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Oxygen-, Sulfur-, and Nitrogen-Containing Molybdenum Complexes That Bind Dinitrogen[1]

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New bis(dinitrogen) complexes of molybdenum are reported containing oxygen, sulfur, and nitrogen ligands. The sodium amalgam reduction of $MoCl_3$(trident), where trident = $(Ph_2PCH_2CH_2)_2O$ (POP), $(Ph_2PCH_2CH_2)_2NR$ [R = H (PNHP); R = Me (PNMeP)], $(Ph_2PCH_2CH_2CH_2)_2S$ (dpps), and $(Ph_2PCH_2CH_2CH_2)_2PPh$ (ttp), in THF solution in the presence of L, where L = PPh_3, $PMePh_2$, and PMe_2Ph, led to the preparation of *trans*-$Mo(N_2)_2$(trident)(L). Formation of *trans*-$Mo(N_2)_2$(dpps)(L) represents the first example of any metal complex with a prior-coordinated sulfur atom binding N_2. Reaction of $Mo(N_2)_2$(trident)(L), where trident = POP and dpps, with HBr in THF afforded ammonia, and with HBr in CH_2Cl_2, ammonia and hydrazine. Complexes $Mo(N_2)_2$(POP)(L) are the first N_2 complexes with an oxygen-containing ligand to produce ammonia. Of the series of amine complexes only *trans*-$Mo(N_2)_2$(PNHP)($PMePh_2$) has been isolated pure. No ammonia was formed upon treatment with HBr/THF and only 1 mol of N_2 was evolved per mole of complex.

Introduction

Bis(dinitrogen) complexes of molybdenum of the type *trans*-$Mo(N_2)_2(triphos)PR_3$, where triphos = $Ph(CH_2CH_2PPh_2)_2$ and PR_3 = PPh_3 and $PMePh_2$, react with excess strong acid to produce ammonia in THF, according to eq 1, and ammonia and hydrazine

$$2Mo(N_2)_2(triphos)PR_3 \xrightarrow{HX,\ THF} 2NH_3 + 2MoX_3(triphos) + 2PPh_3 + 3N_2 \quad (1)$$

in solvents such as CH_2Cl_2 and toluene.[2,3] At least one monodentate ligand is required for ammonia and hydrazine formation. Triphos supports the integrity of the complex during the multistep reaction, enabling the final molybdenum-containing products to be isolated.[2-5] Initial reaction with acid HX (where X = Br or Cl) leads to the formation of a hydrazido(2−) complex, $[MoX(NNH_2)(triphos)(PR_3)]X$, which can be isolated.[2,6] Studies of the mechanisms of the reactions of these hydrazido complexes with acid to form ammonia and hydrazine have been complicated by two factors. (i) The hydrazido complexes occur as a mixture of two isomers as a result of the configuration at the central phosphorus atom of triphos.[7,8] (ii) Each isomer reacts at a very different rate. Although these isomers can be separated[2,7,8] we have decided that mechanistic studies may be better accomplished by making modifications to the triphos ligand. Thus replacing the center PhP unit by a S or O atom will avoid obtaining isomers of the type that we have already seen. To this end we have synthesized an extensive series of trident ligands.

trident = $(Ph_2PCH_2CH_2)_2X$ and $(Ph_2PCH_2CH_2CH_2)_2X$
X = S (PSP) X = S (dpps)
X = O (POP) X = PhP (ttp)
X = NH (PHNP)
X = NMe (PNMeP)

Although there is no definitive information concerning the site of binding of N_2 in nitrogenase, accumulated X-ray absorption data on nitrogenase point to molybdenum in both the MoFe protein and FeMo cofactor as having, in addition to Fe and S, neighboring light atoms, e.g., O, N, or C.[9] The paucity of N_2 complexes that contain these light atoms and yield ammonia provided an additional impetus for this work. Among the results reported in this paper are (i) the first example of any metal complex with a prior-coordinated sulfur atom binding N_2 and (ii) the first N_2 complex containing an oxygen ligand that produces ammonia.

Results and Discussion

All ligands, $MoCl_3$(trident), and bis(dinitrogen) complexes were prepared by methods reported in the literature.

The reduction of $MoCl_3$(PSP) by sodium amalgam in THF in the presence of PPh_3 or $PMePh_2$ under N_2 failed to afford an N_2 complex. This is in complete contrast to facile syntheses of both mono-[10] and bis(dinitrogen)[2] complexes of molybdenum using triphos. Inspection of molecular models suggested that better sulfur–molybdenum orbital overlap might be achieved in a six-coordinate complex if the ethylene backbone in PSP was replaced by propylene. Therefore dpps was synthesized. Indeed reduction of $MoCl_3$(dpps) led to the isolation of a series of bis(dinitrogen) complexes, *trans*-$Mo(N_2)_2(dpps)PR_3$ (**1**), where PR_3 = PPh_3, $PMePh_2$, and PMe_2Ph. We believe that these are the first examples of any metal complex with a prior-coordinated sulfur atom binding N_2. In previous cases of metal–N_2 complexes containing one or more coordinated sulfur atoms, the sulfur-containing ligand was introduced after N_2 was bound to the metal.[11] These complexes are uniformly less stable than their all-phosphorus counterparts and generally give unsatisfactory combustion analyses. However there is little doubt that these new complexes are structurally analogous to the other well-known bis(dinitrogen) complexes of molybdenum. In the infrared spectrum all new complexes display a very strong antisymmetric NN stretch at 1912–1928 cm^{-1} and a weak symmetric NN stretch at 2000–2022 cm^{-1}. The ^{31}P NMR data in C_6D_6 solution reveal a doublet for the dpps phosphorus atoms and a triplet for PR_3. These data together with the satisfactory N_2 analyses of two N_2 per Mo atom strongly support a complex with two trans N_2 ligands and three coordinated phosphorus atoms per molecule. Although we have not identified anything in the infrared spectrum of these complexes

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associated with a Mo–S interaction, we assume that sulfur coordinates to molybdenum in an 18-electron, monomeric complex.

In C_6D_6 solution **1**(PPh_3) displays after 0.7 h resonances in the ^{31}P NMR spectrum due to **1**(PPh_3) and two singlets at 23.6 and −10.1 ppm. The latter resonance is due to free PPh_3 and the former is assigned to $\{Mo(N_2)_2(dpps)\}$. Addition of excess $PMePh_2$ to this solution resulted in the appearance of resonances due to **1**($PMePh_2$) and disappearance of the singlet at 23.6 ppm. In order to determine whether or not PPh_3 dissociation was due to the trans influence of sulfur we prepared the corresponding series of bis(dinitrogen) complexes containing ttp, *trans*-$Mo(N_2)_2(ttp)PR_3$ (**2**), where PR_3 = PPh_3, $PMePh_2$, and PMe_2Ph. In the ^{31}P NMR spectrum of **2**(PPh_3) three sets of resonances were observed; those due to **2**(PPh_3), a singlet due to free PPh_3, and a doublet and triplet assigned to the five-coordinate species $\{Mo(N_2)_2(ttp)\}$. We conclude that dissociation of PPh_3 arises for steric rather than electronic reasons. As the number of atoms in the two chelate rings increases from five (triphos) to six (ttp, dpps), the XMoP(Ph_2) angles will increase from about 80 to close to 90°. This will result in greater steric interaction between the terminal PPh_2 groups and the fourth ligand in the equatorial girdle. The crystal structure of RhCl(ttp) revealed just such an interaction.[12] Undoubtably, as the cone angle of PR_3 decreases so will the steric interaction decrease. Interestingly, J_{PP} is observed between the terminal and central phosphorus atoms in coordinated *mer*-ttp but not in *mer*-triphos.[2,10,13]

It proved possible to prepare bis(dinitrogen) complexes containing POP, *trans*-$Mo(N_2)_2(POP)PR_3$ (**3**), where PR_3 = PPh_3, $PMePh_2$, and PMe_2Ph. There are very few N_2 complexes containing a coordinated oxygen atom.[14] The **3** complexes are more stable than **1**. These new complexes display symmetric and antisymmetric NN stretches in their infrared spectra. The POP complexes showed simple ^{31}P NMR spectra with no evidence of PR_3 dissociation. Evidence for oxygen atom coordination is derived from the following data. (i) The oxygen-bound methylene carbon atoms are shifted downfield by about 6 ppm in the ^{13}C NMR spectra of **3** relative to those in free POP, and (ii) there is considerable reduction in the relative intensity of the ether stretch (C–O–C) in the infrared spectrum of POP upon complexation.

Bis(dinitrogen) complexes with the amine-containing trident ligands were readily prepared from the corresponding $MoCl_3$(trident) complexes. Unfortunately, most of these new complexes could not be isolated as pure solids from the reaction mixtures. Thus, *trans*-$Mo(N_2)_2(PNHP)PR_3$ (**4**), where PR_3 = PPh_3 and $PMePh_2$, and *trans*-$Mo(N_2)_2(PNMeP)PPh_3$ (**5**) were prepared, but so far only **4**($PMePh_2$) has been isolated as a crystalline product.

When observed $\nu(N_2)$ values are compared within each series, the following trends are noted: $\nu(N_2)$ moves to lower frequency when (i) the chelate bite sizes increase from five to six, (ii) the central chelate atom is changed from PhP to S, and (iii) X in $X(CH_2CH_2PPh_2)_2$ is changed from PhP to O to HN.

Complexes **1**–**3** reacted with HBr in THF solution to produce N_2 and ammonia, but no hydrazine, in yields (see Table I) comparable to those obtained from *trans*-$Mo(N_2)_2(triphos)PR_3$ (**6**), where PR_3 = PPh_3 and $PMePh_2$.[2] Complexes **3** are the first N_2 complexes with an oxygen-containing ligand to produce ammonia. When the solvent is changed to CH_2Cl_2, high yields of both ammonia and hydrazine were obtained. Somewhat surprisingly **4**($PMePh_2$) reacted with HBr in THF at room temperature to evolve 1 mol of N_2 but yielded no ammonia or hydrazine.

Summary and Conclusion

Confining sulfur, oxygen, and NR (R = H or Me) to the center position of a potential tridentate ligand containing two phosphorus atoms has led to the preparation of a series of bis(dinitrogen) complexes containing these ligands. Whereas oxygen and NR analogues of triphos, $X(CH_2CH_2PPh_2)_2$ afforded *trans*-$Mo(N_2)_2$(trident)PR_3, the sulfur analogue PSP failed to do so. However, the corresponding ligand dpps with a propylene backbone proved satisfactory. These new sulfur-containing complexes are the first to be synthesized by binding N_2 to a complex containing a prior-coordinated sulfur atom. These results suggest that complexes of molybdenum containing one or more non-phosphorus ligand atoms will bind N_2.

Table I. Yields of Nitrogen-Containing Products from Reactions of Bis(dinitrogen) Complexes with HBr at 25 °C[a]

complex[b]	solvent (mol of HBr)[c]	time, h	mol[c] of product N_2	mol[c] of product NH_3	mol[c] of product N_2H_4	N_2 balance mol[c]	N_2 balance %
1($PMePh_2$)	THF (50)	34	1.02	0.43	0.01	1.25	63
1(PMe_2Ph)	THF (50)	40	0.97	0.25	0.01	1.10	55
2($PMePh_2$)	THF (50)	48	1.47	0.25	nd	1.60	80
2($PMePh_2$)	CH_2Cl_2 (50)	48	1.33	0.35	0.41	1.92	96
3(PPh_3)	THF (50)	48	1.50	0.25	nd	1.63	81
3($PMePh_2$)	THF (50)	48	1.14	0.20	nd	1.24	61
3($PMePh_2$)	CH_2Cl_2 (50)	48	1.07	0.45	0.41	1.71	86
4($PMePh_2$)	THF (50)	48	1.10	nd	nd	1.10	55
6(PPh_3)	THF (19)	62	1.46	0.72	nd	1.82	91
6(PPh_3)	CH_2Cl_2 (20)	60	1.23	0.27	0.19	1.56	78

[a] Reaction vessels were evacuated to 10^{-4} Torr and acid and solvent condensed in at 77 K; nd = not detected. [b] **1**, *trans*-$[Mo(N_2)_2(dpps)PR_3]$; **2**, *trans*-$[Mo(N_2)_2(ttp)PR_3]$; **3**, *trans*-$[Mo(N_2)_2(POP)PR_3]$; **4**, *trans*-$[Mo(N_2)_2(PNHP)PR_3]$, **6**, *trans*-$[Mo(N_2)_2(triphos)PR_3]$. [c] Per mole of Mo.

In general, these new complexes displayed properties similar to those of *trans*-$Mo(N_2)_2(triphos)PR_3$. For example, they reacted with HBr in THF to yield ammonia and with HBr in CH_2Cl_2 to afford ammonia and hydrazine. Complexes **3** are the first N_2 complexes with an oxygen-containing ligand to produce ammonia. A notable exception is *trans*-$Mo(N_2)_2(PNHP)PMePh_2$, which reacted with HBr in THF to liberate 1 mol of N_2 but yielded no ammonia or hydrazine.

Some differences in chemistry may evolve in studies of intermediates formed upon protonation of N_2 in these new complexes. Work is currently under way in this area.

Experimental Section

General Procedures. All preparations and reactions were carried out either under a dry N_2 atmosphere or in vacuo. Compounds were handled in a water- and oxygen-free environment, which was provided by use of Schlenk equipment, glovebags, and a Vacuum Atmospheres Corp. drybox.

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

Physical Measurements. IR spectra were obtained as KBr pellets on a Perkin-Elmer 283 spectrophotometer. ^1H NMR spectra were recorded on either a Varian EM-390 (90 MHz) or VXR-200 (200 MHz) instrument. $^{31}P\{^1H\}$ NMR spectra were obtained on either a Varian VXR-200 or XL-200 (80 MHz) instrument. $^{13}C\{^1H\}$ NMR spectra were obtained on a Varian VXR-200 (50 MHz). All spectra were recorded at ambient temperature unless otherwise stated. All chemical shifts are reported in ppm from Me_4Si (^1H, ^{13}C) or 85% H_3PO_4 (^{31}P) with positive values being to lower field.

Reagents and Materials. All solvents were reagent grade and purchased from commercial sources. Solvents were rigorously dried by heating at reflux over the appropriate drying agent and deoxygenated by bubbling with N_2 for a minimum of 0.5 h prior to use.

Chemicals were purchased from commercial sources and used without further purification. Butyllithium, 1,3-dichloropropane, 2,2′-thiodiethanol, 3,3′-thiodipropanol, diethanolamine, *N*-methyldiethanolamine, 2-chloroethyl ether, diphenylphosphine, thionyl chloride, and tetraphenylphosphonium bromide were purchased from Aldrich Chemical Co., Inc. Other phosphines were purchased from Strem Chemicals, Inc.

Ligand Syntheses. Bis(2-(diphenylphosphino)ethyl) Sulfide, PSP.[15,16] A round-bottom flask (0.5 L) fitted with a condenser and septum-capped

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stopcock was charged with 2,2′-thiodiethanol (16.4 g, 134 mmol). Thionyl chloride (40 g, 2.5-fold excess) was slowly added by syringe and the solution stirred (2 h). Excess thionyl chloride was removed in vacuo. *Caution! The residue is a mustard and must be handled with gloves in a good fume hood.* The resulting residue was dissolved in THF and the solution passed through a cannula into two equivalents of lithium diphenylphosphide (prepared by adding 100 mL of 2.6 M butyllithium in hexanes to diphenylphosphine (50 g, 260 mmol) in THF (250 mL)). After being stirred (1 h), the solution was washed with water (3 × 25 mL) and the organic layer dried ($MgSO_4$). The solution was filtered and solvent removed with a rotary evaporator to yield a colorless solid (ca. 80% yield). ^{1}H NMR ($CDCl_3$): δ 7.3 (m, 10, Ph), 2.4–2.7 (m, 2, CH_2), 2.1–2.3 (m, 2, CH_2).

Bis(3-(diphenylphosphino)propyl) sulfide, dpps,[16] was prepared analogously to PSP starting with 3,3′-thiodipropanol. The product is a viscous yellow oil. ^{1}H NMR ($CDCl_3$): δ 7.3 (m, 10, Ph), 2.5 (t, 2, CH_2), 2.1 (m, 2, CH_2), 1.6 (m, 2, CH_2). ^{13}C NMR ($CDCl_3$): δ 33.9 (d, $^{3}J_{PC}$ = 14 Hz), 28.0 (d, $^{2}J_{PC}$ = 13 Hz), 26.9 (d, J_{PC} = 18 Hz). ^{31}P NMR (CD_3COCD_3): δ −17.9 (s).

Bis(2-(diphenylphosphino)ethyl) Ether, POP. This ligand was prepared analogously to PSP except that 30 mmol of $LiPPh_2$ in THF (25 mL) was added to 15 mmol of 2-chloroethyl ether in THF (25 mL). The product was a light yellow oil. ^{1}H NMR ($CDCl_3$): δ 7.2 (m, 10, Ph), 3.45 (m, 2, CH_2O), 2.30 (t, 2, CH_2P). ^{13}C NMR (C_6D_6): δ 67.7 (d, $^{2}J_{PC}$ = 24 Hz), 28.9 (d, J_{PC} = 14 Hz). ^{31}P NMR (C_6D_6): δ −26.9 (s).

Bis(2-(diphenylphosphino)ethyl)amine, PNHP.[16] This ligand was prepared in the same way as PSP. Diethanolamine (21 mmol) was treated with excess thionyl chloride. The resulting solid was dissolved in water and the solution made basic with 10% NaOH. This solution was extracted with CH_2Cl_2 from which a colorless oil, $HN(CH_2CH_2Cl)_2$, was obtained. *Caution! This compound behaves as a mustard and must be handled with gloves in a good fume hood.* This product (1.86 g, 12.9 mmol) was placed in THF (40 mL) and $LiPPh_2$ (25.8 mmol) in THF (30 mL) added. Workup according to the procedure used for preparing PSP yielded a viscous yellow oil. ^{1}H NMR ($CDCl_3$): δ 7.2 (m, 10, Ph), 2.7 (t, 4, CH_2), 2.2 (t, 4, CH_2), 1.6 (s, 1, NH).

Bis(2-(diphenylphosphino)ethyl)methylamine, PNMeP.[16] This ligand was prepared from *N*-methyldiethanolamine, which was converted to $MeN(CH_2CH_2Cl)_2$ with thionyl chloride in diethyl ether. The final product, PNMeP, was a yellow oil. ^{1}H NMR ($CDCl_3$): δ 7.3 (m, 20, Ph), 2.2–2.6 (m, 4, CH_2), 2.2 (s, 3, CH_3), 1.6–1.9 (m, 4, CH_2).

Bis(3-(diphenylphosphino)propyl)phenylphosphine, ttp. This ligand was prepared by a modification of a procedure of Meek et al.[17] A solution of $Ph_2PCH_2CH_2CH_2Cl$ was prepared by the addition of $LiPPh_2$ (36 mmol) in THF (50 mL) to 1,3-dichloropropane (36 mmol) in THF (80 mL). This solution was then passed via cannula into a slurry of $PhPLi_2$ [$PhPH_2$ (18 mmol) and BuLi (36 mmol) in THF (75 mL)]. The product was worked up as for PSP to yield a colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.2 (m, 25, Ph), 2.0 (m, 4, CH_2), 1.6 (m, 8, CH_2). ^{13}C NMR ($CDCl_3$): δ 29.0 (t, $^{1}J_{PC}$ = 12 Hz), 28.9 (t, $^{1}J_{PC}$ = 12 Hz), 21.7 (t, $^{2}J_{PC}$ = 15 Hz).

Synthesis of $MoCl_3$(trident).[2] These complexes were prepared by the method used to prepare $MoCl_3$(triphos) reported previously, except for $MoCl_3$(PNHP), which was prepared from $[Ph_4P][MoCl_4(THF)_2]$.[18] Thus, a mixture of $[Ph_4P][MoCl_4(THF)_2]$ (2.71 g, 3.75 mmol) and PNHP (1.65 g, 3.75 mmol) in CH_2Cl_2 (30 mL) was heated at reflux (16 h). The volume of solution was reduced by half and sufficient diethyl ether added to precipitate 1.17 g (2.65 mmol, 71%) of product.

All $MoCl_3$(trident) complexes are yellow and were stored in the drybox. No effort has been made to thoroughly characterize these complexes at this time.

Synthesis of Bis(dinitrogen) Complexes. The bis(dinitrogen) complexes were prepared in a 400-mL Fischer-Porter pressure bottle by variations of a published method.[2]

$Mo(N_2)_2(dpps)(PR_3)$ (1). A bottle containing $MoCl_3$(dpps) (2.06 g, 3.0 mmol), PPh_3 (1.51 g, 6.0 mmol) (1 equiv of PR_3 was used for PR_3 = PMe_2Ph and $PMePh_2$), 1% sodium amalgam (50 g), and THF (80 mL) was charged to 65 psi of N_2 and the yellow suspension stirred (18 h). The resulting deep red solution was decanted from the mercury and filtered through a layer of Celite. The filtrate was then rigorously bubbled with N_2 and pentane rapidly added to precipitate 2.9 g (2.2 mmol, 74%) of brick red product.

1(PPh_3). ^{31}P NMR[19] (C_6D_6): δ 55.5 (t, 1, $^{2}J_{P_aP_x}$ = 15.3 Hz, P_x), 19.6 (d, 2, P_a). IR: ν(NN) 2022 (w), 1912 (vs) cm^{-1}.

1(PMe_2Ph). Anal. Calcd for $C_{38}H_{43}MoN_4P_3S$: C, 58.76; H, 5.59; N, 7.21; P, 11.96. Found: C, 58.33, H, 5.62; N, 6.89; P, 11.38. ^{31}P NMR[19] (C_6D_6): δ 21.2 (d, 2, $^{2}J_{P_aP_x}$ = 17.6 Hz, P_a), 8.8 (t, 1, P_x). IR: ν(NN) 2011 (w), 1928 (vs) cm^{-1}.

1($PMePh_2$). Anal. Calcd for $C_{43}H_{45}MoN_4P_3S$: C, 61.57; H, 5.42; N, 6.68; P, 11.07; S, 3.83. Found: C, 60.02; H, 5.63; N, 3.83; P, 10.69; S, 3.98. ^{31}P NMR[19] (C_6D_6): δ 28.5 (t, 1, $^{2}J_{P_aP_x}$ = 16.0 Hz, P_x), 21.2 (d, 2, P_a). IR: ν(NN) 2000 (w), 1925 (vs) cm^{-1}.

$Mo(N_2)_2(ttp)(PR_3)$ (2). Typically, $MoCl_3$(ttp) (900 mg, 1.2 mmol), 1 equiv of PR_3 (2 equiv of PPh_3), and 40 g of 1% sodium amalgam in THF (40 mL) were stirred (18 h) together. Product was obtained after the addition of methanol.

2($PMePh_2$). Anal. Calcd for $C_{49}H_{50}MoN_4P_4{\cdot}C_4H_8O$: C, 64.49; H, 5.94; N, 6.13; P, 12.55. Found: C, 63.11; H, 5.96; N, 6.12; P, 12.54. ^{31}P NMR[19] (C_6D_6): δ 22.1 (dd, 2, $^{2}J_{P_aP_b}$ = 18.5, $^{2}J_{P_aP_x}$ = 24.3 Hz, P_a), 16.6 (dt, 1, $^{2}J_{P_bP_x}$ = 99.7 Hz, P_x), 11.0 (dt, 1, P_b). ^{1}H NMR (C_6D_6): δ 6.7–7.6 (m, Ph), 3.6 (m, 2, CCH_2), 2.6 (m, 4, PCH_2), 2.4 (m, 4, PCH_2), 1.8 (m, 6, CH_2 (ttp and THF)), 1.4 (m, 3, PCH_3). IR: ν(NN) 2000 (w), 1939 (vs) cm^{-1}.

2(PMe_2Ph). Anal. Calcd for $C_{44}H_{48}MoN_4P_4$: N, 6.57. Found: N, 6.29. ^{31}P NMR[19] (C_6D_6): δ 22.3 (dd, 2, $^{2}J_{P_aP_b}$ = 19.7, $^{2}J_{P_aP_x}$ = 23.8 Hz, P_a), 11.9 (dt, 1, $^{2}J_{P_bP_x}$ = 99.6 Hz, P_b), −1.90 (dt, 1, P_x). IR: ν(NN) 2003 (w), 1941 (vs) cm^{-1}.

2(PPh_3). ^{31}P NMR[19] (C_6D_6): δ 40.6 (dt, 1, $^{2}J_{P_aP_b}$ = 24.9, $^{2}J_{P_bP_x}$ = 96.1 Hz, P_x), 24.9 (dd, 2, $^{2}J_{P_aP_x}$ = 18.4 Hz, P_a), 11.7 (dt, 1, P_b). IR: ν(NN) 2009 (w), 1949 (vs) cm^{-1}. The ^{31}P NMR spectrum of **2**(PPh_3) also shows resonances due to free PPh_3 and a non-PPh_3-containing species: δ 26.0 (d, 2, $^{2}J_{P_aP_b}$ = 25.3 Hz, P_a), 21.6 (t, 1, P_b).

$Mo(N_2)_2(POP)(PR_3)$ (3). Methanol was used to cause precipitation of the red product.

3(PPh_3). Anal. Calcd for $C_{46}H_{43}MoN_4OP_3$: C, 64.48; H, 5.07; N, 6.54. Found: C, 63.77; H, 4.53; N, 6.34. ^{31}P NMR[19] (C_6D_6): δ 80.5 (t, 1, $^{2}J_{P_aP_x}$ = 7.23 Hz, P_x), 48.5 (d, 2, P_a). ^{13}C NMR (C_6D_6): δ 73.4 (m, OCH_2), 34.4 (m, PCH_2). IR: ν(NN) 2000 (w), 1939 (vs) cm^{-1}.

3($PMePh_2$). ^{31}P NMR[19] (C_6D_6): δ 52.7 (t, 1, $^{2}J_{P_aP_x}$ = 7.07 Hz, P_x), 50.6 (d, 2, P_a). IR: ν(NN) 1998 (w), 1941 (vs) cm^{-1}.

3(PMe_2Ph). ^{31}P NMR[19] (C_6D_6): δ 51.5 (d, 2, $^{2}J_{P_aP_x}$ = 6.73 Hz, P_a), 34.6 (t, 1, P_x). IR: ν(NN) 2003 (w), 1933 (vs) cm^{-1}.

$Mo(N_2)_2(PNHP)(PMePh_2)$ (4). $MoCl_3$(PNHP) (466 mg, 1.05 mmol), $PMePh_2$ (221 mg, 1.10 mmol), and 40 g 1% sodium amalgam were stirred in THF (50 mL) for 8 h. After filtration, the volume of the deep red solution was reduced to 10 mL by vigorously bubbling with N_2. The solution was cooled to −78 °C and methanol added to cause precipitation of the deep red product. ^{31}P NMR[19] (C_6D_6): δ 52.3 (d, 2, $^{2}J_{P_aP_x}$ = 7.5 Hz, P_a), 40.4 (t, 1, P_x). IR: ν(NN) 1995 (w), 1930 (vs) cm^{-1}.

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Registry No. **1** ($PMePh_2$), 112596-97-1; **1** (PMe_2Ph), 112596-98-2; **1** (PPh_3), 112596-99-3; **2** ($PMePh_2$), 105560-48-3; **2** (PMe_2Ph), 105560-47-2; **2** (PPh_3), 112597-00-9; **3** (PPh_3), 112597-01-0; **3** ($PMePh_2$), 112597-02-1; **3** (PMe_2Ph), 112597-03-2; **4** ($PMePh_2$), 112597-04-3; **4** (PPh_3), 112597-05-4; **5**, 112597-06-5; **6** (PPh_3), 75420-24-5; POP, 50595-38-5; ttp, 34989-06-5; THF, 109-99-9; $MoCl_3$(dpps), 112597-07-6; $MoCl_3$(ttp), 105560-46-1; $MoCl_3$(PNHP), 112597-08-7; $MoCl_3$(POP), 112597-09-8; $MoCl_3$(triphos), 97590-53-9; $MoCl_3$(PNMeP), 112597-10-1; $LiPPh_2$, 4541-02-0; $Ph_2PCH_2CH_2CH_2Cl$, 5713-55-0; CH_2Cl_2, 75-09-2; HBr, 10035-10-6; 2-chloroethyl ether, 111-44-4; 1,3-dichloropropane, 142-28-9; ammonia, 7664-41-7; hydrazine, 302-01-2.

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(19) The labels P_a, P_b, and P_x refer to the terminal and central phosphorus atoms of trident and to monodentate phosphine, respectively.