Formation of Ammonia and Hydrazine from the Reactions of Acids with Bis(dinitrogen) Complexes of Molybdenum. Identification and Isolation of Intermediates. Possible Analogy with the Hydrazine-Forming Property of Nitrogenase[1]

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The reactions of anhydrous HBr and HCl with *trans*-[Mo(N$_2$)$_2$(triphos)(PR$_3$)], where triphos = PhP(CH$_2$CH$_2$PPh$_2$)$_2$ (PR$_3$ = PPh$_3$ (**1**), PMePh$_2$ (**2**)), in tetrahydrofuran (THF) solution to produce ammonia and in benzene solution to produce hydrazine and ammonia have been examined. Complex **1** reacted with HBr in THF to produce 1.5 mol of N$_2$/mol of **1** and routinely ca. 0.72 mol of NH$_3$/mol of **1**, respectively, and MoBr$_3$(triphos) (≥94% yield). No more than a trace of hydrazine was detected. Total nitrogen balance was increased to 100% when amounts of HBr were added periodically during the reaction. The reaction of **1** or **2** with HBr or HCl led to the rapid loss of 1 mol of N$_2$ and the formation of a pair of isomeric hydrazido(2-) complexes, [MoX(NNH$_2$)(triphos)(PR$_3$)]X (PR$_3$ = PPh$_3$ for **1A(X)** and **1B(X)**, PPh$_2$Me for **2A(X)** and **2B(X)**; X = Br, Cl). The same mixtures were formed in the absence of solvent. The presence of two isomers was the result of the position of the phenyl group on the central phosphorus atom of the triphos ligand relative to the hydrazido(2-) ligand. Monitoring the ammonia-forming reactions by ^{31}P{^{1}H} NMR spectroscopy showed the rapid loss of PPh$_3$ from the **B** series of hydrazido(2-) complexes. Addition of excess PMe$_2$Ph to a **1A–1B** mixture led to the rapid replacement of PPh$_3$ in **1B(Br)** by PMe$_2$Ph to form [MoBr(NNH$_2$)-(triphos)(PMe$_2$Ph)]Br, **3B(Br)**. Addition of excess PMe$_2$Ph to a mixture of **1A(Cl)** and **1B(Cl)** in toluene led to the isolation and characterization of **1A(Cl)** and **3B(Cl)**. From the reaction of a **1A(Br)–1B(Br)** mixture with HBr in benzene, a novel molybdenum(III) complex was isolated, MoBr$_4$(Ph$_2$PCH$_2$CH$_2$PPhCH$_2$CH$_2$PHPh$_2$), in which triphos was behaving as a bidentate ligand and the pendant phosphorus atom was protonated. If water was added to an ammonia-forming reaction in THF after PPh$_3$ had been lost from **1B(Br)** (or **1B(Cl)**), ca. 1 h, significant quantities of hydrazine were detected. The yield of hydrazine decreased as the reaction was allowed to proceed longer before hydrolysis until eventually (>12 h) no more than a trace of hydrazine was detected. It was shown that free hydrazine was not present before hydrolysis. It is proposed that following the loss of PPh$_3$ from the **B** hydrazido(2-) complex an intermediate was formed that upon hydrolysis produced hydrazine. The behavior of this intermediate appeared analogous to that of *nitrogenase* during *nitrogen fixation*. The relationship between the chemistry of **1** and nitrogenase is discussed.

Introduction

Considerable interest in the conversion of dinitrogen into ammonia is provided by a desire to (i) find economical alternatives to the Haber–Bosch process for the synthesis of ammonia and (ii) elucidate the mechanism of *nitrogenase*.[4] One approach to achieving these goals has been to study the interaction of dinitrogen with transition-metal ions.[5] This has been carried out in two distinct ways. The first has been to prepare well-defined metal complexes and study their ability to form ammonia.[5–10] The

second has involved the in situ reactions of dinitrogen with metal ions in a reducing media.[11–13]

Bis(dinitrogen) complexes of molybdenum that contain at least one monodentate ligand have been shown to produce significant amounts of ammonia upon treatment with some strong acids. Among these complexes are *cis*-Mo(N$_2$)$_2$(PMe$_2$Ph)$_4$,[6b,7,14] *trans*-Mo(N$_2$)$_2$(PMePh$_2$)$_4$,[6b] *trans*-Mo(N$_2$)$_2$(dppe)(PMePh$_2$)$_2$[6b] (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$), *trans*-Mo(N$_2$)$_2$(triphos)(PPh$_3$) (**1**;[8] triphos = PhP(CH$_2$CH$_2$PPh$_2$)$_2$), and *trans*-Mo(N$_2$)$_2$-(PMePh$_2$)$_2$(Ph$_2$PCH$_2$CH$_2$SMe).[15] The only nitrogen-containing molybdenum species detected[16] or isolated in the above reactions contain the hydrazido(2-) (NNH$_2$) ligand. This area has been extensively reviewed recently.[5c] Occasionally, hydrazine has been detected as a product along with ammonia.[6b,7,17]

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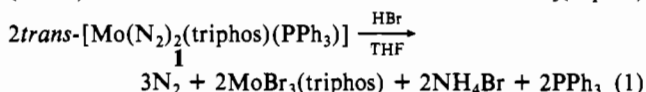(16) Anderson, S. N.; Fakley, M. E.; Richards, R. L.; Chatt, J. *J. Chem. Soc., Dalton Trans.* **1981**, 1973–1980.

Table I. Yields of Nitrogen-Containing Products from Reactions of Acid with Complexes in Tetrahydrofuran Solution

complex[a]	acid (mol)[b]	time, h	mol[b] N$_2$	NH$_3$	N$_2$H$_4$	N$_2$ balance mol[b]	%
1	HBr (18)	1	1.139				
		67	1.502				
1[c]	HBr (19)	62	1.457	0.724	d	1.819	91.0
1	HBr (15)[e]	68	1.480	0.742		1.851	92.5
1	[Ph$_3$PH]Br (13)	1	1.345				
		75	1.509	0.743		1.880	94.0
1	[Ph$_3$PH]Br (6)	1	1.360				
	HBr (6)[f]	68	1.560	0.866		1.993	99.7
1	[Ph$_3$PH]Br (5)[g]	34	1.679	0.641		1.999	100.0
1	HCl (19)	77	1.283	0.585	0.010	1.586	79.3
1	[Ph$_3$PH]BF$_4$ (8)	50	1.035				
		18[h]	1.048	0.003	0.000	1.050	50.3
1	H$_2$SO$_4$ (40)	2	1.0				
		24	1.75	0.000	0.000	1.75	87.5
2	HBr (18)	72	1.52	0.74	0.006	1.89	95.0
5	[Ph$_3$PH]Br (8)	108	1.34	0.064	0.000	1.346	67.3
6	HBr (20)	65	1.493	0.675	0.000	1.831	91.6
1A(Cl)	HBr (20)	168	0.31	0.17	d		
2A(Cl)	HBr (22)	96	0.32	0.17	0.000		
3A(Cl)	HBr (20)	168	0.22	0.03	d		
1A(F)	HBr$_{aq}$ (18)	288		0.088	d		
1A(Br)–1B(Br)[i]		69	1.37	0.29	0.000	1.52	75.1
1A(Br)–1B(Br)[j]		68	1.24	0.18	d	1.33	67.0

[a] **1**, *trans*-[Mo(N$_2$)$_2$(triphos)(PPh$_3$)]; **2**, *trans*-[Mo(N$_2$)$_2$(triphos)(PPh$_2$Me)]; **3**, *trans*-[Mo(N$_2$)$_2$(triphos)(PMe$_2$Ph)]; **5**, *trans*-[Mo(N$_2$)$_2$(dppe)$_2$]; **6**, *trans*-[Mo(N$_2$)$_2$(dppe)(PPh$_2$Me)$_2$]. [b] Per mole of molybdenum complex. [c] 94% MoBr$_3$(triphos) isolated. [d] Trace; <0.001 mol. [e] Increment added after 3, 6, and 68 h, respectively. [f] Increment added after 1, 3, 6, and 8 h, respectively. [g] LiBr (11 mol) dissolved in acetic acid (20 mL) added in vacuo after 0.75 h via a sidearm attached to the reaction flask. [h] 58 °C. [i] HBr removed after evolution of 1 mol of N$_2$. THF added in vacuo. [j] HBr removed after evolution of 1 mol of N$_2$. CH$_2$Cl$_2$ added in vacuo; mixture stirred at −78 °C (0.25 h) and then removed at 0 °C. THF added.

The mode of bonding of N$_2$ in nitrogenase and the relevance of the hydrazido(2−) ligand to nitrogenase are presently unknown. One recognized property of the substrate N$_2$ during turnover of the enzyme is the liberation of hydrazine upon hydrolysis of the enzyme reaction mixture with acid or base.[18,19] On the basis of its chemistry, the hydrazido(2−) ligand has been proposed as the intermediate in N$_2$ fixation that liberates hydrazine upon hydrolysis.[4b,6a,22]

The reaction of **1** with HBr in THF (eq 1) produced 1.5 mol of N$_2$, 0.72–0.87 mol of ammonia/mol of **1**, and MoBr$_3$(triphos) (≤94%).[8a] The isolation and characterization of MoBr$_3$(triphos)

$$2\textit{trans-}[Mo(N_2)_2(triphos)(PPh_3)] \xrightarrow[\text{THF}]{\text{HBr}}$$
$$\mathbf{1}$$
$$3N_2 + 2MoBr_3(triphos) + 2NH_4Br + 2PPh_3 \quad (1)$$

in such high yield was a key to establishing the correct stoichiometry. Subsequently, molybdenum(III) complexes have been isolated from reactions involving *cis*-[Mo(N$_2$)$_2$(PMe$_2$Ph)$_4$][6a] and *trans*-[Mo(N$_2$)$_2$(dppe)(PPh$_2$Me)$_2$],[8b] establishing the generality of this stoichiometry for this series of bis(dinitrogen) complexes of molybdenum. The stoichiometry of the ammonia-forming reaction of bis(dinitrogen) complexes of molybdenum is summarized in eq 2.

$$\{Mo^0(N_2)_2\} \rightarrow \{Mo(III)\} + 1.5N_2 + NH_3 \quad (2)$$
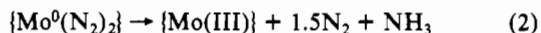
In this paper we report the results of the reactions of **1** with acids to form ammonia and hydrazine. An initial step in the

reaction is the formation of *two isomeric hydrazido(2−) complexes*, one of which is significantly more reactive than the other. The role that phosphine loss plays in the subsequent chemistry leading to ammonia formation has been probed and has led to the isolation of a number of hydrazido(2−) complexes. Hydrolysis of the ammonia-forming reaction mixture shortly after the formation of the hydrazido(2−) complexes led to the detection of hydrazine in yields significantly greater than those of ammonia. The relevance to nitrogenase will be discussed on the basis of this hydrolysis experiment. Some of these results have been reported in preliminary communications.[1,8,17,23]
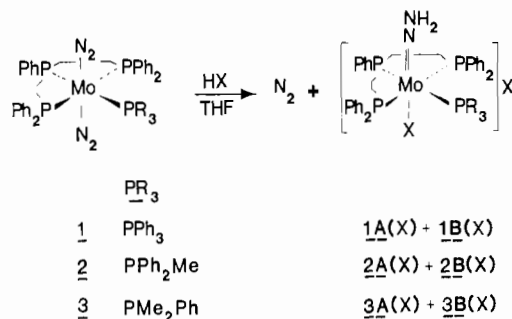
Results

Ammonia Formation in Reactions with HBr and [Ph$_3$PH]Br in Tetrahydrofuran. The first task was to establish the stoichiometry of the reaction between HBr and **1** by determining the identity and yield of products formed under optimum conditions. Reactions were allowed to proceed until no more dinitrogen was evolved (usually >60 h); ca. 1.5 mol of N$_2$/mol of bis(dinitrogen) complex (see Table I). Similar results were obtained with [Ph$_3$PH]Br. The molybdenum-containing product was separated from [NH$_4$]Br and identified as MoBr$_3$(triphos) in yields ≤94%. The remaining nitrogen was found as ammonia and occasionally as traces of hydrazine. In those reactions in which ca. 1.5 mol of N$_2$ were evolved, the yield of ammonia was routinely ca. 0.72 mol/mol of bis(dinitrogen) complex. No increase in the yield of ammonia occurred upon base distillation of the aqueous extract, Kjeldahl digestion of the residue followed by base distillation, or addition of acid before workup commenced. However, increases in the ammonia yield were obtained by adding incremental amounts of acid (HBr or CH$_3$COOH/LiBr) during the early hours of the reaction. In one example (see Table I) 1.993 mol (99.7%) of nitrogen were accounted for.

Although the overall behavior of HBr and [Ph$_3$PH]Br was identical, the amount of N$_2$ liberated after ca. 1 h of reaction was very different. About twice as much N$_2$ was evolved beyond the first mole by using [Ph$_3$PH]Br compared with HBr in the first

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Scheme I

	$\underline{PR_3}$		
$\underline{1}$	PPh_3		$\underline{1A}(X) + \underline{1B}(X)$
$\underline{2}$	PPh_2Me		$\underline{2A}(X) + \underline{2B}(X)$
$\underline{3}$	PMe_2Ph		$\underline{3A}(X) + \underline{3B}(X)$

hour. [Ph$_3$PH]Br is not very soluble in THF.

On the basis of an accumulation of data, the stoichiometry of the ammonia-forming reaction of **1** is represented by eq 1. The complexes *trans*-[Mo(N$_2$)$_2$(dppe)(PMePh$_2$)$_2$] and *trans*-[Mo-(N$_2$)$_2$(triphos)(PMePh$_2$)] (**2**) appeared to behave analogously (see Table I). Complex *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] reacted with HBr and [Ph$_3$PH]Br to produce low yields of ammonia: 4.3 and 6.4%, respectively.[6b]
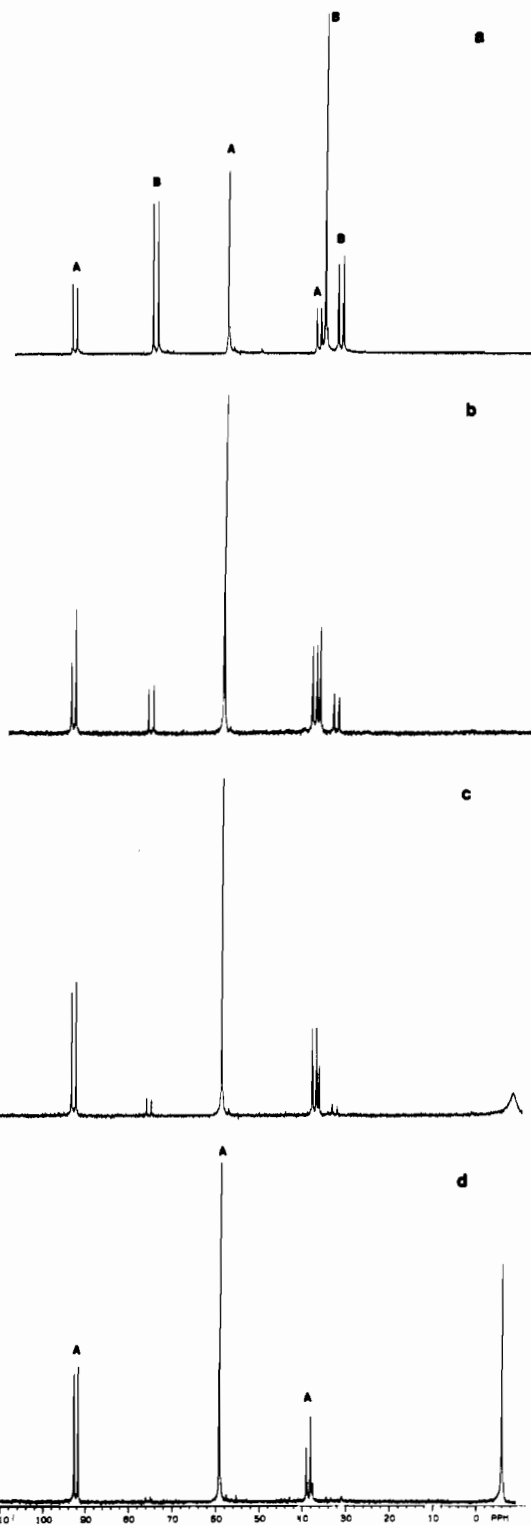
4-Bromobutanol, 1,4-dibromobutane, and water were products that arose from the ring-opening reaction of HBr with THF and the subsequent reaction between the alcohol and HBr. In these reactions the half-life of HBr in THF at room temperature was ca. 0.5 h. As a result of these side reactions, the concentration of HBr decreased rapidly. Addition of water (25 mol/mol of Mo) to a reaction of **1** with HBr in THF had no effect upon the yields of ammonia and hydrazine. Addition of 1 mL of water to a similar reaction resulted in 1.29 mol of N$_2$ and 0.078 mol of ammonia/mol of **1** and a trace of hydrazine.

Reactions of 1 with Other Acids in Tetrahydrofuran. Treatment of **1** with HCl in THF led to the formation of both ammonia and hydrazine (see Table I). Although the yield of hydrazine was low, it was greater than that found in the HBr reactions. The quantity of N$_2$ evolved was less than 1.5 mol but correlated well with the yield of ammonia. In the example cited (see Table I), 0.283 mol of N$_2$ was evolved beyond the first mole of N$_2$, representing 56% reaction. The yield of ammonia was 0.59 mol/mol of **1**.

Sulfuric acid, tetrafluoroboric acid etherate, and [Ph$_3$PH]BF$_4$ behaved differently upon reaction with **1**. The reactions stopped after the loss of 1 mol of N$_2$ and no ammonia was formed. No molybdenum-containing product was isolated from the sulfuric acid reaction, and if the reaction mixture was allowed to sit for a long period of time, further N$_2$ evolved, leading toward a total of 2 mol. Isolation of *trans*-[MoF(NNH$_2$)(triphos)(PPh$_3$)]BF$_4$ was possible by using either tetrafluoroboric acid etherate or [Ph$_3$PH]BF$_4$, although it inevitably contained an unidentified impurity that could only be removed by careful recrystallization. No ammonia was produced when the complex was treated with anhydrous HBr, but aqueous HBr in THF produced 8.8% NH$_3$ together with a trace of hydrazine. Treatment of **1** with acetic acid led to the loss of all nitrogen as N$_2$.

Monitoring of Ammonia-Forming Reactions by ^{31}P NMR Spectroscopy. The ^{31}P NMR spectrum of **1** consisted of two doublets, relative intensities 1:2, due to triphos and a double of triplets, relative area 1, due to PPh$_3$. The absence of observed coupling between the triphos phosphorus atoms greatly simplified this and subsequent ^{31}P NMR spectra.

The reaction of **1** with excess anhydrous HBr in THF occurred with the rapid evolution of N$_2$ (ca. 1.0 mol) to give a golden-brown solution. The solution was filtered into an NMR tube cooled to –78 °C. The ^{31}P{^{1}H} NMR spectrum was recorded at –60 °C (or –40 °C) and revealed two [(triphos)(PPh$_3$)]-containing complexes, **1A**(Br) and **1B**(Br) (see Figure 1a) in the ratio of ca. 1:2[24] and no **1** (see Scheme I). This solution was periodically warmed
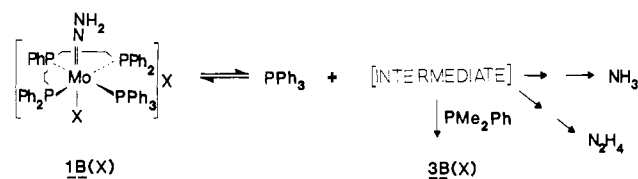
(24) ^{31}P{^{1}H} NMR [THF, –40 °C, PhP$_a$(CH$_2$CH$_2$P$_b$Ph$_2$)$_2$, Ph$_3$P$_x$, $^2J_{P_aP_b}$ = 0.0 Hz]. **1A**(Br): δ 92.6 (d, 1, $^2J_{P_aP_x}$ = 145.2 Hz, P$_a$), 58.6 (d, 2, $^2J_{P_bP_x}$ = 16.3 Hz, P$_b$), 38.0 (dt, 1, P$_x$). **1B**(Br): δ 75.4 (d, 1, $^2J_{P_aP_x}$ = 163.7 Hz, P$_a$), 37.3 (d, 2, $^2J_{P_bP_x}$ = 17.5 Hz, P$_b$), 33.7 (dt, 1, P$_x$).

Figure 1. Successive ^{31}P{^{1}H} NMR spectra (–60 °C) of a mixture of **1A**(Br) and **1B**(Br) showing **1B**(Br) disappearing and PPh$_3$ appearing in THF solution with excess anhydrous HBr initially present: a, at the start (0 min); b, after 16 min at room temperature; c, after 26 min at room temperature; d, after 36 min at room temperature. Resonances marked **A** and **B** correspond to **1A**(Br), and **1B**(Br), respectively. An adjustment in the intensities of the resonances is made between spectra a and b. For P atom assignments, see text.

to 25 °C and maintained at that temperature for fixed periods of time before being cooled back to –60 °C. Following these cycles, the ^{31}P NMR spectra showed the gradual disappearance of resonances due to **1B**(Br). Eventually a resonance, initially broad, due to PPh$_3$ appeared (Figure 1c) as resonances due to **1B**(Br) continued to decrease in intensity. No other new species were observed. Frequently, a gold-colored solid began to pre-

Scheme II

Figure 2. Relative position of the phenyl group on the central phosphorus atom of triphos in **1**, **1A(X)**, and **1B(X)**.

cipitate after ca. 0.5 h. After ca. 1 h, only resonances due to **1A(Br)** and PPh$_3$ (now sharp) were observed in the spectrum. The intensity of resonances due to **1A(Br)** continued to decrease until after ca. 24 h very little was present. Residues from these experiments were shown to contain the ammonium ion.

The reactions of HBr with **2**[25] and HCl with **1**[26] similarly led to the appearance of two [(triphos)(PR$_3$)]-containing hydrazido(2−) complexes (see Scheme I).

The reaction of sulfuric acid with **1** in THF was monitored for 0.1 h following the loss of 1 mol of N$_2$. Resonances due to two species were observed; one species contained both triphos and PPh$_3$[27] and the other triphos[28] but no PPh$_3$. There was no evidence in the spectrum of a second {(triphos)(PPh$_3$)}-containing complex. Beyond this time the resolution of the spectrum deteriorated rapidly.

Reactions of 1 with Hydrogen Halides in the Absence of Solvent. About a 20-fold excess of HBr was condensed onto the surface of solid **1** at −196 °C. As the temperature rose, white solid HBr began to melt and the surface of **1** immediately turned green and bubbling was observed. Once HBr had volatilized, the reaction ceased. The reaction flask was again cooled in order to solidify HBr. Again, upon warming, during the very brief time that HBr was a liquid, a reaction with **1** occurred. By cycling the temperature in this way and monitoring N$_2$ evolution with the Toepler pump, it was possible to achieve N$_2$ losses up to 1.0 mol/mol of **1**, i.e. complete conversion to the hydrazido(2−) complexes.

When the green-brown solid was dissolved at −78 °C in THF, toluene, CH$_2$Cl$_2$, or MeOH and the ^{31}P NMR spectra was recorded at −40 °C, the same mixture of **1A(Br)** and **1B(Br)** was observed and in a similar ratio of ca. 1:2. On the basis of all the data gathered so far, there is no difference between the chemical behavior of a mixture of hydrazido(2−) complexes prepared as a solid or in solution.

Phosphine Incorporation into Hydrazido(2−) Complexes. Since the loss of PPh$_3$ from **1B(Br)** appeared to be an important step in the continuing reaction to form ammonia and no non-PPh$_3$-containing species were observed in the ^{31}P NMR spectra, the effect of the presence of phosphines more basic than PPh$_3$ was explored. It had already been noted that **2** reacted more slowly and produced less ammonia than **1**. Addition of excess PMe$_2$Ph to a **1A(Br)−1B(Br)** mixture in THF in the absence of acid resulted in the appearance of a new hydrazido(2−) complex, **3B(Br)**[29] (Scheme II). As resonances due to **1B(Br)** began to decrease in the ^{31}P NMR spectrum, resonances due to **3B(Br)** began to appear. Within 0.5 h the ratio of **1A(Br)** to **3B(Br)** was almost the same as the original ratio of **1A(Br)** to **1B(Br)**, and no **1B(Br)** was present. After a short time only **1A(Br)**, **3B(Br)**, PPh$_3$, and PMe$_2$Ph were present in the spectrum. Even after 14 h intense resonances due to **3B(Br)** remained. Significantly, very little
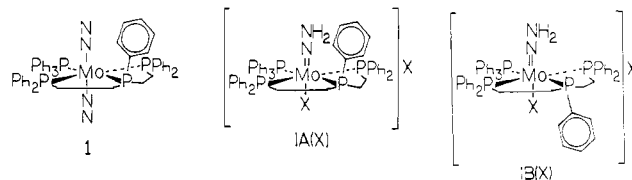
ammonia was present in this reaction mixture after 60 h.[30] Similarly, PPh$_2$Me reacted with a **1A(Br)−1B(Br)** mixture to produce a mixture of **1A(Br)**, **2B(Br)**, PPh$_3$, and PPh$_2$Me.

When 1 mol of P(C$_6$H$_4$-4-OMe)$_3$ was added to a **1A(Br)−1B-(Br)** mixture in THF with HBr present, a set of resonances began to appear in the ^{31}P NMR spectrum due to the new **B** hydrazido(2−) complex. After ca. 0.5 h, resonances due to both **B** hydrazido(2−) complexes were present (their combined intensities being greater than for **1A(Br)**), together with **1A(Br)**, PPh$_3$, and P(C$_6$H$_4$-4-OMe)$_3$. After 12 h, the same resonances were still present in the spectrum and with the same relative intensities. Addition of excess PPh$_3$ to a **1A–1B** mixture caused a similar decrease in the rate of disappearance of **1B(Br)**.

In toluene and CH$_2$Cl$_2$ solutions, **1A(Br)−1B(Br)** mixtures and **1A(Cl)−1B(Cl)** mixtures both showed incorporation of PMe$_2$Ph into the **B** series of hydrazido(2−) complexes forming **3B(Br)** and **3B(Cl)**, respectively. In methanol solution the incorporation of PMe$_2$Ph occurred significantly more slowly.

While the monodentate phosphine in the **B** series of isomers was shown to be labile and could be replaced by other phosphines, no evidence was found for a similar lability in the **A** series of hydrazido(2−) complexes.

Isolation and Characterization of Hydrazido(2−) Complexes. Addition of excess PMe$_2$Ph to a toluene solution of a **1A(Cl)−1B(Cl)** mixture, in the absence of acid, resulted in the formation of a mixture of **1A(Cl)** and **3B(Cl)** (vide supra). Over an 18-h period, a brown crystalline product formed, which analyzed for [MoCl(NNH$_2$)(triphos)(PPh$_3$)]Cl, with a molecule of toluene of solvation, and had a ^{31}P NMR spectrum identical with that of **1A(Cl)**. The resonance due to the hydrazido(2−) ligand protons was observed at δ 8.5, and $ν_{NH}$ appeared over a broad range: 3307, 2872, and 2575 cm^{-1}. When the volume of the filtrate was reduced, a lime green solid formed over 18 h. This product, isolated in low yield, analyzed for [MoCl(NNH$_2$)(triphos)(PMe$_2$Ph)]Cl with one-half of a molecule of toluene of solvation. No resonance due to the hydrazido(2−) ligand protons was observed in the ^{1}H NMR spectrum. Addition of PPh$_2$Me to a **1A(Cl)−1B(Cl)** mixture in toluene similarly led to the isolation of **1A(Cl)** and **2B(Cl)**.

Single-crystal X-ray structure determinations have been carried out on both **1A(Cl)** and **2B(Cl)**.[31] Representations of the structures are shown in Figure 2. The preliminary data showed that **A** and **B** were isomers, with the major difference being the position of the NNH$_2$ group relative to the phenyl group of the central phosphorus atom. In **1A(Cl)** the phenyl group was on the same side of the plane of the four phosphorus (P$_4$) atoms as the NNH$_2$ group. In **2B(Cl)** the phenyl group was on the opposite side of the P$_4$ plane, which resulted in the NNH$_2$ group being more "exposed". Hydrogen bonding between a hydrazido hydrogen atom and the chloride counterion occurred in **2B(Cl)** but not in **1A(Cl)**. The most apparent geometrical consequence of the position of this phenyl group was the difference of ca. 0.36 Å in the position of Mo relative to the phosphorus planes in **1A(Cl)** and **2B(Cl)**. While the Mo atom was displaced 0.28 Å from the P$_4$ plane *toward* the nitrogen atom of the NNH$_2$ group in **1A(Cl)**, the Mo atom was moved 0.08 Å below the P$_4$ plane in **2B(Cl)** in the direction of the coordinated chloride.

(25) ^{31}P{^{1}H} NMR [THF, −40 °C, PhP$_a$(CH$_2$CH$_2$P$_b$Ph$_2$)$_2$, Ph$_2$MeP$_x$, $^2J_{P_aP_b}$ = 0.0 Hz]. **2A**(Br): δ 91.3 (d, $^2J_{P_aP_x}$ = 143.1 Hz, P$_a$), 51.7 (d, $^2J_{P_bP_x}$ = 16.6 Hz, P$_b$), 8.1 (dt, P$_x$). **2B**(Br): δ 71.3 (d, $^2J_{P_aP_x}$ = 162.2 Hz, P$_a$), 37.0 (d, $^2J_{P_bP_x}$ = 18.3 Hz), 5.8 (dt, P$_x$).

(26) ^{31}P{^{1}H} NMR [THF, −40 °C, PhP$_a$(CH$_2$CH$_2$P$_b$Ph$_2$)$_2$, Ph$_3$P$_x$, $^2J_{P_aP_b}$ = 0.0 Hz]. **1B**(Cl): δ 76.7 (d, 1, $^2J_{P_aP_x}$ = 169.3 Hz, P$_a$), 40.3 (d, 2, $^2J_{P_bP_x}$ = 17.4 Hz, P$_b$), 35.3 (dt, 1, P$_x$). For **1A**(Cl), see Experimental Section.

(27) ^{31}P{^{1}H} NMR [THF, −40 °C, PhP$_a$(CH$_2$CH$_2$P$_b$Ph$_2$)$_2$, Ph$_3$P$_x$]: δ 90.8 (dt, $^2J_{P_aP_b}$ = 5.2 Hz, $^2J_{P_aP_x}$ = 153.9 Hz, P$_a$), 59.5 (dd, $^2J_{P_bP_x}$ = 14.9 Hz, P$_b$), 34.8 (dt, P$_x$).

(28) ^{31}P{^{1}H} NMR [THF, −40 °C, PhP$_a$(CH$_2$CH$_2$P$_b$Ph$_2$)$_2$]: δ 101.3 (t, $^2J_{P_aP_b}$ = 17.0 Hz, P$_a$), 50.7 (d, P$_b$).

(29) ^{31}P{^{1}H} NMR [THF, −40 °C, PhP$_a$(CH$_2$CH$_2$P$_b$Ph$_2$)$_2$, PhMe$_2$P$_x$, $^2J_{P_aP_b}$ = 0.0 Hz]. **3B**(Br): δ 72.4 (d, 1, $^2J_{P_aP_x}$ = 162.2 Hz, P$_a$), 42.0 (d, 2, $^2J_{P_bP_x}$ = 19.3 Hz, P$_b$), −2.8 (dt, 1, P$_x$).

(30) In a separate experiment **3B(Cl)** was reacted with HBr in THF (60 h) to give 0.08 mol of ammonia/mol of **3B(Cl)** and no hydrazine.

(31) Gebreyes, K.; George, T. A.; Koczon, L. M.; Tisdale, R. C.; Zubieta, J. A., manuscript in preparation.

Table II. Yields of Nitrogen-Containing Products from Reactions of Acids with Complexes in Different Solvents

complex[a]	acid (mol)	solvent	time, h	N_2	NH_3	N_2H_4
1[c]	HCl (20)	C_6H_6	108	1.36	0.30	0.24
1[c,d]	HCl (20)	C_6H_6	17	1.35	0.18	0.29
1[c]	HBr (20)	C_6H_6	20	1.08	0.17	0.29
1[c,e]	HBr (20)	C_6H_6	72	1.33	0.21	0.24
1[c,f]	HBr (200)	C_6H_6	60	1.33	0.31	0.33
1[c]	HBr (20)	CH_2Cl_2	60	1.23	0.27	0.19
1[c]	HBr (20)	CH_3OH	84	1.36	0.19	0.005
1[c]	HBr (20)	DME	60	1.42	0.36	0.14
1[c]	HBr (20)	CF_3COOH	48	1.39	0.48	0.22
1[c]	HCl (20)	CF_3COOH	18	1.15	0.28	0.15
1[c,g]	HBr (20)	CF_3COOH	41	1.09	0.41	0.05
1[c,h]	HBr (20)	CF_3SO_3H	15	1.19	0.29	0.42

[a] 1 *trans*-$Mo(N_2)_2$(triphos)(PPh_3). [b] Per mole of 1. [c] Acid added to solid 1. Solvent added after evolution of 1 mol of N_2. [d] Heated at 45 °C after addition of solvent. [e] Volatiles removed after 72 h. CH_2Cl_2 added in vacuo and stirred for a further 48 h. [f] Same as in footnote e except stirred for 20 h in CH_2Cl_2. [g] Acid removed and 12 mL of CF_3COOH added in vacuo. [h] Acid removed and 1 mL of CF_3SO_3H added in vacuo.

One consequence of the configuration at the central phosphorus atom of triphos was the inequivalence of the two N_2 ligands in **1**. This was manifested in the preferential protonation of the less hindered N_2 ligand, resulting in more of the **B** than the **A** isomer being formed.

Unfortunately we were not able to develop a successful strategy for the isolation of the more reactive **1B(Br)** and **1B(Cl)** hydrazido(2−) complexes.

Reactions of a Mixture of the Hydrazido(2−) Complexes with and without Acid. With acid present, **1A(Br)** and **1B(Br)** reacted further in THF solution to give ammonia and 0.5 mol of N_2. In the absence of acid, the reaction occurred similarly although not to completion. In the ^{31}P NMR spectrum, a mixture of **1A(Br)** and **1B(Br)** in THF in the absence of acid showed the rapid appearance of a sharp resonance due to PPh_3, in contrast to its absence until later in the reaction when acid was present. Resonances due to **1B(Br)** decreased at a slower rate than with acid present, such that after 3 h some **1B(Br)** still remained together with **1A(Br)**. Considerable solid was present after 3 h.

The reaction of HBr with a **1A(Br)**–**1B(Br)** mixture in methanol proceeded to produce much less ammonia than in THF (see Table II). After an initial decrease in the intensity of resonances due to **1B(Br)**, resonances due to **1A(Br)** and **1B(Br)** persisted for many days.

In toluene solution, in the absence of acid, **1A(Br)** and **1B(Br)** showed no evidence of reaction. In the presence of acid, a reaction occurred slowly. In the ^{31}P NMR spectrum, after 5 h, resonances due to **1B(Br)** were still present, being one-half of the intensity of those due to **1A(Br)**. After 24 h, there was no evidence of **1B(Br)**, but a substantial amount of solid had formed in the NMR tube. This solid was dissolved in CH_2Cl_2, but only weak resonances due to **1A(Br)** were observed. Analysis of the residue revealed ammonia and, for the first time in these studies of **1**, *a substantial amount of hydrazine* (see later).

Effect of Halide Ion. When approximately equimolar amounts of a **1A(Br)**–**1B(Br)** mixture and a **1A(Cl)**–**1B(Cl)** mixture were dissolved together in THF solution the ^{31}P NMR spectrum revealed four distinct species. Within 0.33 h, resonances due to **1B(Br)** had almost disappeared while resonances due to **1B(Cl)** gradually decreased over a 12-h period. Thus **1B(Br)** reacted more rapidly than **1B(Cl)**. During the first 0.33 h, no decrease in the intensities of resonances due to **1A(Br)** and **1A(Cl)** occurred.

Addition of LiBr to a **1A(Br)**–**1B(Br)** mixture in THF showed no effect upon the ratio of **1A(Br)** to **1B(Br)** or the rate of disappearance of **1B(Br)**. However, addition of a saturated solution of LiCl in methanol to a mixture of **1A(Br)**–**1B(Br)** and **1A(Cl)**–**1B(Cl)** complexes in THF resulted in the rapid increase in the intensities of resonances due to **1B(Cl)** and a commensurate decrease in resonances due to **1B(Br)** in the ^{31}P NMR spectrum. In a similar experiment LiCl (20 mol/mol of Mo) in a 30% methanol in THF solution was added to a **1A(Br)**–**1B(Br)** mixture in the absence of acid. After 2.5 days, the filtrate contained **1A(Cl)**, **1B(Cl)**, and PPh_3. Therefore, given enough time, the

coordinated bromide ion of **1A(Br)** will exchange as well. No similar exchange of coordinated chloride was observed. Thus, when excess LiBr in a 20% methanol in THF solution was added to a **1A(Cl)**–**1B(Cl)** mixture no change in the ^{31}P NMR occurred over a 49-h period. Only resonances due to **1A(Cl)**, **1B(Cl)**, and PPh_3 were present.

Addition of excess tetrabutylammonium fluoride in THF to a **1A(Br)**–**1B(Br)** mixture at −78 °C was carried out to investigate the possibility of fluoride ion incorporation. The ^{31}P NMR spectrum was run at −40 °C, without warming to room temperature, and resonances due to **1A(Br)** were present but not **1B(Br)**. Instead, intense resonances due to **1** were observed. After the solution was allowed to stand at room temperature for 0.1 h, the spectrum was run at −40 °C. This time only resonances due to **1** were present. Fluoride ion appeared to have deprotonated both hydrazido(2−) complexes.
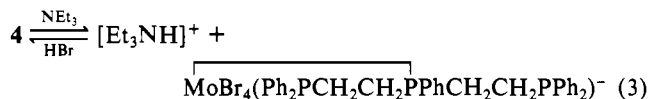
Hydrazine Formation in Reactions with HCl and HBr. Benzene and excess HBr were condensed onto **1** at −196 °C. As the temperature rose, a forest green powder formed (where **1** was exposed to liquid HBr). As the benzene began to melt, substantial gas evolution was observed, a turbid solution was generated, and a brown oil appeared. A golden yellow solid was often observed to form after ca. 0.5 h. Evolved N_2 (1.12–1.13 mol/mol of **1**) was measured after 24 h. After all volatiles were removed in vacuo, a tan solid remained. Qualitatively, the same results were obtained by using toluene and CH_2Cl_2 as solvent. Monitoring these reactions by ^{31}P NMR spectroscopy in toluene solution, which required occasional filtering of the sample, showed that after 24 h of reaction a substantial amount of **1A(Br)** remained in solution. In fact, in the reaction **1**–HCl–CH_2Cl_2, **1A(Cl)** was still present in solution after 48 h.

Analysis of these reactions carried out in benzene, toluene, or CH_2Cl_2 after >48 h revealed the presence of ammonia and, for the first time, hydrazine in more than trace quantities (see Table II). All these yields were significantly different from those obtained by using HBr/THF. In none of these reactions was a complete nitrogen balance achieved. In many cases this was due to unreacted **1A(Br)** or **1A(Cl)** remaining at the time the reaction was terminated.

Isolation of Molybdenum-Containing Product. The reaction of HBr with **1** in benzene (48 h) produced a brownish orange powdery solid and a yellow gold solution. Volatiles were removed, and CH_2Cl_2 was added. The resulting orange solution was filtered immediately from hydrazinium and ammonium bromide. Orange crystals began to form after about 1 h and were filtered off after 48 h. The orange product exhibited ν_{P-H} at 2350 cm^{-1} in the IR spectrum, and the elemental analysis supported a ratio of Mo: Br:triphos of 1:4:1. Complex **4** was formulated as a molybdenum(III) complex coordinated with four bromine atoms and with triphos behaving as a bidentate ligand. The pendant phosphorus atom was protonated. The complex was insoluble in all common organic solvents. However, the addition of triethylamine to a suspension of **4** in CH_2Cl_2 rapidly produced a clear orange solution.

4
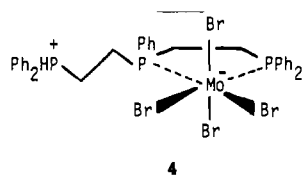
A magnetic susceptibility measurement (Evans method) was made on this solution giving a μ_{eff} of 4.00 μ_B, close to that expected for a molybdenum(III) complex.[32] Addition of HBr to the solution precipitated **4** (eq 3).

$$\mathbf{4} \underset{HBr}{\overset{NEt_3}{\rightleftharpoons}} [Et_3NH]^+ +$$

$$MoBr_4(Ph_2PCH_2CH_2PPhCH_2CH_2PPh_2)^- \quad (3)$$

Hydrolysis Experiments. In many of the reactions of a **1A**-(Br)–**1B**(Br) mixture with HBr or HCl in THF or toluene, a gold colored solid began to form after ca. 0.5 h at room temperature. This solid was isolated (by filtration in a glovebag using a water aspirator). Analysis confirmed the presence of both hydrazine and ammonia. Evidently hydrazine could be formed in a reaction that when allowed to proceed for >60 h, produced no more than a trace of hydrazine.

To further investigate this result **1A**(Br)–**1B**(Br) mixtures were reacted with HBr in THF in a series of experiments. Each experiment was stopped at a particular time by removing volatiles in vacuo, extracting the solid with a CH_2Cl_2–H_2O mixture and analyzing the aqueous layer for ammonia and hydrazine (see Table III). These results are presented as yield (mol/mol of Mo) of ammonia and of hydrazine plotted against time (see Figure 3). Early in the reaction, a rapid buildup of hydrazine was observed while the amount of ammonia produced was small and little N_2 was evolved. As the reaction proceeded, a maximum yield of hydrazine was observed after ca. 1.0 h (ca. 0.16 mol/mol of **1**) beyond which time the yield of hydrazine decreased. The ammonia yield and N_2 evolution increased steadily with time. No change in the amount of hydrazine formed after 1 h was noted upon the use of scrupulously outgassed water. When hydrolysis was conducted in vacuo a small amount of N_2 was evolved. No obvious relationship existed among the amounts of N_2, ammonia, and hydrazine formed at this early stage in the ammonia-forming reaction.

Two feasible explanations were available to account for these unusual results. (i) Hydrazine was being generated in the reaction and subsequently reduced to ammonia and N_2 (eq 4) by a mo-

$$N_2H_5^+ + 3H^+ + 2e^- \rightarrow 2NH_4^+ \quad (4)$$
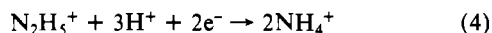
lybdenum complex. (ii) An intermediate complex was being converted to hydrazine as a result of the procedures employed for the analysis of ammonia and hydrazine. The latter scenario is very similar to the behavior of nitrogenase: no free hydrazine was detected in the functioning enzyme, but hydrolysis of the functioning enzyme gave hydrazine.[18]

To help clarify the situation, the following experiment was conducted. To a **1A**(Br)–**1B**(Br) mixture, from which excess HBr was not removed, were added $^{15}N_2H_4$[33] and THF at -196 °C. The reaction mixture was allowed to stir for 60 h at room temperature. When the mixture was cooled to -196 °C, the evolved gases were collected. Following the usual workup, the aqueous extract was treated with a NaOBr solution and the evolved gases were collected. Mass spectral determination of the ratio of N_2 isotopomers provided no evidence that $^{15}NH_4^+$ (as determined from $^{29}(N_2)$) had been produced in yields any greater than the background. In other words, there was no evidence of incorporation of $^{15}N_2H_4$ (present as $^{15}N_2H_5Br$) into the ammonia-forming sequence of reactions.[34]

Table III. Yields of Ammonia and Hydrazine upon Hydrolysis of the Reaction of HBr with *trans*-[Mo(N_2)_2(triphos)(PPh_3)] in THF at Different Times[a]

|	mol[b]			mol[b]	
time, h	NH_3	N_2H_4	time, h	NH_3	N_2H_4
0.25	0.045	0.051	2	0.14	0.15
0.5	0.055	0.11	3	0.23	0.13
1	0.12	0.16	6	0.41	0.065
1.5	0.13	0.15	12	0.48	0.002

[a] For conditions, see Experimental Section. [b] Per mole of molybdenum complex.

TIME (hours)
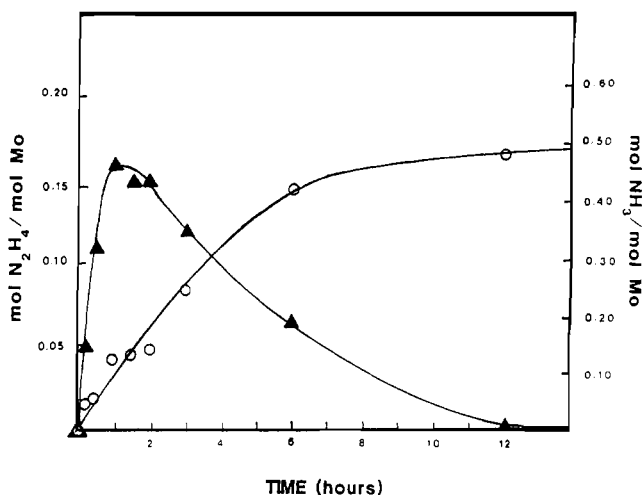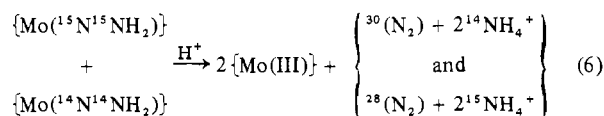
Figure 3. Variations in yields of hydrazine (▲) and ammonia (O) vs. time. In separate experiments the reaction of *trans*-[Mo(N_2)_2(triphos)(PPh_3)] (1) with HBr in THF was stopped after set periods of time (see Table III). At 60 h or longer, the yields of ammonia and hydrazine were routinely ca. 0.72 and <0.0015 mol/mol of **1**.

Nitrogen-15 Labeling Experiments and Electron Transfer. In order to investigate the mechanism of ammonia and hydrazine formation beyond the hydrazido(2–) stage, a series of experiments were carried out to (i) study the loss of the 0.5 mol of N_2/mol of hydrazido(2–) complex and (ii) probe for evidence of inner-sphere or outer-sphere electron-transfer steps.

(i) The conversion of the hydrazido(2–) ligand to 0.5 N_2 and ammonia at a single metal center (eq 5) would require coupling

$$\{Mo(NNH_2)\} \xrightarrow{H^+} \{Mo(III)\} + 0.5N_2 + NH_4^+ \quad (5)$$
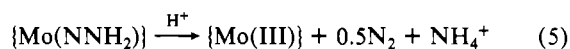
of nitrogen species at some stage, leading to the formation of new N–N bonds. To probe for new nitrogen–nitrogen bonds, the following experiment was carried out.[8a] To a mixture of **1** and $^{15}N_2$-labeled **1** was added HBr and THF. After the mixture was stirred for 72 h, the evolved N_2 was collected. Mass spectral analysis of the gases showed that the amount of $^{29}(N_2)$ was no greater than the background. Therefore, each N_2 ligand of **1** gave either N_2 or 2 mol of ammonia, and no new nitrogen–nitrogen bonds were formed. In terms of the overall conversion of the hydrazido(2–) complex to ammonia and N_2, the above results can be summarized in eq 6. The reaction occurring at a single metal

$$\begin{matrix} \{Mo(^{15}N^{15}NH_2)\} \\ + \\ \{Mo(^{14}N^{14}NH_2)\} \end{matrix} \xrightarrow{H^+} 2\{Mo(III)\} + \begin{Bmatrix} ^{30}(N_2) + 2^{14}NH_4^+ \\ \text{and} \\ ^{28}(N_2) + 2^{15}NH_4^+ \end{Bmatrix} \quad (6)$$

center (eq 5) can be eliminated since in the above labeling experiment the 0.5N_2 would have shown a distribution of $^{28}(N_2)$,

(32) See for example: Anker, M. W.; Chatt, J.; Leigh, G. J.; Wedd, A. G. *J. Chem. Soc., Dalton Trans.* **1975**, 2639–2645.

(33) Prepared from [$^{15}N_2H_6$]SO_4: Browne, A. W.; Welsch, T. W. B. *J. Am. Chem. Soc.* **1911**, *33*, 1728–1734.

(34) The transitory existence of hydrazine within a solvent cage or bound to a metal cannot be eliminated by this experiment. However, the large yields of hydrazine determined early in the reaction after workup argue against this likelihood.

$^{29}(N_2)$, and $^{30}(N_2)$ based upon the original ratio of **1** to $^{15}N_2$-labeled **1**.

(ii) In an attempt to identify electron-transfer steps in the reaction, hydrazido(2–) complexes that did not generate ammonia with acid were added to **1**. Although these hydrazido(2–) complexes did not themselves give ammonia, they might still behave as redox reagents toward intermediates generated from **1** during an ammonia-forming reaction. Thus, increased yields of ammonia in the reaction of **1** with HBr–THF would support this behavior. To a mixture of 1 mol of **1** and 3 mol of [MoF($^{15}N^{15}NH_2$)-(triphos)(PPh₃)]Br was added HBr and THF. After the mixture was stirred for 36 h, the evolved N₂ was collected. Following the normal workup procedure, the aqueous extract was treated with NaOBr solution and evolved gases were collected. No $^{29}(N_2)$ or $^{30}(N_2)$ was detected above the background level. The ammonia yield was normal (0.73 mol/mol of **1**). Similar results were obtained when **1** and [MoBr(NNH₂)(dppe)₂]Br (prepared in situ[35]) were reacted with HBr in THF. At the conclusion of the reaction no increase in the ammonia yield was found.

Discussion

Reaction Stoichiometry. Routinely, the yields of ammonia were less than stoichiometric (eq 1) in the reaction of HBr–THF with **1**. Two factors may have contributed to this. (i) All HBr was consumed by reaction with THF before the ammonia-forming reaction was complete. (ii) The presence of 4-bromobutanol, 1,4-dibromobutane, and water in the reaction mixture. The nitrogen balance was exact when amounts of HBr were added periodically in vacuo to the reaction of [Ph₃PH]Br with **1**. A similar result was obtained upon adding a solution of LiBr and acetic acid in THF, although some decomposition of **1** due to reaction with acetic acid led to more than 1.5 mol of N₂ being liberated. Addition of an increment of HBr only after 1.5 mol of N₂ had been liberated (ca. 60 h) led to no increase in the ammonia yield. So far, no evidence has been found for the formation of organic nitrogen compounds in these reactions.

Intermediate Hydrazido(2–) Complexes. The reaction of **1** with HBr in THF led to the rapid loss of 1.0 mol of N₂ followed by the subsequent slower loss of a further 0.5 mol of N₂. Isolation of the molybdenum(III) product, MoBr₃(triphos), established that a net transfer of three electrons was occurring from each molybdenum to a coordinated N₂. Although the formation of the hydrazido(2–) ligand upon protonation of N₂ complexes of molybdenum and the intermediacy of this ligand in reactions leading to ammonia and hydrazine are well established, no information is available on the mechanism of the conversion of the hydrazido(2–) complex to either ammonia or hydrazine. An earlier suggestion[6b] that ammonia arose as the result of the disproportionation of the hydrazido(2–) ligand (3N₂H₂ → 2NH₃ + 2N₂) was proposed before the stoichiometry of the reaction had been established.

We observed the formation of not one but two hydrazido(2–) complexes, **1A(Br)** and **1B(Br)**, upon the loss of 1.0 mol of N₂ from **1** on treatment with either HBr–THF or liquid HBr. Similar results were obtained by using HCl. Our original structural assignment for the **A** and **B** isomers was based upon a desire to account for the greater lability of the monodentate phosphine in the **B** series. We proposed that during the formation of the **B** isomers the monodentate phosphine migrated with the result that it became trans to the hydrazido(2–) ligand.[17,23] Thus the lability of the phosphine would be due to the strong trans effect of the multiply bonded hydrazido(2–) group. This argument totally ignored the ^{31}P NMR data that showed $^2J_{P_aP_x}$ between the monodentate phosphorus and unique phosphorus atom of triphos in the **B** series was even larger than $^2J_{P_aP_x}$ in the **A** series.

Inspection of the proposed structure of **1** (Figure 2) reveals that the two dinitrogen ligands are not in identical environments. The presence of the bulky phenyl group on the central triphos phosphorus atom might be expected to favor protonation of one N₂
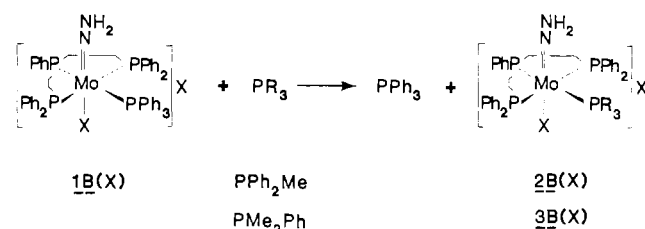
over the other. In fact this is what has been observed in all the reactions with HBr and HCl. Protonation occurred preferentially on the least hindered N₂ ligand to give a predominance of the **B** hydrazido(2–) complexes.

Isolated [MoF(NNH₂)(triphos)(PPh₃)]BF₄ appeared to belong to the **A** series since it did not incorporate PMe₂Ph (17 h in THF). A second (triphos-PPh₃)-containing complex was observed as a minor complex in the ^{31}P NMR spectrum while following the reaction of excess HBF₄·OEt₂ with **1** in THF. The ^{31}P NMR data (see Experimental Section) strongly suggested that it was the **B** isomer. However, considering the ease with which fluoride ion deprotonated **1B(Br)** in THF at –40 °C (vide supra), it is likely the same fate befell this **B** isomer.

It is not obvious from the X-ray crystallographic data why the monodentate phosphine is relatively labile in the **B** series of hydrazido(2–) complexes are not in the **A** series. One possible reason may be the greater "openness" of the {MoNNH₂} moiety in the **B** series.[31]

Phosphine Loss. Loss of the monodentate phosphine from a **B** hydrazido(2–) complex appears to be the next step toward ammonia formation. Following the formation of the **1A(Br)**–**1B(Br)** mixture, **1B(Br)** reacted rapidly in THF solution but no new species except PPh₃ were observed in the ^{31}P NMR spectrum. It was assumed that further species in solution were either paramagnetic or in very low steady-state concentrations. About this time a gold colored solid was often observed. The reaction to give ammonia was successfully blocked by adding PMe₂Ph to a solution of **1A(Br)**–**1B(Br)** in which **3B(Br)** was formed rapidly from **1B(Br)**: *very little ammonia was detected.*[17,30] One interpretation of these results is shown in Scheme III. Loss of PPh₃ from **1B(Br)** would lead to a five-coordinate intermediate that could become involved in redox reactions leading to ammonia formation. In the presence of a more basic phosphine such as PPh₂Me and PMe₂Ph, the five-coordinate intermediate was trapped to form **2B(Br)** and **3B(Br)**, respectively. Even the addition of P(C₆H₄-4-OMe)₃ or PPh₃ was able to dramatically slow the rate of further reaction.

A second interpretation is that electron transfer preceded phosphine loss. We have discounted this possibility on the basis of reported electrochemical studies of similar hydrazido(2–) complexes of molybdenum that afforded ammonia.[36] For complexes such as MoBr₂(NNH₂)(PMe₂Ph)₃, [MoCl(NNH₂)-(PMe₂Ph)₃(C₅H₅N)]Cl, and [Mo(NNH₂)(quin)(PMe₂Ph)₃]X, where quin = 8-hydroxyquinolinate and X = Cl or Br, in dichloromethane solution no reduction wave was observed in the cyclic voltammogram at potentials above that of solvent discharge.

The **A** hydrazido(2–) complexes do not appear to have a labile monodentate phosphine and seem relatively unreactive compared with their **B** analogues. In fact, the **A** hydrazido(2–) complex was often present in solution after many days of reaction. At this time, it is not clear how the **A** hydrazido(2–) complex reacts but many reactions with pure, isolated **1A(Cl)** have shown that it will afford either ammonia or ammonia and hydrazine depending upon the conditions.[16]

We believe that the failure of the reaction of **1** with sulfuric acid in THF to give ammonia at room temperature was due to the coordinating sulfate (or hydrogen sulfate) ion becoming a bidentate ligand once PPh₃ loss occurred. This would have trapped

Scheme III

$$\mathbf{1B(X)} \quad + \quad PR_3 \quad \longrightarrow \quad PPh_3 \quad + \quad \mathbf{2B(X)}$$

PPh₂Me   →   **2B(X)**
PMe₂Ph   →   **3B(X)**

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

(36) Chatt, J.; Pearman, A. J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1978**, 1766–1776.

the five-coordinate intermediate and blocked the reaction pathway leading toward ammonia formation. Complex [Mo(N$_2$)$_2$-(dppe)(PPh$_2$Me)$_2$], which contains two monodentate ligands, did react with sulfuric acid to produce ammonia.[6b] Also, a 1A-(Br)–1B(Br) mixture reacted with H$_2$SO$_4$ in THF to give small amounts of ammonia and hydrazine.[37]

Role of Acid. Additional acid was required for the stoichiometric conversion of a 1A(Br)–1B(Br) mixture to ammonia. However, additional acid was not required for some ammonia formation to occur. Thus an acid-free 1A(Br)–1B(Br) mixture in THF (but not in toluene) continued to react, although more slowly than when acid was present, and [NH$_4$]Br, 1A(Br), and MoBr$_3$(triphos) were detected in the infrared spectrum of products after removal of solvent. It is possible that the hydrazido(2–) ligand protons were sufficiently acidic to play the role of acid. The observed increase in the rate of disappearance of 1B(Br) in the presence of acid compared with that in the absence of acid could be due to the displacement of the equilibrium shown in Scheme III by formation of the phosphonium ion (eq 7).

$$PPh_3 + H^+ \rightleftharpoons [Ph_3PH]^+ \qquad (7)$$

Solvent Effects. Solvent has a dramatic effect upon the yields and nature of the reduced nitrogen species formed in acid reactions of bis(dinitrogen) complexes of molybdenum and tungsten and their derivatives, as previously noted by other workers.[6b,7,16] Particularly dramatic effects were noted in this work upon changing from THF to methanol and from THF to benzene or toluene. It was not clear why methanol inhibited the ammonia-forming reaction. Two factors that differentiate methanol and THF and that may be important are the higher dielectric constant and hydrogen bonding ability of the former.

In benzene solution with HBr hydrazine was the major reduced-nitrogen product. A significant difference between the reactions carried out in THF and benzene was the effective concentration of HBr (or HCl) at any given time. Initially, HBr concentrations were similar (large excess), but HBr reacted with THF, hence rapidly lowering the concentration of HBr. Therefore, after a few hours the effective concentration of HBr in THF was zero, but in benzene it remained high throughout the reaction. The same results were observed with other solvents of low dielectric constant that did not react with HBr (or HCl) such as toluene, CH$_2$Cl$_2$, and CF$_3$COOH, although the relative yields of ammonia and hydrazine varied. The presence of hydrazine among the products of the reaction of HCl with 1 in THF may also have reflected the slower rate of reaction of HCl with THF and hence a higher effective acid concentration for a longer period of time. Two dramatic examples of the influence of high effective acid concentration were found in the results from the reactions of a 1A(Br)–1B(Br) mixture with HBr in CF$_3$SO$_3$H and CF$_3$COOH, respectively. The yields of ammonia and hydrazine per mole of Mo were 0.29 and 0.42, and 0.48 and 0.22, respectively.[38]

At what stage of the reaction conditions favor ammonia over hydrazine and vice versa remains to be determined, although at this time we may conclude that it occurs beyond the A–B hydrazido(2–) stage. Hidai[7a] has proposed that the formation of hydrazine in the reaction of cis-[Mo(N$_2$)$_2$(PMe$_2$Ph)$_4$] with HCl in monoglyme arose via a pathway involving protonation of a hydrazido(2–) complex at the metal to form a hydride–hydrazido(2–) complex. We have not detected a metal hydride spectroscopically but cannot totally eliminate the possibility of such a complex in our reactions.

Molybdenum-Containing Products. The molybdenum-containing product in the reaction of HX with 1 in THF was

MoX$_3$(triphos), where X = Br or Cl.[8a] The same reaction carried out in benzene solution in which hydrazine and ammonia were formed led to the isolation of crystalline 4, a molybdenum(III) complex. The filtrate contained some unreacted 1A(Cl). In CH$_2$Cl$_2$ solution MoCl$_3$(triphos) reacted with HX (X = Br, Cl) to form an analogous monoprotonated bidentate triphos complex.[1a] Thus, if MoBr$_3$(triphos) was the product of the ammonia-forming reaction in benzene, it would be converted into 4. The presence of only one molybdenum-containing product suggests one of two possibilities: (i) A single reaction pathway led to the formation of both ammonia and hydrazine and one metal-containing product. (ii) Ammonia and hydrazine were formed in two separate reactions, but coincidently the metal-containing product from each reaction was the same. In the latter case the molybdenum-containing product initially formed after hydrazine formation could be either (i) a molybdenum(II) complex (eq 8) that was oxidized

$$2Mo(NNH_2)^+ \xrightarrow{H^+} N_2H_5^+ + N_2 + 2Mo(II) \qquad (8)$$
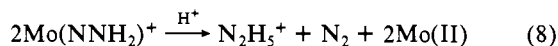
subsequently by HBr to 4, (ii) a molybdenum(IV) hydride that lost H to form 4,[38] or (iii) a molybdenum(IV) complex (eq 9) that

$$Mo(NNH_2)^+ \xrightarrow{H^+} N_2H_5^+ + Mo(IV) \qquad (9)$$
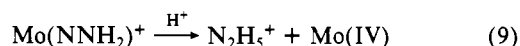
was reduced to 4. The facile opening of one of the chelate rings of the tridentate ligand in the presence of acid poses the question of the role that metal–triphos phosphorus bond cleavage may play during these reduction reactions. The pendant phosphonium ion would provide a high local acid concentration.

Hydrolysis Reactions. The detection of hydrazine upon hydrolysis of a reaction mixture of 1A(Br)–1B(Br) and HBr in THF early in the reaction has a number of important consequences. First, it points to a relationship between the chemistry of 1 and one aspect of the chemistry of nitrogenase. Second, it provides information about one or more steps in the ammonia-forming sequence. Third, a possible relationship between the ammonia- and hydrazine-forming reactions is established.

The relatively rapid buildup of a hydrazine-forming intermediate corresponded very closely with the disappearance of 1B(Br). We are led to conclude that the loss of PPh$_3$ from 1B(Br) leads to the early buildup in concentration of an intermediate in the ammonia-forming reaction that upon reaction with H$_2$O generates hydrazine. No new species other than PPh$_3$ were observed in the ^{31}P NMR spectrum, despite the apparent high concentration of intermediate. It was the addition of a large quantity of water that led to the formation of hydrazine. Small additions had no effect.

If the proposed intermediate is common to both ammonia and hydrazine formation in THF, why was hydrazine not a product, particularly when increments of HBr were added at 1, 3, 6, and 8 h, respectively? Similarly, addition of CF$_3$COOH (20 mol/mol of 1) or CH$_3$COOH (20 mL) early in the reaction produced no hydrazine. Part of the answer may rest with an inherent difference in the reactivity of the metal complex with the acid compared with water: the formation of a species with a Mo=O bond would be a driving force for hydrolysis. Pez and co-workers[10d] have shown that (μ_3-N$_2$)[(η^5:η^5-C$_{10}$H$_8$)(η-C$_5$H$_5$)$_2$Ti$_2$][(η^1:η^5-C$_5$H$_4$)(η-C$_5$H$_5$)$_3$Ti$_2$]·[(η-C$_5$H$_5$)$_2$(C$_6$H$_{14}$O$_3$)Ti]·C$_6$H$_{14}$O$_3$ reacted with THF–H$_2$O to give N$_2$H$_4$ and NH$_3$ but with HCl/diglyme to give mainly N$_2$.

Relevance to Nitrogenase. In biological N$_2$-fixing systems, the nitrogenase enzyme converts N$_2$ to ammonia. The ligation of N$_2$ to a single metal site or a multimetal site is presently the only reasonable model for the initial uptake of N$_2$ by nitrogenase. Studies of nitrogenase have led to the identification of two properties of the substrate N$_2$ *during* turnover of the enzyme. These are (i) the N$_2$-dependent formation of HD in the presence of D$_2$[19,41] and (ii) the detection of hydrazine upon hydrolysis of the enzyme.[18] On the basis of the chemistry of hydrazido(2–) complexes of molybdenum and tungsten, it has been proposed that

(37) Yields of N$_2$, NH$_3$, and N$_2$H$_4$ per mole of Mo were 0.39, 0.05, and 0.12, respectively.

(38) George, T. A.; Koczon, L. M., unpublished results.

(39) (a) The reaction of metal hydrides with halocarbons is well documented. One example involving a tungsten–hydrazido–hydride complex reacting with CH$_2$Cl$_2$ has been reported.[40] (b) Kao, S. C.; Spillett, C. T.; Ash, C.; Lusk, R.; Park, Y. K.; Darensbourg, M. Y. *Organometallics* **1985**, *4*, 83–91 and references cited therein.

(40) Chatt, J.; Fakley, M. E.; Hitchcock, P. B.; Richards, R. L.; Luong-Thi, N. T. *J. Chem. Soc., Dalton Trans.* **1982**, 345–352.

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the dinitrogen hydride intermediate that liberates hydrazine upon hydrolysis is the hydrazido(2–) ligand.[18] The present work suggests that hydrazine is liberated from an intermediate dinitrogen hydride that is formed following loss of phosphine and probably following electron transfer. Successful identification of the intermediate in this molybdenum system may provide a chemical and structural model for a dinitrogen hydride intermediate during N_2 fixation by nitrogenase.

Summary

In this paper we have examined reactions of **1** and **2** with HBr and HCl in a number of different solvents. In all cases a pair of isomeric hydrazido(2–) complexes was formed. The isomers arose as a consequence of the inequivalence of the two N_2 ligands in **1** and **2**, which was caused by the stereochemistry at the central phosphorus atom of triphos. Thus, the phenyl group bonded to the central phosphorus atom of triphos could be on the same side of the plane of four phosphorus (P_4) atoms as the hydrazido(2–) ligand (**A** isomer) or on the other side (**B** isomer). Mixtures of the **A**–**B** hydrazido(2–) complexes reacted with HBr in THF solution to yield ammonia and MoBr₃(triphos). However, in benzene solution both ammonia and hydrazine were formed together with a novel molybdenum(III) complex **4**. When a large quantity of water was added to the mixture of **1A(Br)–1B(Br)** and HBr in THF after ca. 1 h of reaction, a significant quantity of hydrazine was detected: a reaction that normally gave no more than a trace of hydrazine after 60 h. The formation of free hydrazine as an intermediate in the ammonia-forming reaction was shown not to be occurring. Experiments carried out with mixtures of the **A**–**B** hydrazido(2–) complexes, formed by reaction of **1** or **2** and HBr or HCl in the absence of solvent, led to the observations that the monodentate phosphine is labile in the **B** series but not in the **A** series. Thus addition of PPh₂Me to a **1A(Br)–1B(Br)** mixture led to the formation of **2B(Br)** but not **2A(Br)**.

Addition of PMe₂Ph to a **1A(Br)–1B(Br)** mixture in THF resulted in the formation of **3B(Br)** with very little ammonia being formed. In this way it was possible to prepare both **2B(Cl)** and **3B(Cl)** and separate them from **1A(Cl)**. It was not possible to isolate the more reactive **1B(Br)** or **1B(Cl)**. The addition of excess PMe₂Ph to a mixture of **1A(Br)–1B(Br)** significantly inhibited the ammonia-forming reactions.

The results from the work support the following conclusions.

(1) The stoichiometry of the reaction of **1** with HBr in THF solution is best represented by eq 1 in which two molybdenum centers are involved in the reduction of one N_2 ligand to give 2 mol of ammonia.

(2) The loss of PPh₃ from **1B(Br)** or **1B(Cl)** appears to be the crucial next step on the pathway to ammonia formation. Loss of PPh₃ is reversible, and the reaction is inhibited by addition of excess PPh₃ or a more basic phosphine.

(3) Electron transfer follows phosphine loss.

(4) Following loss of PPh₃ from **1B(Br)** or **1B(Cl)** in THF solution, an intermediate is believed to be formed relatively rapidly. This intermediate if not disturbed proceeds to yield ammonia and dinitrogen. However, if excess water is added to the intermediate significant amounts of hydrazine are detected.

(5) The reactions of this intermediate in yielding hydrazine upon hydrolysis resembles similar behavior exhibited by nitrogenase and suggests a chemical resemblance between the two systems at this particular stage in the reduction of dinitrogen.

Experimental Section

General Procedures. All preparations and reactions were carried out either under a dinitrogen atmosphere or in vacuo. Compounds were handled in a water- and oxygen-free environment, which was provided by use of Schlenk equipment,[42] glovebags, and a Vacuum Atmospheres Corp. drybox. A general utility vacuum line capable of attaining pressures <10⁻⁶ torr was employed for all reactions in which anhydrous acids were used, and N_2 evolution measurements were made by Toepler pump.

Elemental analyses were performed by either Schwarzkopf Microanalytical Laboratory, Inc., Woodside, NY, or Galbraith Laboratories, Inc., Knoxville, TN.

Reagents and Materials. All solvents were reagent grade and purchased from commercial sources. Solvents were rigorously dried by heating at reflux over an appropriate drying agent followed by distillation in a dinitrogen atmosphere and were saturated with dinitrogen immediately before use by bubbling the gas through the solvent for a minimum of 0.5 h.

Chemicals were purchased from commercial sources and used without purification except for the following. Hydrogen halides were purified by a series of trap-to-trap distillations on the vacuum line and stored in glass bulbs. Triphenylphosphine was recrystallized from a benzene/methanol solution. Triphenylphosphonium bromide was made by a known procedure,[43] and triphenylphosphonium tetrafluoraborate was prepared similarly (triphenylphosphine and anhydrous tetrafluoroboric acid etherate). Dinitrogen-30 (^{15}N, 99.89 atom %; ^{14}N, 0.11 atom %; N_2, 99.99 mol %; CO_2, 0.01 mol %) was obtained from Monsanto Research Corp. Mound Facility, Miamisburg, OH 45342, and [$^{15}N_2H_6$]SO₄ ($^{15}N^{15}N$ 95%) was obtained from Cambridge Isotope Laboratories, Cambridge, MA 02139.

The following complexes were prepared by published procedures: MoCl₄(THF)₂[44] (when this complex was filtered, it was washed with dry acetone, THF, and finally pentane before being dried in vacuo), *trans*-Mo(N₂)₂(dppe)₂[45] (dppe = Ph₂PCH₂CH₂PPh₂), and *trans*-Mo(N₂)₂-(dppe)(PMePh₂)₂.[46] Improved methods for the preparation of MoCl₃-(triphos)[46] and *trans*-Mo(N₂)₂(triphos)(PPh₃) (**1**)[46] are given below.

MoCl₃(triphos). To a THF (50 mL) solution of PPh₃ (1.87 g, 7.14 mmol) and triphos (1.31 g, 2.45 mmol) were added 1.00 g (2.62 mmol) of MoCl₄(THF)₂ and 0.47 g (4.0 mmol) of amalgamated granular tin. Immediately upon addition of MoCl₄(THF)₂ a dark brown solid appeared. Within seconds the entire reaction mixture became a dark brown gel. The gel broke down over several minutes to form a suspension of a dark brown solid that gradually changed color to tan and finally to yellow. The reaction mixture was stirred for 8 h at room temperature (up to 48 h for larger scale preparations). The reaction mixture was swirled to suspend the product, then decanted from the tin onto a frit, and the suspension filtered. Successive portions of THF were added to the reaction flask to remove any remaining product from the reaction flask and to wash the product on the frit. The solid was dried in vacuo. The yield of bright yellow MoCl₃(triphos) was 1.67 g (2.26 mmol, 92.4%). Yields are lower when PPh₃ is omitted from the reaction.

***trans*-Mo(N₂)₂(triphos)(PPh₃) (1).** In the drybox, a 1% sodium amalgam (0.80 g Na, 80 g Hg) was added to a Fischer and Porter bottle (250 mL) containing MoCl₃(triphos) (4.0 g, 5.4 mmol), PPh₃ (2.8 g, 11 mmol), THF (100 mL), and an egg-shaped magnetic stirbar. The vessel was sealed, removed from the drybox, and cooled to 0 °C in an ice bath. The bottle was connected to a dinitrogen cylinder, the connecting line flushed, and the bottle pressurized to 60 psi. The reaction mixture was stirred for 6 h at 0 °C and a further 14 h at room temperature. At this time the excess pressure was released and the bottle opened in a glovebag. The dark solution was decanted from the amalgam and filtered through Celite on a fine frit. The reaction bottle and frit were washed with THF (15 mL). Dinitrogen was bubbled through the dark orange filtrate to reduce the volume to ca. 50 mL. Methanol (ca. 20 mL) was added slowly to this solution. Within 0.2 h orange crystals formed. Methanol (ca. 2 vol) was added *slowly* over 4 h to complete precipitation. The orange crystals were filtered off, washed with methanol and pentane, and suction dried. The yield of orange-red **1·THF** was 3.6 g (3.7 mmol, 69%). $^{31}P\{^1H\}$ NMR (C₆H₆, PhP$_a$(CH₂CH₂P$_b$Ph₂)₂, Ph₃P$_x$): δ 101.8 (d, 1, $^2J_{P_aP_b}$ = 0.0 Hz, $^2J_{P_aP_x}$ = 113.6 Hz, P$_a$), 63.6 (d, 2, $^2J_{P_bP_x}$ = 14.0 Hz, P$_b$), 52.5 (dt, 1, P$_x$). IR (KBr): ν_{NN} 2035 (w), 1950 (vs) cm⁻¹.

Somewhat lower yields were obtained in similar reactions by adding methanol (2 vol) and heptane (1 vol) to the original filtrate and allowing the crystals to precipitate.

Reduction times varied but were never less than 3 h at 0 °C followed by 12 h at room temperature.

The dinitrogen-30-labeled complex was prepared similarly. IR (KBr): ν_{15N15N} 1892 (vs) cm⁻¹ (2025 (w), 1970 (m), 1932 (w) cm⁻¹).

***trans*-Mo(N₂)₂(triphos)(PMePh₂) (2).** This complex was prepared similarly to **1**. Sodium amalgam (0.4 g Na, 40 g Hg), MoCl₃(triphos) (2.0 g, 2.7 mmol), PMePh₂ (0.80 mL, 3.8 mmol), THF (40 mL), N_2 (60 psi). Addition of methanol produced a dark oil, which slowly dissolved and deposited clusters of crystals. The yield of orange crystalline product was 1.5 g (1.6 mmol, 61%). Anal. Calcd for C₄₇H₄₆MoN₄P₄·¹/₂THF:

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C, 63.78; H, 5.46; N, 6.07. Found: C, 63.20; H, 5.41; N, 5.70. ^{1}H NMR (C$_6$D$_6$, 90 MHz): δ 1.8 (d, $^2J_{PH}$ = 3.6 Hz, Ph$_2$PCH$_3$). ^{31}P{^{1}H} NMR (C$_6$H$_6$, PhP$_a$(CH$_2$CH$_2$P$_b$Ph$_2$)$_2$, Ph$_3$P$_x$): δ 102.8 (d, 1, $^2J_{P_aP_b}$ = 0.0 Hz, $^2J_{P_aP_x}$ = 112.3 Hz, P$_a$), 64.6 (d, 2, $^2J_{P_bP_x}$ = 14.2 Hz, P$_b$), 22.7 (dt, 1, P$_x$). IR (KBr): ν_{NN} 2009 (m), 1960 (vs) cm^{-1}.

trans-Mo(N$_2$)$_2$(triphos)(PMe$_2$Ph) (3). This compound could not be prepared pure. IR (KBr): ν_{NN} 1970 cm^{-1}.

trans-[MoF(NNH$_2$)(triphos)(PPh$_3$)]BF$_4$. 1·$^1/_2$THF (1.1099 g, 1.127 mmol) and [Ph$_3$PH]BF$_4$ (1.5825 g, 4.520 mmol) were stirred together in THF (20 mL). After 18 h, the mixture was filtered and the solid washed with THF (3 mL). Dinitrogen was bubbled through the orange filtrate until the volume was about 10 mL. Diethyl ether (2 mL) was added, and the brown-white solid that formed was removed by filtration. Addition of heptane (5 mL) produced an oil that partially solidified after 2 h. The pale orange supernatant was decanted and the oil dissolved in 6 mL of a methanol–dichloromethane (1:1 by vol) solvent mixture. Crystals were obtained by adding pentane (2 mL) and storing at 0 °C for 2 days. The orange-looking crystals were filtered, washed with pentane, and suction dried. The yield was 0.4964 g (0.4826 mmol, 42.8%). Anal. Calcd. for C$_{52}$H$_{50}$BF$_5$MoN$_2$P$_4$·$^1/_2$CH$_2$Cl$_2$: C, 58.86; H, 4.81; N, 2.62. Found: C, 58.60; H, 5.01; N, 2.47. ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$, PhP$_a$(CH$_2$CH$_2$P$_b$Ph$_2$)$_2$, Ph$_3$P$_x$): δ 83.2 (dd, 1, $^2J_{P_aP_b}$ = 0 Hz, $^2J_{P_aP_x}$ = 171.4 Hz, $^2J_{P_aF}$ = 34.4 Hz, P$_a$), 51.7 (dd, 2, $^2J_{P_bP_x}$ = 17.4 Hz, $^2J_{P_bF}$ = 46.5 Hz, P$_b$), 30.3 (ddt, 1, $^2J_{P_xF}$ = 24.3 Hz, P$_x$). IR (KBr): ν_{NH} 3330, 3255, 3155 cm^{-1}. Usually, a small amount of impurity was present in crystals of product that had the following poorly resolved ^{31}P NMR spectrum (CH$_2$Cl$_2$): δ 108.4 (t, 1, $^2J_{P_aF}$ = 33.8 Hz, P$_a$), 88.1 (t, 2, $^2J_{P_bF}$ = 33.3 Hz, P$_b$). No resonance due to coordinated PPh$_3$ was observed. When the reaction of 1 with excess HBF$_4$·OEt$_2$ in THF solution was followed by ^{31}P{^{1}H} NMR spectroscopy a second (triphos–PPh$_3$)-containing complex was observed in low yield: δ 72.8 (dd, $^2J_{P_aP_b}$ = 0 Hz, $^2J_{P_aP_x}$ = 185.7, $^2J_{P_aF}$ = 20.7 Hz, P$_a$), 39.6 (dd, $^2J_{P_bP_x}$ = 17.5, $^2J_{P_bF}$ = 19.3 Hz, P$_b$), 29.1 (ddt, $^2J_{P_xF}$ = 41.7 Hz, P$_x$).

General Procedure for Acid Reactions. The bis(dinitrogen) complex (0.1000–0.2000 g, 0.1000–0.2000 mmol) to be reacted was placed in a tared round-bottom flask and its mass determined. (In those reactions in which a triphenylphosphonium salt was used, the solid acid was added and the flask reweighed.) A magnetic stirbar was added and the flask sealed with a high-vacuum stopcock by which the apparatus was attached to the vacuum line. The flask was evacuated until less than 10^{-6} torr of residual pressure remained. The flask was immersed in liquid nitrogen and cooled to −196 °C. Hydrogen halide (2–3 mmol) was distilled into the flask, followed by the appropriate solvent 6–15 mL). The solvent had previously been degassed by several freeze–pump–thaw cycles. After all transfers were complete, the flask was evacuated to less than 10^{-6} torr at −196 °C.

The reactions were initiated by closing the stopcock to isolate the reaction mixture and then warming the flask to the desired temperature, usually room temperature. At about 0 °C, vigorous bubbling was observed and a homogeneous solution resulted (except when insoluble triphenylphosphonium salts were used) that was golden in color.

The evolution of N$_2$ was monitored by allowing the reaction to proceed for the desired length of time. The reaction flask was cooled (−196 °C). After the solution had frozen, N$_2$ was measured by quantitative transfer to a calibrated part of the vacuum line. Frequently, a gold solid would appear after ca. 0.5 h.

To isolate the molybdenum-containing product in the reaction all volatiles were removed by vacuum distillation. The oily residue was stirred with methanol (20 mL) for several hours. The suspension was filtered through a preweighed frit. Successive portions of methanol and pentane were used to transfer all the solid from the flask and wash the solid. The solid was dried in a stream of dinitrogen. Analytically pure samples of MoBr$_3$(triphos) (≥94%) and MoCl$_3$(triphos) were obtained.

Ammonia and hydrazine were analyzed in one of two ways. (i) Several drops of aqueous hydrogen bromide (48%) were added to the filtrate from the isolation of the molybdenum complex, and volatiles were removed by vacuum distillation. Dichloromethane (15 mL) was added to the residue and extracted with three or four portions of water. The combined aqueous extract was added to a 25-mL volumetric flask and the volume brought up to the mark. (ii) Volatiles were removed from the original reaction mixture in vacuo, and the oily residue was extracted with dichloromethane and water as outlined above. The oily appearance of the residue was due to 1,4-dibromobutane and 4-bromobutanol (comparison with authentic samples, gc retention times).

The aqueous extract was analyzed for ammonia by the indophenol method[47] (three 50-μL aliquots, three blanks, and three 0.0101 M ammonium chloride standards) and for hydrazine by the procedure of Watt and Chrisp[48] using p-(dimethylamino)benzaldehyde (1.0-mL aliquot).

Dinitrogen evolution and ammonia and hydrazine analyses data are given in Tables I–III.

Acid Reactions with No Solvent. These reactions using HBr or HCl were carried out similarly to those described above except no solvent was added. The acid condensed as a white solid upon the surface of the orange bis(dinitrogen) complex. When the mixture was warmed to room temperature, a dramatic color change (orange to green) occurred during the very brief period of time that the acid was in the liquid phase. Bubbling was often observed at this point. Usually, five to ten freeze-thaw cycles with stirring of the solid were necessary to complete the reaction (1.0 mol of N$_2$/mol of Mo complex). Extent of reaction was monitored by using the Toepler pump. The final solid was a green-brown color.

Crystalline bis(dinitrogen) complexes were finely ground in a mortar before use.

Following the reaction with acid, acid was left or removed depending upon the subsequent reaction. Typically, acid was removed in vacuo and the solid pumped on for at least 0.5 h. Frequently, cycles of dissolution and evaporation using CH$_2$Cl$_2$ were carried out to ensure minimum acid concentration. However, it is possible that acid remains due to strong hydrogen bonding with the hydrazido(2−) complexes.

Monitoring Reactions by ^{31}P NMR Spectroscopy. Many reactions were monitored by ^{31}P{^{1}H} NMR spectroscopy. The reactions between acid and bis(dinitrogen) complexes were carried out as detailed above until the first mole of N$_2$ was evolved. (In those reactions carried out in a solvent, this was judged to have occurred when the reaction mixture was almost homogeneous.) To those reactions carried out without solvent was added the appropriate solvent. Solutions were rapidly filtered into an NMR tube, cooled at −78 °C. The capped tube was inserted into the NMR probe set at the desired temperature (−60 or −40 °C), and the spectrum (zero time) was recorded. The tube was removed and warmed to room temperature. After a fixed period of time the tube was cooled again and the spectrum recorded. This process was repeated at various time intervals during the reaction.

[MoCl(NNH$_2$)(triphos)(PPh$_3$)]Cl (1A(Cl)) and [MoCl(NNH$_2$)(triphos)(PPhMe$_2$)]Cl (3B(Cl)). HCl (9.2 mmol) was added to solid 1·$^1/_2$THF (0.45 g, 0.46 mmol) at −196 °C. As the temperature was allowed to increase, the solid rapidly turned green. Following six freeze–thaw cycles, excess acid was removed (in vacuo). Toluene (35 mL) was condensed onto the green-brown solid and the mixture allowed to warm with stirring. A yellow solid began to precipitate as the reaction approached room temperature. After a few minutes (<0.1 h), the yellow solid was removed by filtration and PPhMe$_2$ (6 drops, excess) added to the filtrate. After stirring for 18 h, brown crystalline 1A(Cl) was filtered off and washed with toluene and pentane. The yield was 0.10 g (0.09 mmol, 20%). Anal. Calcd for C$_{52}$H$_{50}$Cl$_2$MoN$_2$P$_4$·C$_7$H$_8$: C, 64.76; H, 5.34; N, 2.56. Found: C, 64.86; H, 5.59; N, 2.67. ^{1}H NMR (CD$_2$Cl$_2$, 90 MHz): δ 2.4 (s, CH$_3$), 2.6 (br, CH$_2$), 6.8–7.8 (m, Ph), 8.5 (br, NH$_2$; disappeared upon adding of D$_2$O). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$, PhP$_a$(CH$_2$CH$_2$P$_b$Ph$_2$)$_2$, Ph$_3$P$_x$): δ 92.0 (d, 1, $^2J_{P_aP_b}$ = 0 Hz, $^2J_{P_aP_x}$ = 152.2 Hz, P$_a$), 57.5 (d, 2, $^2J_{P_bP_x}$ = 16.6 Hz, P$_b$), 36.1 (dt, 1, P$_x$). IR (KBr): ν_{NH} 3307 (w), 2872 (m, br), 2575 (m, vbr) cm^{-1}.

The volume of the green-brown filtrate from the above reaction was reduced by half in vacuo, and the filtrate was allowed to stand. After 18 h, a lime green powder was filtered off and washed with toluene and pentane. The yield of 3B(Cl) was 0.07 g (0.08 mmol, 17%). Anal. Calcd for C$_{42}$H$_{46}$Cl$_2$MoN$_2$P$_4$·$^1/_2$C$_7$H$_8$: C, 59.38; H, 5.48; N, 3.04. Found: C, 58.82; H, 5.52; N, 3.02. ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$, PhP$_a$-(CH$_2$CH$_2$P$_b$Ph$_2$)$_2$, Ph$_3$P$_x$): δ 70.6 (d, 1, $^2J_{P_aP_b}$ = 0.0 Hz, $^2J_{P_aP_x}$ = 171.0 Hz, P$_a$), 39.8 (d, 2, $^2J_{P_bP_x}$ = 19.3 Hz, P$_b$), 0.6 (dt, P$_x$). IR (KBr): ν_{NH} 3210 (w), 2895 (m), 2730 (s, br) cm^{-1}.

In a similar reaction, PPh$_2$Me (0.25 mL) was added dropwise with swirling to a toluene solution of 1A(Cl)–1B(Cl). From this solution crystals of both 1A(Cl) and 2B(Cl) were obtained in less than 10% yield, respectively.[31]

Isolation of MoBr$_4$(Ph$_2$PCH$_2$CH$_2$PPhCH$_2$CH$_2$PHPh$_2$) (4). HBr (3.0 mmol) and benzene (20 mL) were condensed onto solid 1·$^1/_2$THF (0.20 g, 0.20 mmol) at −196 °C. The mixture was allowed to warm to room temperature and was stirred for 48 h. The initial green solution became yellow-gold with a brownish orange solid. Volatiles were removed in vacuo and CH$_2$Cl$_2$ (20 mL) added. The solid dissolved promptly to give a reddish brown solution with a light, flocculent solid suspended in it. This solid was immediately filtered off and shown to be a mixture of N$_2$H$_5$Br and NH$_4$Br according to the IR spectrum. Within 0.5–1 h of dissolution, crystals of 4 began to form. After 24 h, the dark orange crystals were filtered off, washed with CH$_2$Cl$_2$ and pentane, and

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dried in a stream of N_2. The yield was 50%. Anal. Calcd for **4**·[1]/$_2CH_2Cl_2$, $C_{34.5}H_{35}Br_4ClMoP_3$: C, 41.8; H, 3.55; Br, 32.2; P, 9.37; Mo, 9.67. Found: C, 41.6; H, 3.62; Br, 33.0; P, 9.42; Mo, 9.52.

Hydrolysis Experiments. In separate experiments, the reaction of **1** with HBr in THF (assembled as described above) was stopped by removing volatiles in vacuo. To the residue were added CH_2Cl_2 (10 mL) and increments (ca. 3 mL) of water (25 mL total). Ammonia and hydrazine were analyzed for as described above. In those experiments carried out for less than 12 h, a mixture of **1A**(Br) and **1B**(Br) was prepared in the absence of solvent to which THF was added. The 12-h experiment was carried out by mixing **1**, HBr, and THF.

Instrumentation and Techniques. IR spectra (4000–200 cm⁻¹) were recorded on a Perkin-Elmer 283 spectrophotometer. Solid samples were run as potassium bromide pellets. ¹H NMR spectra were recorded by using a Varian EM-390 (90 MHz) spectrometer or a Nicolet NMC 360 (361.06 MHz) spectrometer with a 1180E data processor. All ³¹P NMR spectra were run on a Nicolet NMC 360 (146.17 MHz) spectrometer

using a 12-mm tube and broadband decoupling of protons. About 10% by volume of the appropriate perdeuterated solvent was added for locking purposes. All spectra were recorded at ambient temperature unless otherwise stated. All chemical shifts are reported in ppm downfield from Me_4Si (¹H) or 85% H_3PO_4 (³¹P) with positive values being to lower field.

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Syntheses, Structures, and Mechanism of Formation of *trans*-Chlorohydrobis(trimethylphosphine)platinum(II) and *trans*-Dihydrobis(trimethylphosphine)platinum(II). Energetics of Cis–Trans Isomerization

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The reaction between *cis*-$PtCl_2(PMe_3)_2$ (**1**) and Na(np) (np = naphthalene) under a H_2 atmosphere yields *trans*-$PtHCl(PMe_3)_2$ (**2**). Addition of a second 1 equiv of Na(np) produces *cis*- and *trans*-$PtH_2(PMe_3)_2$ (*cis*-**3** and *trans*-**3**). Complex **3** was crystallized in the presence of np to yield *trans*-**3**·np. Both the latter complex and **2** were characterized by X-ray diffraction at −145 °C. Crystals of **2** belong to the space group $P2_1/n$ with $Z = 4$, $a = 10.241$ (5) Å, $a = 19.012$ (11) Å, $c = 6.300$ (4) Å, $\beta = 96.36$ (1)°, and $V = 1227$ (1) Å³. For the 1259 unique reflections that had $I_o > 3\sigma(I_o)$ the Patterson solution and least-squares refinement led to final $R = 0.063$ and $R_w = 0.082$. Crystals of *trans*-**3**·np belong to the space group $A2/m$ with $Z = 2$, $a = 6.146$ (2) Å, $b = 10.204$ (3) Å, $c = 14.925$ (4) Å, $\beta = 99.17$ (1)°, and $V = 936$ (1) Å³. For the 864 unique reflections that had $I_o > 3\sigma(I_o)$ solution by direct methods and least-squares refinement led to final $R = 0.049$ and $R_w = 0.062$. Complex **2** adopts a square-planar geometry, P(1)–Pt–P(2) = 176.0 (2)°, with the Pt–Cl distance, 2.423 (6) Å, significantly lengthened because of the trans influence of hydride. The *trans*-**3**·np complex exhibits no interaction between *trans*-**3** and np, verifying the role of np as a crystallization agent. Electronic spectra of *trans*-**3**/np mixtures in *n*-hexane solvent did not provide evidence for a charge-transfer complex. Crystals of *trans*-**3**·np are extremely sensitive and lose H_2 under a N_2 atmosphere. They are stable under a H_2 atmosphere. In solution **3** exists as an equilibrium mixture of cis and trans isomers with the highest cis/trans ratios being observed in polar solvents (e.g. 3.3 in DMF). Study of the equilibrium ratios in acetone between −40 and −80 °C yielded $\Delta H = 0.3 \pm 0.1$ kcal/mol and $\Delta S = +3.7$ cal/(mol K) for the *trans*-**3** to *cis*-**3** equilibrium. The difference in reactivities and stabilities of the cis isomer between **3** and bulkier analogues is attributed to steric effects of the phosphine ligands. The source of hydride for the conversion **1** → **2** has been confirmed to be H_2 by deuterium-labeling studies. Analysis of organic products shows that Na(np) functions only as an electron-transfer agent for the **1** → **2** → **3** conversion. Addition of H_2 to dinuclear intermediates explains the sequential formation of **2** and **3**.

Introduction

Dihydrobis(phosphine)platinum(II) complexes exhibit a rich chemistry,[2-16] and have been postulated as intermediates in the catalysis of olefin hydrogenation[17] and the water gas shift reaction.[18] Previous experimental studies have been limited to sterically hindered compounds. Several theoretical investigations of unhindered $PtH_2(PH_3)_2$ and $PtH_2(PMe_3)_2$ systems have examined the mechanism of oxidative addition of hydrogen to the platinum center.[19-24] Important concerns are the facility of

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