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Reactions of Mono(dinitrogen) Complexes of Molybdenum. Isolation and Characterization of Hydrazido(2–) and Mono- and Dihydride Complexes. Crystal Structure of $MoBr[PhP(CH_2CH_2PPh_2)_2](Me_2PCH_2PMe_2)\cdot{}^1/_2C_5H_{12}$[1]

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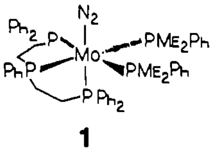
Received January 11, 1990

The reactions of a series of mono(dinitrogen) complexes of molybdenum $Mo(N_2)(dpepp)(L_2)$ [where dpepp = $PhP(CH_2CH_2PPh_2)_2$ and L_2 = 2 PMe_2Ph (**1**), $Me_2PCH_2PMe_2$ (dmpm) (**2**), 1,2-$(Me_2As)_2C_6H_4$ (diars) (**3**), $Ph_2PCH_2PPh_2$ (dppm) (**4**), $Ph_2PCH_2CH_2PPh_2$ (dppe) (**5**)] with acids are reported. Reactions of **1** with excess HX (X = Br, Cl) in the solid state or HX (2 mol) in toluene led to the isolation of the hydrazido(2–) complexes $[MoX(NNH_2)(\eta^2\text{-dpepp})(PMe_2Ph)_2]X$ [**6** (X = Cl) and **7** (X = Br)] in which dpepp is bidentate. Similar results were obtained with CF_3SO_3H. Heating a toluene solution of **7** led to the loss of one PMe_2Ph and reincorporation of the pendant phosphine to form *mer*-$[MoBr(NNH_2)(dpepp)(PMe_2Ph)]Br$. Complexes **6** and **7** yielded ammonia and hydrazine when treated with HCl and HBr. The pendant phosphine can be protonated (HBr) and alkylated. Complex **1** reacted with HBr (1 mol) to initially (0.25 h) produce an equimolar mixture of **1** and **7**. These two complexes reacted (15 h) to give an almost quantitative yield of $Mo(H)Br(dpepp)(PMe_2Ph)$ (**10**). With HBr (1 mol), **10** produced $Mo(H)_2Br_2(dpepp)(PMe_2Ph)$. Solid **2** reacted with excess HX (X = Br, Cl, SO_3CF_3) to produce the unstable hydrazido(2–) dication $[Mo(NNH_2)(dpepp)(dmpm)]^{2+}$ without loss of a ligand. In solution the stability of the dication increased with decreasing basicity of the anion: Cl < Br < SO_3CF_3. $[Mo(NNH_2)(dpepp)(dmpm)][SO_3CF_3]_2$ was isolated. Decomposition of the dication in solution led to loss of N_2 and formation of a pair of isomeric eight-coordinate dihydrides, $[Mo(H)_2Cl(dpepp)(dmpm)][HCl_2]$ (**16**). Reaction of **2** with HBr (1 mol) in benzene led to the isolation of $[Mo(H)_2Br(dpepp)(dmpm)]Br$ (**13**, single isomer), $MoBr(dpepp)(dmpm)$ (**14**), and $Mo(H)Br(dpepp)(dmpm)$ (**15**, single isomer). A similar reaction with HCl produced $Mo(H)Cl(dpepp)(dmpm)$ (**17**) as a pair of isomers. Complex **14** crystallizes with 0.5 mol of pentane in the monoclinic space group $P2_1/c$ with a = 12.452 (2) Å, b = 15.738 (2) Å, c = 21.677 (3) Å, β = 98.94 (1)°, and Z = 4. Complexes **3**–**5** gave evidence of hydrazido(2–) formation upon treatment with acid, but in solution N_2 was rapidly evolved and hydrides were formed. Structural assignments of new complexes are based upon ^{31}P and ^1H NMR spectral data. Dpepp is shown to adopt both *fac* and *mer* configurations. The protonation of metal–N_2 complexes is discussed.

Introduction

The enzyme nitrogenase is responsible for the reduction of N_2 to ammonia. Despite extensive studies, the site at which N_2 binds and is reduced in nitrogenase remains unknown.[3] Thus efforts to prepare synthetic analogues that model the behavior of nitrogenase are based upon little information. Low-valent molybdenum and tungsten complexes form bis(dinitrogen) complexes, and in certain cases the complexes react with strong acid to form ammonia, often in high yield.[4-7] In addition, these same complexes afford the only intermediates that have been detected and identified during the reduction of N_2 to ammonia.[8] In this paper we report (i) the first examples of intermediates isolated during the reduction of mono(dinitrogen) complexes to ammonia (very few of the more than 100 known mono(dinitrogen) complexes afford more than a trace of ammonia) and (ii) proof that it is not necessary to have at least two N_2 ligands attached to a single metal in order to afford ammonia upon treatment with acid as had been supposed previously. In addition to the hydrazido(2–) complexes prepared, we also report many new metal hydrides formed following the dehydrohalogenation and subsequent denitrification of hydrazido(2–) complexes. The mono(dinitrogen) complexes $Mo(N_2)(dpepp)(L_2)$ (**1**–**5**) studied are as follows, where dpepp = $PhP(CH_2CH_2PPh_2)_2$:[9-11] **1**, L_2 = PMe_2Ph; **2**, L_2 = $Me_2PCH_2PMe_2$ (dmpm); **3**, L_2 = 1,2-$(Me_2As)_2C_6H_4$ (diars); **4**, L_2 = $Ph_2PCH_2PPh_2$ (dppm); **5**, L_2 = $Ph_2PCH_2CH_2PPh_2$ (dppe).



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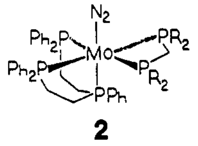

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Results

Isolation and Characterization of Hydrazido(2–) Complexes from 1 (Scheme I). The reaction of **1** with either 2 mol of HX (X = Br, Cl) in toluene or excess (ca. 20 mol) of HX in the absence of solvent afforded a hydrazido(2–) complex in moderate yield (eq 1). The latter method was better. Addition of THF

$$Mo(N_2)(dpepp)(PMe_2Ph)_2 \xrightarrow{HX} [MoX(NNH_2)(\eta^2\text{-dpepp})(PMe_2Ph)_2]X \quad (1)$$
$$X = Cl\ (\mathbf{6}),\ Br\ (\mathbf{7})$$

to the green-brown solid (X = Cl) resulted in a solution from which **6** was isolated. A THF-insoluble fraction was also obtained, and although not characterized, it did afford substantial amounts of ammonia and hydrazine when treated with HBr in CH_2Cl_2.

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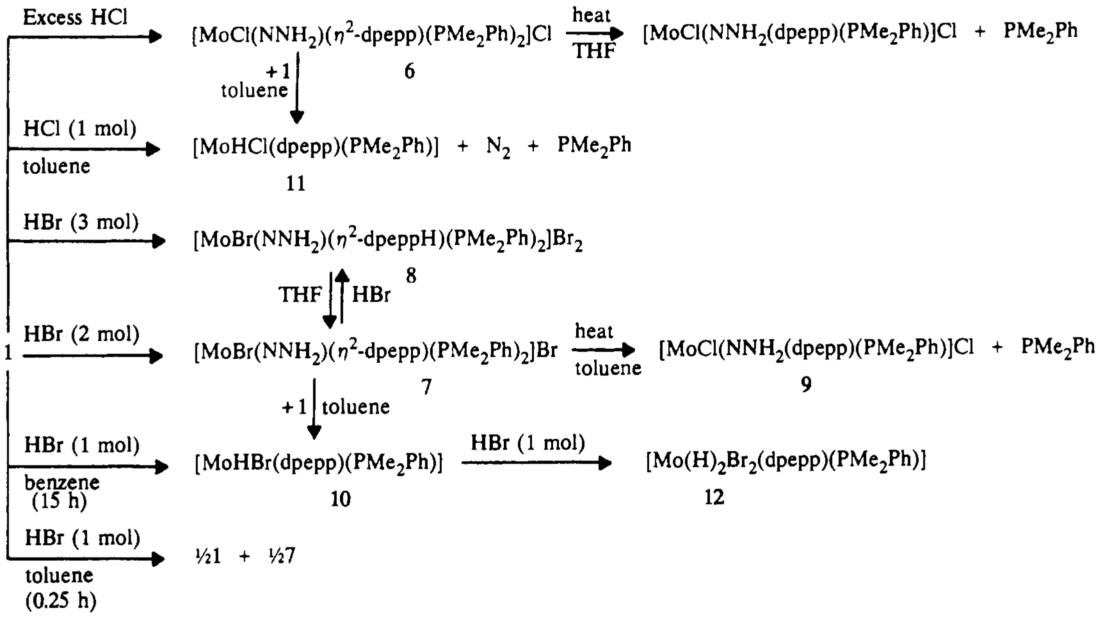
Scheme I. Reactions of 1 with HBr and HCl



The IR spectrum of **6** showed an extremely broad absorption at 2800–2500 cm^{-1} corresponding to ν(NH) of a hydrazido(2–) ligand that is hydrogen-bonded. Exchange of chloride ion with BPh_4^- resulted in ν(NH) appearing at 3350 (w) and 3250 (m) cm^{-1}. More compelling evidence for the presence of the hydrazido(2–) ligand was obtained from the ^{15}N NMR spectrum. Richards and co-workers[12] have reported extensive data for hydrazido(2–) complexes of molybdenum with chemical shift values for N_α (MoN) falling in the range –68 ± 10 ppm and those for N_β in the range –226 ± 12 ppm, relative to CD_3NO_2. ^{15}N NMR data for hydrazido(2–) complexes reported in this paper fall within these ranges.

The ^{31}P NMR spectrum of **6** showed the presence of four coordinated phosphorus atoms, and the large coupling constants confirmed that they occupy a plane within the coordination sphere.[6a,14] A fifth phosphorus atom was observed as a doublet at δ –17.19 ppm, very near the position for the terminal phosphorus atom of free dpepp. The data suggest that dpepp is behaving as a bidentate ligand with P_a (center) and P_b coordinated and P_c pendant. In the ^1H NMR spectrum the (NNH_2) protons appeared as a broad resonance centered at 10.6 ppm that shifted to 5.2 and 5.4 ppm in the BPh_4 and PF_6 salts, respectively. An X-ray crystal structure of $FeCl_2(dpepp)_2$ revealed that one phosphorus atom of each dpepp is pendant.[15]

Initially, only a small quantity of **7** was obtained from the reaction of **1** and HBr, with the majority of material being THF-insoluble. However, continuous extraction of the solid with THF or, better, heating the solid with THF afforded a red solution from which **7** was obtained in yields greater than 90%. A small quantity of $[HPMe_2Ph]Br$ was also isolated. IR and ^{15}N, ^{31}P, and ^1H NMR spectral data were all consistent with **7** being analogous to **6**.

Reaction of **1** with 3 mol of HBr in toluene resulted in the formation of **8** in 93% yield. The IR spectrum showed ν(PH) at 2360 cm^{-1} as well as ν(NH) at 2700–2500 cm^{-1}. The ^{31}P NMR spectrum was identical with that of **7** except for the absence of the resonance ascribed to the pendant phosphine and the appearance of two broad resonances at 23.8 (43%) and 5.8 (57%) ppm, whose combined integration was equivalent to one phosphorus atom. The data support **8** being the phosphonium salt of **7**. Reaction of **1** with 4 mol of HBr in toluene led to the isolation of **8** as a mixture of Br/HBr_2 salts whose ^{31}P NMR spectrum was identical with that of **8**, including the two resonances for the pendant phosphonium, P_c. Stirring solid **8** in THF led to the gradual formation of a red solution from which **7** was isolated, due to the reaction of the acid (phosphonium proton) with THF. It is clear that the THF-insoluble fraction formed in the reaction of **1** and HBr (vide supra) was in fact **8**. Reaction of **6** with HCl gave no trace of a phosphonium complex. However, the addition of 1 mol of MeI to a solution of **6** in CD_2Cl_2/C_6D_6 (1:1) in an NMR tube led to the identification of the methylphosphonium salt. The phosphonium phosphorus atom appeared as a doublet at 23.13 ppm.

Heating either **6** or **7** in toluene solution resulted in the loss of 1 mol of PMe_2Ph/mol of complex and the recoordination of P_c to form $[MoX(NNH_2)(dpepp)(PMe_2Ph)]X$ (**9**, X = Br), with *mer*-dpepp and the phenyl group on P_a above the plane of the four phosphorus atoms and on the same side (syn) as the NNH_2 group.[13] This was confirmed by comparison of the ^{31}P NMR data with those of similar complexes prepared from *mer,trans*-$[Mo(N_2)_2(dpepp)(PPh_3)]$, which formed a mixture of *anti,mer*- and *mer,syn*-$[MoX(NNH_2)(dpepp)(PR_3)]X$ with HX (X = Br, Cl).[6a,13]

Reactions of triflic acid with **1** under various conditions led to the identification of similar hydrazido(2–) complexes.

Isolation and Characterization of Hydrides from 1 (Scheme I). From the reaction of **1** with 1 mol of HBr was isolated the dark green hydride *mer*-Mo(H)Br(dpepp)(PMe_2Ph) (**10**) in quantitative yield. The corresponding chloride **11** was obtained in lower yield. Each complex exhibited ν(MoH) in the IR spectrum at 1876 (**10**) and 1874 (**11**) cm^{-1}. The hydride resonance appeared as a double doublet of triplets in the ^1H NMR spectrum at –3.60 (**10**) and –3.82 (**11**) ppm, respectively. The ^{31}P NMR spectrum of each complex was interpreted as arising from a *mer*-dpepp arrangement (equivalent terminal P atoms) and PMe_2Ph trans to P_a. The spectra of these 16-electron complexes differ in two respects from those of other complexes containing a *mer*-dpepp–PR_3 arrangement: (i) Cis coupling was observed between P_a and $P_{b,c}$, and (ii) P_a chemical shift was upfield of $P_{b,c}$ for these and other hydride complexes (vide infra). The triplet associated with the hydride in the ^1H NMR spectrum arises from the equivalent P_b and P_c atoms, and the double doublet is due to coupling with P_a and P_d, respectively. Free PMe_2Ph was identified in the ^{31}P NMR spectrum of the reaction mixture, and 0.9 mol of N_2 was evolved.

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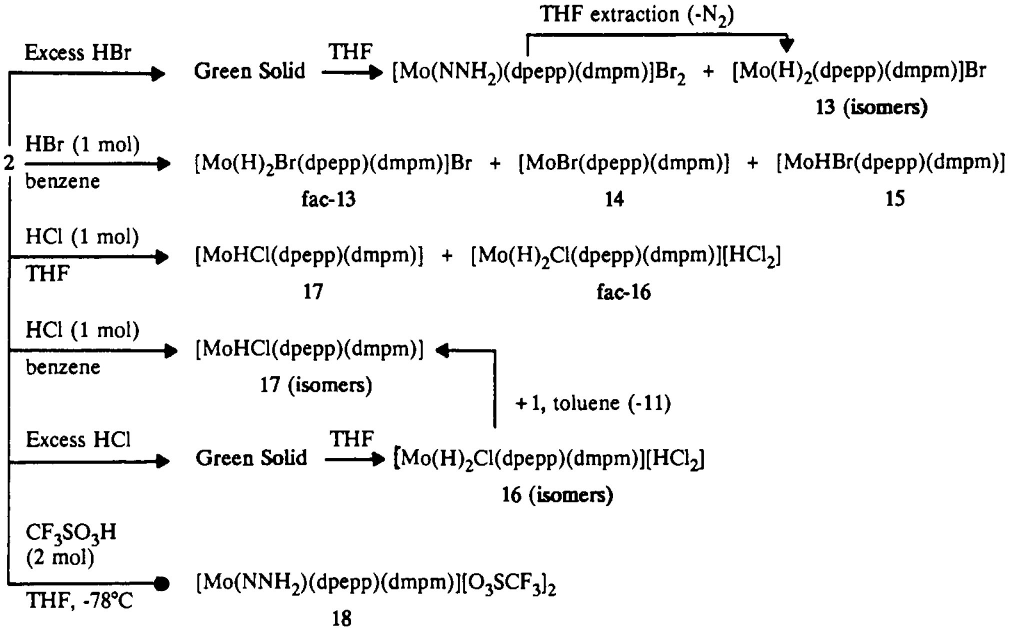
Scheme II. Reactions of **2** with Acids



The green color of the hydride was only observed after stirring the reaction mixture at room temperature for ca. 0.5 h. When **1** was reacted with HBr (1 mol) in toluene for 0.25 h, addition of pentane caused precipitation of **7** (82%) and a mixture of **10** and Mo(H)$_2$Br$_2$(dpepp)(PMe$_2$Ph) (**12**). Removal of solvent from the filtrate produced a red amber oil, which was **1** contaminated with a small amount of PMe$_2$Ph. The mass distribution at the end of the reaction corresponded closely to a 1:1 mixture of **1** and **7**. A similar result was obtained when **1** was reacted with HCl (1 mol) in THF at −15 °C for 15 h. These results showed that **1** reacted with 1 equiv of HX to produce 0.5 mol of **6** or **7**, leaving 0.5 mol of unreacted **1**. However, if left together, these compounds further reacted to produce 1 mol each of **10** or **11** and N$_2$. These results are summarized in Scheme I. To confirm this latter proposal, equimolar amounts of **1** and **7** were allowed to react. **1** and **7** were mixed as solids in an NMR tube that was evacuated (10^{-6} Torr) for 9 days. Onto the brown/yellow powder was condensed C$_6$D$_6$ and the tube sealed. The ^{31}P NMR spectrum of the resulting green solution showed only **10** and free PMe$_2$Ph. A similar reaction carried out in toluene but without any evacuation of the solid gave the same result. Thus in the presence of **1** both **6** and **7** were effectively dehydrohalogenated and denitrified to yield a hydride, with **1** being converted into the same product.

The reaction of **10** with HBr (1 mol) resulted in the very rapid formation of the orange eight-coordinate dihydride Mo(H)$_2$Br$_2$(dpepp)(PMe$_2$Ph) (**12**). In the IR spectrum ν(MoH) appeared at 1878 cm^{-1}, and in the ^{1}H NMR spectrum the hydride resonance occurred as a multiplet at −5.90 ppm. The equivalence of the terminal phosphorus atoms in the ^{31}P NMR spectrum and the large coupling constant observed between P$_a$ and PMe$_2$Ph (identical with that in **10**) suggests *mer*-dpepp and PMe$_2$Ph occupying a plane around molybdenum.

Hydrazido(2−) and Hydride Complexes from 2–5 (Scheme II). Reaction of solid **2** with excess HBr led to the formation of a green solid with no evolution of noncondensable gas. Workup with THF led to the isolation of an olive green solid (70%) and a yellow filtrate. The solid exhibited ν(NH) at 2700–2150 cm^{-1} and a ^{31}P NMR spectrum consistent with *fac*-dpepp and five phosphorus atoms coordinated to molybdenum. Treatment with excess acid produced significant quantities of ammonia and hydrazine. The ^{31}P and ^{1}H NMR spectra of the yellow solid isolated from the filtrate were interpreted as being due to a mixture of two isomeric hydrides (**13**), *fac*-[Mo(H)$_2$Br(dpepp)(dmpm)]Br and *mer*-[Mo(H)$_2$Br(dpepp)(dmpm)]Br. Similar complexes were isolated from reactions of HCl with **2** (vide infra). The olive green solid could be continuously extracted with THF to afford the same yellow solid, suggesting a slow transformation of the hydrazido(2−) complex into the dihydride.

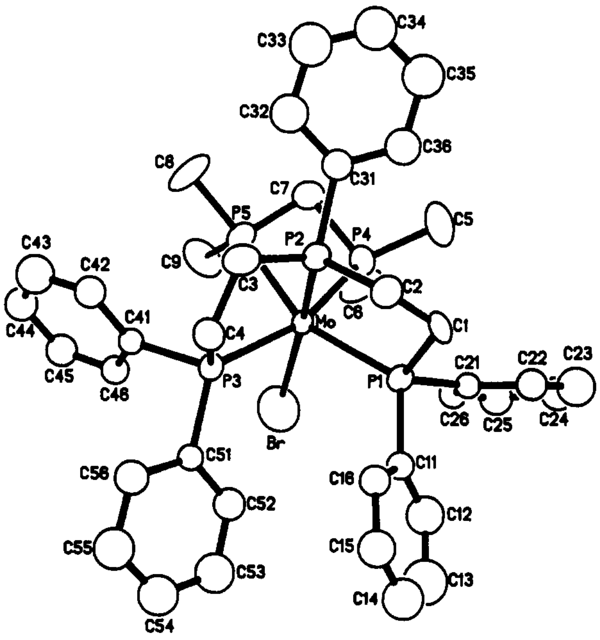


Figure 1. ORTEP view of the structure of MoBr(PhP(CH$_2$CH$_2$PPh$_2$)$_2$)(Me$_2$PCH$_2$PMe$_2$) (**14**) showing the atom-labeling scheme.

The reaction of HBr (1 mol) in benzene with **2** gave a number of products, of which three were characterized. Stirring the solution for 15 h resulted in the isolation of *fac*-[Mo(H)$_2$Br(dpepp)(dmpm)]Br (**13**), which corresponded to about half of the total mass recovered. Addition of pentane caused precipitation of a few milligrams of an orange solid that was not characterized. Allowing the filtrate to stand under N$_2$ resulted in the formation of air-stable orange needles of **14**. The structure of **14** was established by an X-ray diffraction study (vide infra) as a molybdenum(I) complex, MoBr(dpepp)(dmpm) (Figure 1). The magnetic susceptibility (Evans' method[14]) was determined to be 1.87 μ_B at room temperature. Allowing the filtrate to stand for a further 48 h resulted in the formation of a small quantity of air-stable amber prisms of **15**. The IR [ν(MoH) 1957 cm^{-1}] and ^{1}H [δ(MoH), multiplet] NMR spectra of **15** were in accordance

Table I. Yields of Dinitrogen, Ammonia, and Hydrazine

complex[a]	acid (amt, mol)[b]	solvent[c]	time, h	T, °C	yield[d]			N balance[e]
					N_2	NH_3	N_2H_4	
6	HBr (10)	A	16	25	27	27	13	54
6	HBr (80)	A	16	25	29	15	24	61
6	HBr (10)	A	13	50	37	17	34	80
6	HBr (10)	A	40	50	40	44	32	94
6	HCl (10)	A	40	25	24	10	42	71
6	HCl (10)	A	39	52	41	23	46	99
6	HBr (80)	B	40	25	27	25	24	64
6	HCl (80)	B	16	50	34	39	37	91
6	HCl (80)	B	38	55	33	37	45	97
7	HBr (10)	A	40	47	38	18	43	90
7	HCl (10)	A	37	54	36	21	39	86
7	HBr (80)	B	12	55	28	33	27	72

[a] **6** = $[MoCl(NNH_2)(\eta^2\text{-dpepp})(PMe_2Ph)_2]Cl$; **7** = $[MoBr(NNH_2)(\eta^2\text{-dpepp})(PMe_2Ph)_2]Br$. [b] Per mole of complex. [c] A = CH_2Cl_2; B = toluene. [d] (mol/mol of complex) × 100. [e] (mol of N/2 per mol of complex) × 100.

with the presence of a hydride ligand. The ^{31}P NMR spectrum was qualitatively similar to that of **2**. The most likely formulation of **15** is seven-coordinate *fac*-Mo(H)Br(dpepp)(dmpm).

Reaction of solid **2** with excess HCl produced a green solid with no evolution of noncondensable gas. Addition of THF, even at low temperature, resulted in the formation of a yellow filtrate and isolation of a small quantity of $N_2H_4{\cdot}HCl$. From the filtrate was obtained a yellow solid whose spectral and elemental analysis data supported its formulation as a mixture of isomeric dihydrides (**16**) as hydrogen dichloride salts: *fac*- and *mer*-$[Mo(H)_2Cl(dpepp)(dmpm)][HCl_2]$ in the ratio 4:1. There was a ν(MoH) at 1885 cm^{-1} in the IR spectrum and two hydride resonances in the ^1H NMR spectrum. The ^{31}P NMR spectrum revealed two sets of resonances of different intensities. The major isomer displayed five different phosphorus resonances with the largest coupling constants being $J_{P_bP_d}$ (110 Hz) and $J_{P_cP_e}$ (115 Hz). These data suggest a structure based upon that of **2** with *fac*-dpepp and $P_{b,c,d,e}$ arranged in an unsymmetrical plane. This isomer, designated *fac*-**16**, displayed one hydride resonance as an apparent doublet of quartets in the ^1H NMR spectrum at 25 °C. This same isomer was isolated as a single species from the reaction of **2** with 1 mol of HCl in THF solution. The ^{31}P NMR spectrum of the minor isomer displayed equivalent P_b and P_c, suggesting *mer*-dpepp with P_a trans to P_d ($J_{P_aP_d}$ = 184 Hz). This isomer, *mer*-**16**, showed a single broad hydride resonance in the ^1H NMR spectrum. The ^{31}P NMR spectrum of **13** can similarly be interpreted as an equal mixture of *fac*-**13** and *mer*-**13**. The chemical shifts of dpepp phosphorus atoms changed little between *fac*-**16** and *fac*-**13** and between *mer*-**16** and *mer*-**13**, respectively. However, large chemical shift changes arose in the dmpm phosphorus resonances upon changing from the isomers of **16** to those of **13**. This may reflect the larger size of bromine and the greater ease of perturbing dmpm than dpepp in the coordination sphere.

Upon reaction of **2** with HCl (1 mol) in benzene, the initial red color turned green upon stirring for 15 h. Workup produced a small quantity of uncharacterized material. Eventually from the filtrate were obtained amber prisms whose spectral data supported the presence of a mixture (3:1) of isomeric monohydrides, Mo(H)Cl(dpepp)(dmpm) (**17**). The evidence for two isomers is as follows: (i) the presence of two very different ν(MoH) at 1950 and 1840 cm^{-1}, of different intensities in the IR spectrum, (ii) the presence of two hydride resonances at −6.75 and −7.95 ppm, of very different intensities in the ^1H NMR spectrum, and (iii) two sets of resonances of different intensities in the ^{31}P NMR spectrum. The minor isomer displayed three resonances in the ratio 1:2:2 with large coupling constants between P_b and P_c and the phosphorus atoms of dmpm. Therefore, dpepp must be *fac* with $P_{b,c,d,e}$ comprising a plane. The major isomer displayed five different resonances in the ^{31}P NMR spectrum with moderately large coupling constants between P_b,P_c and P_d,P_e ($J_{PP} \approx 122$ Hz). These data fit a structure with *fac*-dpepp and $P_{b,c,d,e}$ nonplanar. This same monohydride isomer (ν(MoH) 1840 cm^{-1}) was the major product obtained from the reaction of **2** with HCl (1 mol) in THF at −78 °C for 15 h. No evidence of the other isomer was obtained. The other product in this latter reaction was *fac*-$[Mo(H)_2Cl(dpepp)(dmpm)]HCl_2$ with no evidence for the presence of the *mer* isomer.

Triflic acid (2 mol) was added to **2** in THF at −78 °C. Within 0.25 h the red solution had turned green. The major product **18** (74%) isolated from this reaction was a light blue solid with ν(NH) at 3207 cm^{-1}. The ^{31}P NMR spectrum was similar to that of **2** and supported the assignment of **18** as the six-coordinate complex *fac*-$[Mo(NNH_2)(dpepp)(dmpm)][SO_3CF_3]_2$ with P_a trans to the (NNH_2) ligand. This is the first example of a hydrazido(2−) complex containing five phosphine ligands. In solution, **18** showed signs of decomposition above −10 °C.

Reactions of **3**–**5** with acid gave initial evidence for the formation of a hydrazido(2−) complex with no liberation of noncondensable gas. For example, solid **3** reacted with HBr to form a green powder whose IR spectrum showed ν(NH) at 2700–2200 cm^{-1}. Similarly, solid **4** reacted with HBr to produce a green powder. Removal of excess acid in vacuo produced a rusty green powder. The IR spectrum showed ν(NH) at 2800–2200 cm^{-1}. Reaction of this product with HBr or HCl in CH_2Cl_2 or toluene produced ammonia and hydrazine and in THF, just ammonia. This same product decomposed with evolution of gas when dissolved in CH_2Cl_2 or THF. With HCl, **4** behaved differently. Reaction of HCl with solid **4** afforded a green powder with no liberation of noncondensable gas. However, upon prolonged evacuation the solid became red-orange. The final yellow-orange powder displayed ν(MoH) at 1885 and ν(MoCl) at 290 cm^{-1}. The ^{31}P NMR spectrum suggested a mixture of two isomeric dihydride complexes in a ratio of 2:1. Each complex showed the presence of five coordinated phosphorus atoms with dpepp in an apparent facial configuration. Elemental analysis supported the formulation $[Mo(H)_2Cl(dpepp)(dppm)][HCl_2]$. Reaction of **4** with 1 mol of HBr in THF for 15 h resulted in the formation of an approximately equimolar mixture of a dihydride and unreacted **4**. Finally **5** reacted with excess HCl analogously to **4** to yield a hydride product.

Reactions of Hydrazido(2−) Complexes with Acid: Ammonia and Hydrazine Formation. Complexes **6** and **7** were reacted with 10 and 80 mol of HBr and HCl for about 12 and 40 h at 25 and ca. 50 °C in toluene, CH_2Cl_2, and THF, and yields of ammonia, hydrazine, and N_2 were determined. In toluene solution the reaction mixture rapidly became heterogeneous due to precipitation of the corresponding phosphonium salt as an oil. However the highest yields of both ammonia and hydrazine were achieved in toluene at ca. 50 °C. The reactions of **6** and **7** with HBr in THF gave low yields of ammonia and no hydrazine, and this system will not be included in the generalization presented below.

A sampling of the $N_2/NH_3/N_2H_4$ yield data to illustrate the general trends observed is collected in Table I. In all reactions investigated increasing the temperature had the single largest effect upon increasing yields of ammonia and hydrazine. Generally, reactions with HCl favored hydrazine formation whereas with HBr ammonia was favored. With increasing time at 25 °C the yield of ammonia increased but not at the expense of hydrazine production; there was no evidence for hydrazine decomposition with increasing time of reaction.

Reactions of Hydrazido(2–) Complexes with Base. Attempts were made to generate diazenido (NNH) complexes by monodeprotonation of **6** and **7** with base.[16] These reactions were monitored by ^{31}P NMR spectroscopy. Reaction of **6** (C_6D_6) with Et_3N (1 mol) and **7** (THF) with Proton Sponge (Aldrich) (1 or 5.5 mol) led to loss of N_2 whereas no reaction occurred between **6** (toluene) and Proton Sponge. In none of these experiments was evidence found for a new diamagnetic species, only unreacted **6** or **7**, in reactions with 1 mol of base. At this stage we must conclude that if a diazenido complex was formed, it rapidly reacted with loss of N_2. Since base would remove available protons, no hydride complex was formed.

Description of Structure. The structure of **14** is illustrated in Figure 1. Crystal data are given in Table II, relevant bond lengths and angles in Table III, and atom coordinates in Table IV.

The complex displays a distorted octahedral coordination environment about Mo with four phosphorus atoms loosely defining an equatorial plane about molybdenum while the central phosphorus atom of dpepp and the bromine atom occupy the axial positions. However, there are few angles close to 90 or 180° about Mo: Br–Mo–P2 is 167.1 (1)°. Dpepp adopts a facial configuration with P–Mo–P angles close to 80° and similar to those found in two molybdenum hyrazido(2–) complexes in which dpepp is meridional[13] and in *fac*-Mo(CO)$_3$(dpepp).[17] The Mo–P2 distance is shorter than the other four Mo–P distances, and the Mo–P1 and Mo–P3 distances are just slightly shorter than the Mo–P(dmpm) distances. Mo–P(dpepp) distances are shorter than Mo–P(dpepp) in *fac*-Mo(CO)$_3$(dpepp).[17] The P1–Mo–P3 and P4–Mo–P5 angles are 105.0 (1) and 66.7 (1)°, respectively. P1 and P3 are displaced toward P2 above a plane containing Mo that is normal to a vector through Mo and P2. P4 is displaced below this plane. All Br–Mo–P angles are ≥ca. 90°.

Discussion

Detailed studies of the reactions of controlled amounts of acid with **1**, **2**, and **4** were conducted. These reactions led to the isolation and characterization of hydrides and hydrazido(2–) complexes.

Hydrazido(2–) Formation. The reactions of **1** with 1 or 2 mol of acid even at low temperature led to the detection (by ^{31}P NMR spectroscopy) and isolation of a hydrazido(2–) complex in which the phosphorus atom of dpepp previously trans to N_2 was no longer coordinated to molybdenum. In its place was a halide ion (**6** and **7**) or triflate ion. Thus **1** was behaving much like the bis(dinitrogen) complexes of molybdenum that form hydrazido(2–) complexes with a conjugate base coordinated in place of N_2 trans to NNH_2.[4] In contrast, reactions of **2** with acid (2 mol) led to the formation of an unstable hydrazido(2–) complex without loss of a ligand. This is only the second example of coordinated N_2 being protonated without loss of a ligand; the first occurred with $Mo(N_2)(RCN)(dppe)_2$.[18] This result suggests that there is no inherent instability associated with dpepp in a facial configuration. Rather, the dissociation of P_b trans to N_2 in **1** is due to a combination of electronic (trans NNH_2 group) and steric effects. The PPh_2 group that dissociates is uniquely cis to four phenyl-substituted phosphorus atoms. Dissociation probably occurs after diprotonation. When the complexes are heated in solution, the pendant phosphorus atom of **6** and **7** recoordinates to give *mer*-dpepp with the loss of one PMe_2Ph ligand. The dissociation of one arm of coordinated dpepp has previously been noted among products of the reaction of *trans*-Mo(N$_2$)$_2$(dpepp)(PPh$_3$) with excess acid in CH_2Cl_2.[6a] For example, MoBr$_4$(η^2-dpeppH) has been isolated in which the pendant phosphorus atom is protonated.[19] The apparent facile dissociation of one arm of dpepp and similar ligands[20,21] raises the question of the role that a neighboring base (and its protonated form) may have upon the mechanism of reduction of hydrazido(2–) complexes to ammonia and hydrazine.

Reactions of **2**–**5** with acid all gave evidence of formation of a hydrazido(2–) complex. However, they were all unstable, decomposing with loss of N_2 to form a variety of different hydrides. In solution, the stability of the dication derived from **2** increased in the order Cl < Br < CF_3SO_3, reflecting the decreasing basicity of the counterions. The hydrazido(2–) complexes derived from **2**–**5** are clearly stable in solution in the presence of excess acid where eventually Mo–P (and Mo–As) bond cleavage occurs leading to ammonia formation.

Decomposition of the Hydrazido(2–) Ligand: Hydride Formation. In an attempt to identify and isolate products arising from the monoprotonation of **1**, **2**, and **4**, reactions were carried out with 1 mol of acid in solution at low temperature. Under these conditions **1** reacted rapidly to form **6** or **7**. In the ^{31}P NMR spectrum resonances due to equimolar amounts of unreacted **1** and **6** or **7** were observed. When the reaction (HBr/**1**) was allowed to proceed, a quantitative yield of **10** was obtained. In solution, **6** and **7** are stable in ether and hydrocarbon solvents. However, upon addition of **1**, the hydrazido(2–) complexes lost N_2, one PMe_2Ph ligand, and HX to form the monohydride **10** or **11** in which dpepp adopts the *mer* configuration. During this reaction, **1** was also converted into **10** or **11** with loss of one PMe_2Ph ligand and rearrangement of dpepp from *fac* to *mer*. With less than 1 mol of **1**, unreacted hydrazido(2–) remained in solution. In solution and in the solid state, **1** loses N_2 to form five-coordinate [Mo(dpepp)(PMe$_2$Ph)$_2$] (**19**).[9]

The initial step in the decomposition of the hydrazido(2–) complex is likely to be monodehydrohalogenation. This would initially be either by (i) protonation of **19** by the hydrazido complex to form a cationic metal hydride and a diazenido complex or (ii) coordination of halide ion to **19** to form an anion followed by protonation and generation of the diazenido complex. The effectiveness of **1** or **19** as a reagent for dehydrohalogenation has been demonstrated in the reaction of **1** with [Mo(H)$_2$Cl(dpepp)(dmpm)][HCl$_2$] to form Mo(H)Cl(dpepp)(dmpm) and **11**. Subsequent decomposition of the diazenido ligand by intramolecular hydrogen migration and loss of N_2 would lead to monohydride formation.[22] Eight-coordinate hydrides were formed by protonation of [Mo(H)X(dpepp)(PMe$_2$Ph)]. Seven- and eight-coordinate hydrides were formed from the decomposition of $[Mo(NNH_2)(dpepp)(dmpm)]^{2+}$ and reactions of **2** with 1 mol of HX (see Scheme II).

The formation of a metal hydride rather than a complex containing a nitrogen–hydride ligand is a frequent result when many metal–N_2 complexes are treated with acid. These results have been rationalized as arising from direct protonation of the metal followed by loss of N_2 (eq 2). The same net reaction would result

$$\{MN_2\} + H^+ \rightarrow \{MH\} + N_2 \qquad (2)$$

$$\{MN_2\} + H^+ \rightarrow \{MNNH\} \rightarrow \{MH\} + N_2 \qquad (3)$$

if protonation of N_2 occurred first followed by fast hydrogen migration (eq 3). In this work we have shown the net decomposition of two different classes of hydrazido(2–) complex: one that decomposes in solution to liberate N_2 and form a hydride complex[23] and the second that reacts with **1**, a "labile" N_2 complex, with loss of N_2 and formation of a hydride complex. These reactions illustrate that hydride formation can occur from the hydrazido(2–) ligand as an alternate pathway to direct protonation of the metal followed by loss of N_2.[24]

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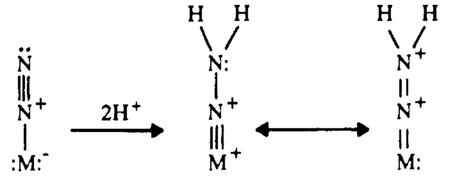
Hydride Structures. The structures of these new hydrides, formed as secondary products, are assigned on the basis of their single-temperature ^{1}H and ^{31}P NMR spectra. A common denominator throughout these complexes is tridentate dpepp. In the ^{1}H NMR spectrum of both **10** and **11**, coupling between the hydride and three different phosphorus atoms was resolved at 25 °C, suggesting a stereochemically rigid structure for the 16-electron complexes. Protonation of **10** with 1 mol of HBr rapidly yielded the dihydride **12** for which the ^{31}P NMR spectrum indicated one species. There are a number of complexes of the type $MH_2X_2P_4$ for which crystal structures have been determined.[25-28] These structures are reported as either distorted square antiprismatic or distorted dodecahedral in which the two hydride ligands are cis. The presence of the dpepp ligand in **12** precludes an idealized polyhedral structure. The similarity of the large coupling between P_a and P_d in the ^{31}P NMR spectra of **12** and six-coordinate complexes containing dpepp and PR_3 with P_a trans to P_d[13] suggests that the structure of **12** is best described as bicapped octahedral with equivalent $P_{b,c}$ not necessarily coplanar with $P_{a,d}$.

The seven- and eight-coordinate hydrides derived from **2** are interesting because of the apparent formation of isomers. Isomers may be expected to arise because of the difficulty of interconverting different arrangements of the bi- and tridentate ligands. Different arrangements of the phosphorus atoms are suggested by the ^{31}P NMR spectra. However, more definitive spectroscopic studies are required before firm structural assignments can be made.

Protonation of Metal–N_2 Complexes. The successful protonation of coordinated N_2 in complexes **1** and **2** is important for two reasons: (i) It clearly demonstrates that it is not necessary to have a *bis(dinitrogen)* complex for effective protonation to form a hydrazido(2–) complex. (ii) Protonation of end-on bound N_2 can be achieved without any change in the other ligands coordinated to the metal. The question to ask now is, why has protonation of end-on bound N_2 been demonstrated in so few complexes? The answer can be divided into three parts: (i) The coordinated N_2 has to be sufficiently "negative" as a result of back-donation of electron density from the metal in order for protonation of N_2 to occur. This is not the most important criterion because the Re(I)–N_2 complexes that show $\nu(N_2)$, at lower energy than all the bis(dinitrogen) complexes of molybdenum are protonated at the metal.[29] (ii) Protonation of end-on bound N_2 is accompanied by oxidation of the metal. In the case of hydrazido(2–) formation, this involves the formal four-electron oxidation of the metal.[30]



For example, in reactions of bis(dinitrogen) complexes of molybdenum and tungsten with a high effective concentration of acid, the metal is oxidized from M(0) to M(IV). Deprotonation of the hydrazido(2–) complex with base under N_2 frequently regenerates the starting bis(dinitrogen) complex.[16] The transformation of Mo(0) to Mo(IV) requires no change in coordination geometry since six-coordination is common to the two oxidation states. (iii) The decomposition of nitrogen hydrides such as hydrazine is frequently catalyzed by transition-metal ions. The hydrazido(2–) ligand is stabilized by the π-accepting M(IV) ions of molybdenum and tungsten. In summary, the conditions that appear to be necessary for the conversion of N_2 into the H_2NN^{2-} ion are rather restrictive and preclude similar transformation for most single-metal N_2 complexes. Of course, there are many other nitrogen hydride intermediates possible that will be realized especially in polymetal complexes and in cases where an external source of electrons is employed.

Summary

1. Complex **1** reacted with HX (≥2 mol; X = Br, Cl) to form stable hydrazido(2–) complexes in which dpepp is bidentate. The coordinated phosphorus atom of dpepp trans to N_2 was displaced by X, while the two monodentate ligands remained coordinated. These complexes reacted with excess HX to afford high yields of ammonia and hydrazine. Treatment of the hydrazido(2–) complexes with **1** (1 mol) resulted in their "denitrification" and formation of a monohydride complex (2 mol). This same hydride was formed almost quantitatively (X = Br) when **1** was treated with HX (1 mol). The six-coordinate 16-electron monohydrides can be protonated to yield eight-coordinate dihydrides.

2. Complex **2** reacted with acid (≥2 mol) to yield an unstable hydrazido(2–) dication *without* loss of a ligand. The stability of the hydrazido(2–) dication increased as the basicity of the anion decreased: Cl < Br < CF_3SO_3. The hydrazido(2–) complexes decomposed in solution to yield pairs of eight-coordinate isomeric dihydrides. Reactions of **2** with HBr (1 mol) in benzene yielded a dihydride, *fac*-**13**, a monohydride, **15**, and a paramagnetic molybdenum complex, **14**, identified as MoBr(dpepp)(dmpm) by an X-ray crystal structure determination. A similar reaction with HCl afforded in high yield the monohydride MoHCl(dpepp)(dmpm) as a pair of isomers.

3. Complexes **3**–**5** reacted with acid in the solid state to give evidence (color changes, no noncondensable gas evolution, and in the case of **3** an IR spectrum) of formation of hydrazido(2–) complexes. All decomposed in solution with loss of N_2 and the formation of hydride complexes, of which only one was characterized.

Experimental Section

General Procedures. All preparations and reactions were carried out either under an N_2 atmosphere or in vacuo. Compounds were handled in a water- and oxygen-free environment, which was provided by using Schlenk techniques,[31] glovebags, and a Vacuum Atmospheres Corp. drybox. A general utility vacuum line capable of attaining pressures <10^{-5} Torr was employed for all reactions in which anhydrous acids were used, and N_2 evolution measurements were made by using a Toepler pump.

Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Reagents and Materials. All solvents were reagent grade and were purchased from commercial sources. Solvents were rigorously dried by heating at reflux over an appropriate drying agent and distilled under N_2. Immediately before use, solvents were either vigorously bubbled with N_2 for >1 h or subjected to >5 freeze–pump–thaw cycles. Chemicals were purchased from commercial sources and used without purification except for the following. Anhydrous HX was purified by a series of trap-to-trap distillations on the vacuum line and stored in glass bulbs. Nitrogen-15 (99.89 atom %; ^{14}N, 0.11 atom %; N_2, 99.99 atom %; CO_2, 0.01 mol %) was obtained from Monsanto Research Corp., Mound Facilities, Miamisburg, OH 45342, and phosphine and arsine ligands were from Strem Chemicals, Inc. All N_2 complexes were prepared by a published procedure.[9]

Ammonia, Hydrazine, and Dinitrogen Analyses. The general procedure for carrying out the reactions of anhydrous acid with N_2 or dinitrogen hydride complexes and the determination of amounts of ammonia, hy-

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Table II. Crystallographic Data for $MoBr(PhP(CH_2CH_2PPh_2)_2)(Me_2PCH_2PMe_2)\cdot{}^1/_2C_5H_{12}$ (**14**)

chem formula $MoBrC_{41.5}H_{53}P_5$	fw = 882.59
a = 12.452 (2) Å	space group $P2_1/c$ (No. 14)
b = 15.738 (2) Å	T = 23 °C
c = 21.677 (3) Å	λ = 0.71073 Å
β = 98.94 (1)°	ρ_{calcd} = 1.39 g cm^{-3}
V = 4196.4 (12) Å^3	μ = 7.9 cm^{-1}
Z = 4	transm coeff = 0.86–0.92
R^a = 0.073	$R_w{}^b$ = 0.077

[a] $R = \sum[|F_o| - |F_c|/\sum|F_o|]$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/[\delta(F_o) + g^*(F_o)]$; g = 0.002.

Table III. Selected Bond Lengths (Å) and Bond Angles (deg) for $MoBr(dpepp)(dmpm)\cdot{}^1/_2C_5H_{12}$ (**14**)

Mo–Br	2.684 (3)	Mo–P1	2.438 (4)
Mo–P2	2.383 (4)	Mo–P3	2.427 (4)
Mo–P4	2.466 (4)	Mo–P5	2.477 (4)
Br–Mo–P1	94.8 (1)	Br–Mo–P2	167.1 (1)
P1–Mo–P2	81.9 (1)	Br–Mo–P3	89.3 (1)
P1–Mo–P3	105.0 (1)	P2–Mo–P3	79.6 (1)
Br–Mo–P4	90.8 (1)	P1–Mo–P4	92.9 (1)
P2–Mo–P4	101.8 (1)	P3–Mo–P4	162.1 (1)
Br–Mo–P5	96.3 (1)	P1–Mo–P5	156.8 (1)
P2–Mo–P5	91.3 (1)	P3–Mo–P5	95.5 (1)
P4–Mo–P5	66.7 (1)	P4–C7–P5	96.4 (1)

Table IV. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3) for Non-Phenyl Atoms of MoBr(dpepp)(dmpm)

atom	x	y	z	U^a
Mo	3335 (1)	−528 (1)	−2179 (1)	21 (1)
Br	3652 (2)	−2084 (2)	−2627 (1)	85 (1)
P1	1356 (3)	−619 (2)	−2377 (2)	28 (1)
P2	2944 (3)	931 (3)	−2024 (2)	31 (1)
P3	3831 (3)	86 (2)	−3123 (2)	28 (1)
P4	3445 (3)	−1104 (3)	−1113 (2)	39 (2)
P5	5163 (3)	−383 (3)	−1548 (2)	35 (1)
C1	780 (11)	400 (10)	−2121 (7)	40 (6)
C2	1465 (10)	1172 (9)	−2238 (7)	35 (6)
C3	3503 (13)	1650 (9)	−2562 (7)	38 (6)
C4	3452 (12)	1241 (8)	−3207 (6)	31 (5)
C5	2558 (15)	−946 (15)	−517 (8)	84 (10)
C6	3812 (14)	−2222 (10)	−963 (8)	63 (7)
C7	4708 (12)	−531 (11)	−807 (7)	47 (6)
C8	6088 (14)	537 (12)	−1401 (9)	72 (8)
C9	6126 (13)	−1254 (13)	−1587 (8)	68 (8)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{iso}$ tensor.

drazine, and N_2 produced has been reported.[6a] The nitrogen content of some complexes was measured by oxidative decomposition with bromine in CH_2Cl_2.

Instrumentation. IR spectra (4000–200 cm^{-1}) were recorded on a Perkin-Elmer 283 spectrophotometer. Solid samples were run as KBr pellets. Proton NMR spectra were recorded by using either a Varian EM-390 or a Varian XL-200 spectrometer. ^{31}P NMR (80.984 MHz; broad-band decoupling of protons) and ^{15}N NMR (20.280 MHz, coaxial tubes; not proton decoupled) spectra were obtained by using a Varian XL-200 spectrometer. All spectra were recorded at ambient temperature unless otherwise stated. All chemical shifts are reported in ppm relative to Me_4Si (^1H), 85% H_3PO_4 (^{31}P), and CD_3NO_2 (^{15}N) with positive values being to low field. Phosphorus atom assignments are $PhP_a(CH_2CH_2P_{b,c}Ph_2)_2$; others are d and e, respectively.

[MoCl(NNH$_2$)(η^2-dpepp)(PMe$_2$Ph)$_2$]Cl (6). Complex **1** (0.44 g, 0.47 mmol) was placed in a 50-mL round-bottomed flask with a magnetic stir bar. The flask was rapidly evacuated to ca. 10^{-3} Torr, and immediately excess HCl (10 mmol) was condensed onto the solid at −196 °C. The flask was sealed by means of a vacuum stopcock and allowed to warm slowly to room temperature. The solid reacted as the acid thawed to initially form a green powder that after ca. 0.5 h formed a red-orange paste. At this time, excess acid was removed in vacuo. The flask was transferred to a glovebag where THF (ca. 30 mL) was added to afford a red suspension. Filtration yielded a few milligrams of an uncharacterized orange solid. To the deep red filtrate was added rapidly ca. 25 mL of pentane, which caused precipitation to occur. The resulting solid was filtered off, washed (3 × 20 mL) with pentane, and dried in vacuo to yield an air-sensitive pinkish yellow powder (0.32 g, 0.31 mmol, 68%). Anal. Calcd for $C_{50}H_{57}Cl_2MoN_2P_4$: C, 59.6; H, 5.70; N, 2.78; P, 15.4; Cl, 7.04. Found: C, 56.7; H, 5.66; N, 2.33; P, 15.2; Cl, 7.94. ^{31}P NMR (C_6D_6): δ 43.21 (dd, 1, $^2J_{P_bP_e}$ = 149.8 Hz, $^2J_{P_bP_d}$ = 18.6 Hz, P_b), 36.30 (complex dt, 1, $^2J_{P_aP_d}$ = 161.2 Hz, $^2J_{P_aP_c}$ = 23.5 Hz, $^2J_{P_aP_e}$ = 18.8 Hz, P_a), −7.10 (complex dt, 1, $^2J_{P_dP_e} \approx$ 20 Hz, P_d), −7.65 (complex dt, 1, P_e), −17.19 (d, 1, P_c). ^1H NMR (C_6D_6): δ 10.63 (broad, 2, NNH_2), 8.0–6.7 (m, Ph), 2.37 (broad, 4, CH_2), 2.01 (broad, 4, CH_2), 1.83 (d, 3, $^2J_{PH}$ = 7.3 Hz, Me), 1.61 (d, 3, $^2J_{PH}$ = 7.3 Hz, Me), 1.40 (d, 3, $^2J_{PH}$ = 7.3 Hz, Me), 1.18 (d, 3, $^2J_{PH}$ = 7.3 Hz, Me). ^{15}N NMR (THF): δ −63.34 (m, 1, N_α), −212.30 (m, 1, N_β). IR: ν(NH) 2800–2500 cm^{-1}.

[MoBr(NNH$_2$)(η^2-dpepp)(PMe$_2$Ph)$_2$]Br (7). Complex **7** was prepared according to the procedure for **6** with yields typically >90%. The single difference was that, upon addition of THF, the suspension was heated (45 °C) with stirring for ca. 0.5 h to afford a red solution. ^{31}P NMR (C_6D_6): δ 42.98 (dd, 1, $^2J_{P_bP_e}$ = 143.9 Hz, $^2J_{P_bP_d}$ = 19.8 Hz, P_b), 35.88 (complex dt, 1, $^2J_{P_aP_d}$ = 152.6 Hz, $^2J_{P_aP_c}$ = 20.3 Hz, $^2J_{P_aP_e} \approx$ 20 Hz, P_a), −6.20 (complex dt, 1, $^2J_{P_dP_e} \approx$ 20 Hz, P_d), −7.29 (complex dt, 1, P_e), −17.06 (d, 1, P_c). ^1H NMR (C_6D_6): 10.34 (broad, 2, NNH_2). ^{15}N NMR (THF): δ −64.21 (m, 1, N_α), −234.54 (m, 1, N_β). IR: ν(NH) 2700–2500 cm^{-1}.

[MoBr(NNH$_2$)(η^2-dpeppH)(PMe$_2$Ph)$_2$]Br$_2$ (8). Complex **1** (688 mg, 0.74 mmol) was placed in a 50-mL flask equipped with a high-vacuum stopcock and a magnetic stir bar. After evacuation for 0.1 h at ca. 1 × 10^{-3} Torr, toluene was condensed onto **1** at −196 °C. Onto the frozen mixture was condensed HBr (2.22 mmol). The stopcock was closed and the flask allowed to warm to room temperature. After the gray turbid sludge was stirred for ca. 0.04 h, the color became sandy. The reaction mixture was stirred (15 h) before being filtered. The solid was washed (3 × 20 mL) with pentane and dried in vacuo to yield 0.81 g (0.68 mmol, 93%) of yellow, air-sensitive product. ^{31}P NMR (CD_2Cl_2): δ 42.94 (dd, 1, $^2J_{P_bP_e}$ = 144.0 Hz, $^2J_{P_bP_d} \approx$ 19 Hz, P_b), 36.57 (complex dt, 1, $^2J_{P_aP_d}$ = 156.3 Hz, $^2J_{P_aP_c} \approx {}^2J_{P_aP_d} \approx$ 20 Hz, P_a), 23.8 (broad, 0.4, P_c), 5.8 (broad, 0.6, P_c), −6.20 (complex dt, 1, $^2J_{P_dP_e} \approx$ 20 Hz, P_d), −7.29 (complex dt, 1, P_e). IR: ν(NH) 2700–2500, ν(PH) 2360 cm^{-1}.

***mer*-Mo(H)Br(dpepp)(PMe$_2$Ph) (10).** Complex **1** (1.27 g, 1.36 mmol) was placed in a round-bottomed flask equipped with a high-vacuum stopcock and a magnetic stir bar. After the flask was briefly evacuated, benzene (10 mL) and HBr (1.36 mmol) were successively condensed onto the solid at −196 °C. At room temperature the solution was red, but after being stirred for 15 h, it became green. The solution was filtered and pentane (0.2 L) added with rapid swirling. The resulting solid was collected by filtration, washed (2 × 20 mL) with pentane, and dried in vacuo to afford 1.10 g (1.29 mmol, 95%) of a green powder. Anal. Calcd for $C_{42}H_{45}BrMoP_4$: C, 59.4; H, 5.34. Found: C, 59.0; H, 5.32. ^{31}P NMR (C_6D_6): δ 126.94 (dd, 2, $^2J_{P_aP_b}$ = 22.0 Hz, $^2J_{P_bP_d}$ = 14.0 Hz, $P_{b,c}$), 95.16 (dt, 1, $^2J_{P_aP_d}$ = 160.7 Hz, P_a), 4.83 (dt, 1, P_d). ^1H NMR (C_6D_6): δ 7.9–6.9 (m, Ph), 2.56 (broad d, J = 40 Hz, CH_2), 1.63 (broad d, J = 40 Hz, CH_2), 1.31 (d, $^2J_{PH}$ = 7.3 Hz, Me), −3.82 (double dt, 1, J_{PH} = 73.4, 50.6, and 13.4 Hz, hydride). IR: ν(MoH) 1874 cm^{-1}.

***mer*-Mo(H)Cl(dpepp)(PMe$_2$Ph) (11).** Toluene (20 mL) was condensed onto the surface of a sample of **1** (972 mg, 1.04 mmol) in a round-bottomed flask equipped with a high-vacuum stopcock and a stir bar. While the temperature was maintained at −196 °C, HCl (1.04 mmol) was condensed onto the solid. The reaction flask was filled with N_2 and the mixture warmed to 25 °C to afford a red solution. While being stirred (38 h), the solution turned green. After filtering, pentane (0.25 L) was added to the filtrate. A precipitate formed over a period of 15 h. The volume was reduced to ca. 90 mL and the suspension cooled by passing N_2 rapidly across the surface. The product was collected by filtration, washed (2 × 20 mL) with pentane, and dried in vacuo to yield 0.30 g (0.37 mmol, 36%) of dark green prisms. ^{31}P NMR (C_6D_6): δ 127.80 (dd, 2, $^2J_{P_aP_b}$ = 22.0 Hz, $^2J_{P_bP_d}$ = 14.5 Hz, $P_{b,c}$), 92.20 (dt, 1, $^2J_{P_aP_d}$ = 166.4 Hz, P_a), 3.84 (dt, 1, P_d). ^1H NMR (C_6D_6): δ 8.0–6.9 (m, Ph), 2.58 (broad d, J = 40 Hz, CH_2), 1.60 (broad d, J = 40 Hz, CH_2), 1.20 (d, $^2J_{PH}$ = 7.3 Hz, Me), −3.90 (double dt, J_{PH} = 74.4, 49.8, and 13.1 Hz, hydride). IR: ν(MoH) 1876, ν(MoCl) 301 cm^{-1}.

***mer*-Mo(H)$_2$Br$_2$(dpepp)(PMe$_2$Ph) (12).** Toluene (20 mL) and HBr (0.77 mmol) were successively condensed onto **10** (845 mg, 0.77 mmol) in a round-bottomed flask at −196 °C. Upon thawing, the dark green solution rapidly (5 s) became a gray turbid sludge and within a further 20 s acquired an orange hue. After the mixture was stirred (15 h), the solid was collected by filtration, washed (2 × 20 mL) with pentane, and dried in vacuo to afford 0.51 g (0.55 mmol, 71%) of bright orange powder. Anal. Calcd for $C_{42}H_{46}Br_2MoP_4$: C, 54.2; H, 4.98; P, 13.3; Br, 17.2. Found: C, 54.4; H, 4.85; P, 13.0; Br, 16.8. ^{31}P NMR (C_6D_6): δ 59.84 (dd, 2, $^2J_{P_aP_b}$ = 10.4 Hz, $^2J_{P_bP_d}$ = 22.6 Hz, $P_{b,c}$), 53.99 (dt, 1, $^2J_{P_aP_d}$ = 167.0 Hz, P_a), −9.23 (dt, 1, P_d). ^1H NMR (C_6D_6): δ 8.3–6.6 (m, Ph), 3.3–2.3 (broad d, 8, CH_2), 1.67 (d, 3, $^2J_{PH}$ = 8.1 Hz, Me), −5.90 (m, hydride). IR: ν(MoH) 1878 (b) cm^{-1}.

***mer,syn*-[MoBr(NNH$_2$)(dpepp)(PMe$_2$Ph)]Br (9).** Toluene (20 mL) was added to **7** (405 mg, 0.37 mmol) and the red solution stirred (30 h) at 45 °C. The resulting suspension was filtered and the solid washed (2 × 20 mL) with pentane and dried to afford 238 mg (0.30 mmol, 80%) of pale yellow product. ^{31}P NMR (CH$_2$Cl$_2$): δ 89.50 (dt, 1, $^2J_{P_aP_d}$ = 145.2 Hz, $^2J_{P_aP_b}$ = 8.2 Hz, P$_a$), 48.51 (dd, 2, $^2J_{P_bP_d}$ = 17.8 Hz, P$_{b,c}$), −9.70 (dt, 1, P$_d$). ^{1}H NMR (CD$_2$Cl$_2$): δ 7.6–6.8 (m, Ph), 3.1 (broad, 4, CH$_2$), 2.78 (broad, 4, CH$_2$), 1.74 (d, J_{PH} = 7.7 Hz, Me). IR: ν(NH) 3301, 2752 cm^{-1}. Addition of pentane to the filtrate resulted in the recovery of unreacted **7** (70 mg, 0.06 mmol).

Reactions of 2 with HCl. (i) Excess HCl (20 mol) was condensed (−196 °C) onto a sample of **2** (ca. 0.20 g, 0.25 mmol). Upon warming, the solid reacted as the acid thawed to afford a green powder. A series of three freeze–thaw cycles were conducted. The solid was agitated with a magnetic stir bar. Excess acid was removed from the solid. THF (30 mL) was added to the resulting forrest green powder to afford a yellow-green suspension. Filtration yielded a few milligrams of a white solid whose IR spectrum indicated the presence of N$_2$H$_4$·2HCl. To the yellow filtrate was rapidly added pentane (ca.0.1 L), which caused precipitation to occur. The solid was collected by filtration, washed (3 × 20 mL) with pentane, and dried to yield ca. 0.15 g (0.17 mmol, 68%) of yellow product. ^{31}P NMR (CD$_2$Cl$_2$): for *fac*-**16**, δ 80.35 (dt, 1, $^2J_{P_aP_d} \approx$ 30 Hz, $^2J_{P_aP_b} \approx {}^2J_{P_aP_c} \approx$ 16 Hz, P$_a$), 71.30 (dm, 1, $^2J_{P_bP_d}$ = 110.1 Hz, P$_b$), 61.45 (dt, 1, $^2J_{P_cP_e}$ = 115.4 Hz, $^2J_{P_bP_c}$ = 12.6 Hz, P$_c$), −11.73 (dt, 1, P$_d$), −22.08 (dt, 1, P$_e$); for *mer*-**16**, δ 66.33 (dd, 2, $^2J_{P_aP_b}$ = 11.3 Hz, $^2J_{P_bP_d}$ = 23.5 Hz, P$_{b,c}$), 58.66 (dt, 1, $^2J_{P_aP_d}$ = 183.7 Hz, P$_a$), 2.15 (dt, 1, P$_d$), −0.45 (m, 1, P$_e$). ^{1}H NMR (CD$_2$Cl$_2$): δ 11.50 (broad), 9.45 (broad), 8.1–7.0 (m, Ph), 4.8–0.8 (m, CH$_2$), −3.58 (broad, hydride), −5.15 (dq, $^2J_{PH}$ = 54.8 Hz, $^2J_{PH}$ = 33.3 Hz, hydride). Anal. Calcd for C$_{39}$H$_{50}$Cl$_3$MoP$_5$: C, 53.47; H, 5.75; Cl, 12.14; P, 17.68. Found: C, 53.06; H, 6.13; Cl, 12.00; P, 17.50. IR: ν(MoH) 1885 (b) cm^{-1}.

(ii) Benzene (20 mL) and HCl (0.73 mmol) were successively condensed (−196 °C) onto a sample of **2** (580 mg, 0.73 mmol). After warming to room temperature, the red suspension was stirred (15 h). The resulting greenish amber suspension was filtered to afford a few milligrams of an uncharacterized green powder. Addition of pentane (0.2 L) caused precipitation of a few milligrams of a purple-gray solid, which was not characterized. Following filtration, the filtrate was allowed to stand under N$_2$ (24 h), during which time amber prisms formed. The product was collected by filtration, washed (2 × 20 mL) with pentane, and dried to yield ca. 0.3 g (0.4 mmol, 50%) of **17**. ^{31}P NMR (C$_6$D$_6$): for major isomer, δ 94.05 (dt, 1, $^2J_{PP}$ = 47.1 Hz, $^2J_{PP}$ = 22.3 Hz, P$_a$), 84.24 (dm, 1, $^2J_{P_bP_d}$ = 131.5 Hz, P$_b$), 74.26 (dt, 1, $^2J_{P_cP_e}$ = 124.0 Hz, $^2J_{PP}$ = 18.5 Hz, P$_c$), −12.47 (dq, 1, $^2J_{PP}$ = 26.9 Hz, P$_d$), −19.96 (dm, 1, P$_e$); for minor isomer, δ 114.70 (t, 1, $^2J_{P_aP_d} \approx {}^2J_{P_aP_e}$ = 24.4 Hz, P$_a$), 61.04 (complex m, 2, $^2J_{PP} \approx$ 119 Hz, P$_{b,c}$), 24.52 (complex m, 2, P$_{d,e}$). ^{1}H NMR (C$_6$D$_6$): δ 8.5–6.5 (m, Ph), 4.0–1.5 (broad m, CH$_2$), 1.5–0.5 (m, Me), −6.75 (m, hydride, major isomer), −7.95 (m, hydride). IR: ν(MoH) 1950 (wb, minor isomer), 1840 (mb) cm^{-1}.

(iii) A reaction similar to (ii) was carried out by using THF and **2** (1.13 g, 1.42 mmol). The initial mixture was warmed to −78 °C to afford a red suspension. When this was warmed to 25 °C and stirred (0.5 h), a bright orange suspension formed. The mixture was cooled to −78 °C (15 h) and filtered at room temperature; the solid was washed (2 × 10 mL) with pentane and dried to yield 172 mg (0.20 mmol, 14%) of pure *fac*-**16**. Addition of pentane (0.25 L) to the filtrate caused precipitation of a yellow powder that upon isolation (as above) yielded 167 mg of impure *fac*-**16**. Upon cooling of the filtrate (0 °C) and reduction of the volume to ca. 30 mL with a stream of N$_2$ across the surface of the solution, crystals formed (1 h). Collection of the product (as above) afforded 521 mg (0.64 mmol, 45%) of orange dendritic crystals of the major isomer of **17**. IR: ν(MoH) 1840 cm^{-1}. ^{31}P NMR [C$_6$D$_6$/CH$_2$Cl$_2$ (1:1)]: δ 96.83 (m, 1, P$_a$), 88.30 (dm, 1, $^2J_{P_bP_d} \approx$ 131 Hz, P$_b$), 76.29 (dm, 1, $^2J_{P_cP_e} \approx$ 126 Hz, P$_c$), −14.40 (dm, 1, P$_d$), −22.59 (dm, 1, P$_e$).

Reaction of 2 with HBr. (i) Excess HBr (20 mol) was condensed (−196 °C) onto a sample of **2** (0.47 g, 0.60 mmol). Upon warming, the solid reacted as the acid thawed to give an olive green powder. A series of freeze–thaw cycles were performed. The solid was agitated with a magnetic stir bar. No noncondensable gas was evolved during this reaction. Excess acid was removed and THF (50 mL) added to afford a yellow-green suspension. The solid was collected by filtration, washed (3 × 20 mL) with pentane, and dried to yield 0.4 g of an olive green powder. IR: ν(NH) 2700–2150 cm^{-1}. Washing the solid with THF afforded a yellow solution. Addition of pentane caused precipitation to occur. Collection (as above) yielded a small amount of a tan-yellow powder. ^{31}P NMR (CD$_2$Cl$_2$, −55 °C): for *fac*-**13**, δ 81.10 (m, 1, P$_a$), 65.83 (dm, 1, $^2J_{P_bP_e}$ = 114.8 Hz, P$_b$), 56.15 (dt, 1, $^2J_{P_cP_d}$ = 105.6 Hz, P$_c$), −20.00 (dt, 1, P$_d$), −30.58 (dt, 1, $^2J_{PP}$ = 24.7 Hz, P$_e$); for *mer*-**13**, δ 62.97 (t, 2, $^2J_{PP}$ = 22.3 Hz, P$_{b,c}$), 55.09 (dt, 1, $^2J_{P_aP_d}$ = 152.2 Hz, $^2J_{PP}$ = 20.1 Hz, P$_a$), −7.86 (dt, 1, $^2J_{PP}$ = 22.3 Hz, P$_d$), −14.50 (m, 1, P$_e$). ^{1}H NMR (CD$_2$Cl$_2$, −55 °C): δ 12.69 (broad), 11.93 (broad), 11.39 (broad), 10.67 (broad), 10.20 (broad), 6.8–5.0 (m, Ph), 4.0–0.8 (m, CH$_2$), −2.65 (m, hydride), −5.90 (m, J = 26 Hz, hydride).

(ii) Benzene (15 mL) and HBr (1.62 mmol) were successively condensed (−196 °C) onto a sample of **2** (1.29 g, 1.62 mmol). After warming to room temperature, the red solution was stirred (15 h). The resulting tan-orange suspension was filtered and the solid washed (2 × 10 mL) with pentane and dried to yield 556 mg (0.60 mmol, 37%) of light green powder, *fac*-**13**. IR: ν(MoH) 1890 cm^{-1}. ^{31}P NMR (CD$_2$Cl$_2$): δ 84.63 (dt,1, J_{PP} = 36.0 Hz, J_{PP} = 19.8 Hz, P$_a$), 72.66 (dm, 1, $^2J_{P_bP_e}$ = 114.0 Hz, P$_b$), 59.14 (dt, 1, $^2J_{P_cP_d}$ = 115.8 Hz, J_{PP} = 13.1 Hz, P$_c$), −17.79 (dt, 2, J_{PP} = 30.6 Hz, P$_d$), −28.4 (dt, 1, J_{PP} = 13.1 Hz, P$_e$). Addition of pentane (0.2 L) to the filtrate resulted in a small amount of precipitate that was removed by filtration. Allowing the filtrate to stand under N$_2$ for ca. 24 h resulted in the formation of crystals. Collection of product (as above) afforded 150 mg (0.18 mmol, 10%) of air-stable orange needles of **14**. Anal. Calcd for C$_{39}$H$_{47}$BrMoP$_4$: C, 55.3; H, 5.60; Br, 9.44; P, 18.3. Found: C, 54.9; H, 5.89; Br, 9.16; P, 18.1. μ_{eff} = 1.87 μ_B (Evans' method[14]).

Allowing the filtrate to stand under N$_2$ for another 48 h resulted in the formation of amber prisms (50 mg, 0.06 mmol, 4%), which were collected as described above. IR: ν(MoH) 1957 (s) cm^{-1}. ^{31}P NMR (C$_6$D$_6$): δ 91.03 (t, 1, J_{PP} = 16.2 Hz, P$_a$), 67.64 (complex m, 2, P$_{b,c}$), −21.88 (complex m, 2, P$_{d,e}$). ^{1}H NMR (C$_6$D$_6$): δ 12.03 (s), 9.05 (s), 7.8–6.5 (m, Ph), 3.0–1.4 (m, CH$_2$), 1.24 (d, $J_{PH} \approx$ 7 Hz, Me), 0.42 (d, $J_{PH} \approx$ 7 Hz, Me), −8.74 (m, hydride). This air-stable complex was assigned the formula Mo(H)Br(dpepp)(dmpm) (**15**).

***fac*-[Mo(N$_2$H$_2$)(dpepp)(dmpm)][CF$_3$SO$_3$]$_2$ (18).** Triflic acid (0.12 mL, 1.40 mmol) was added dropwise to a stirred red solution of **2** (554 mg, 0.70 mmol) in THF (15 mL) cooled to −78 °C. Within 0.25 h, the reaction mixture was a green suspension. After standing (2 h) at −78 °C, the suspension was filtered and the solid washed (2 × 10 mL) with pentane and dried to afford 566 mg (0.52 mmol, 74%) of a light blue powder. IR: ν(NH) 3207 cm^{-1}. ^{31}P NMR [MeCN/CD$_2$Cl$_2$ (1:1), −10 °C]: δ 55.81 (complex m, 2, P$_{b,c}$), 47.14 (tt, 1, $^2J_{P_aP_b}$ = 6.7 Hz, $^2J_{P_aP_d}$ = 26.6 Hz, P$_a$), −27.28 (complex m, 2, P$_{d,e}$). Anal. Calcd for C$_{41}$H$_{49}$F$_6$MoN$_2$O$_6$S$_2$: N, 2.98. Found: N, 2.70.

Reaction of 4 with HCl. Hydrogen chloride (20 mol) was condensed (−196 °C) onto a sample of **4** (230 mg, 0.22 mmol). The solid reacted as the acid thawed to afford a forest green powder. Following a series of freeze–thaw cycles, while the solid was agitated with a magnetic stir bar, excess acid was removed after confirming that no noncondensable gas was evolved. Upon prolonged evacuation, the solid turned red-orange. IR: ν(MoH) 1885 cm^{-1}, ν(MoCl) 290 cm^{-1}. ^{31}P NMR (CD$_2$Cl$_2$, −78 °C): δ 91.77 (t, 1, J_{PP} = 31.3 Hz, P$_a$), 48.68 (complex m, 2, P$_{b,c}$), −7.91 (complex m, 2, P$_{d,e}$), 78.80 (m, 1, P$_{a'}$), 62.00 (dm, 1, P$_{b'}$), 48.20 (dm, 1, P$_{c'}$), −2.2 (dm, 2, P$_{d',e'}$). The solid was dissolved in THF at −78 °C, and the solution was filtered. Pentane (−78 °C) was then added to cause precipitation. The solid was collected by filtration, washed (3 × 20 mL) with pentane, and dried to yield 0.2 g (0.18 mmol, 82%) of yellow powder. Anal. Calcd for C$_{59}$H$_{58}$Cl$_3$MoP$_5$: C, 63.03; H, 5.20; N, 0.0; P, 13.78; Cl, 9.46. Found: C, 62.74; H, 5.19; N, 0.0; P, 13.70; Cl, 8.24.

Reaction of Hydrazido(2−) Complexes with Base. Complex **6** was reacted with Et$_3$N (1 mol) in C$_6$D$_6$ at 25 °C in an NMR tube. The solution changed from red to greenish amber. The ^{31}P NMR spectrum showed the presence of only **6** and free PMe$_2$Ph. A similar experiment carried out by using Proton Sponge (1 and 5.5 mol) afforded no reaction. In contrast, reaction with **7** in THF with Proton Sponge (2 mol) led to a rapid color change, red to bright green, and gas evolution. The ^{31}P NMR spectrum showed only **7**.

X-ray Crystallography. Full details of the crystallographic methodologies may be found in ref 32. Crystallographic data are given in Table II. The Mo atom position was located in a three-dimensional sharpened Patterson map; all non-hydrogen atoms were located on subsequent difference Fourier maps. Hydrogen atoms were included as fixed contributors in the final refinement cycle. Data were corrected for background, attenuators, and Lorentz and polarization effects.

Acknowledgment. This work was supported by the National Science Foundation through Grant CHE83-05478.

Supplementary Material Available: Tables of crystal data and experimental details, bond lengths, bond angles, anisotropic temperature factors, H atom coordinates and temperature factors, and atom coordinates and temperature factors (10 pages); a listing of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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