Articles

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Synthesis of Mono(dinitrogen) Complexes of Molybdenum. Formation of Ammonia and Hydrazine[†,1]

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The synthesis and reactivity of a series of mono-N_2 complexes of molybdenum are reported. Reduction of $MoCl_3$(triphos), where triphos = $PhP(CH_2CH_2PPh_2)_2$, with sodium amalgam in the presence of 2L or L_2 and with a regulated amount of N_2 led to the formation of $Mo(N_2)$(triphos)(L_2) (**1**–**5**): **1**, L = 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. Complexes **3** and **5** were each a mixture of two isomeric mono-N_2 complexes. Complexes **1**–**5** reacted with excess HX (X = Br, Cl) to afford varying yields of ammonia, hydrazine, and N_2 (and some H_2). Loss of N_2 occurred readily from **1** when it was evacuated in the solid state to give **7**. Five-coordinate **7** reacted with H_2, CO, and C_2H_4 in the solid state to form MoH_2(triphos)$(PMe_2Ph)_2$ (**8**), Mo(CO)(triphos)$(PMe_2Ph)_2$ (**9**), and $Mo(C_2H_4)$(triphos)$(PMe_2Ph)_2$ (**10**), respectively. Reaction of solids **7**, **8**, and **10** with N_2 regenerated **1**. Structural assignments of the new complexes are based upon ^{31}P and ^1H NMR spectral data. Triphos is shown to adopt both *fac* and *mer* configurations.

Introduction

We have prepared a series of mono-N_2 complexes of molybdenum (eq 1, where triphos = $PhP(CH_2CH_2PPh_2)_2$) and begun

$$MoCl_3(\text{triphos}) + L_2 \text{ (or 2L)} \xrightarrow[\text{THF}]{\text{Na/Hg}} Mo(N_2)(\text{triphos})(L_2) \quad \begin{array}{l} \mathbf{1},\ L = PMe_2Ph \\ \mathbf{2},\ L_2 = \text{dmpm} \\ \mathbf{3},\ L_2 = \text{diars} \\ \mathbf{4},\ L_2 = \text{dppm} \\ \mathbf{5},\ L_2 = \text{dppe} \end{array} \tag{1}$$

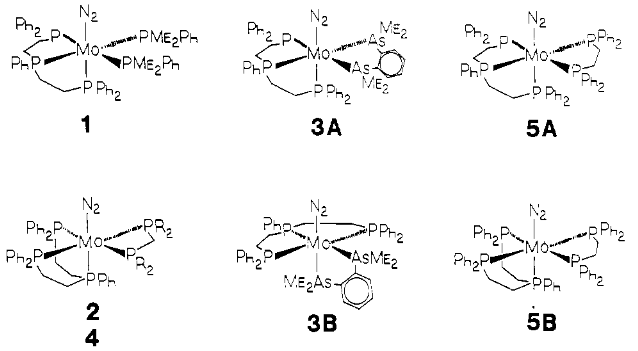
a study of their chemistry.[2,3] These complexes break new ground because few of the more than 100 well-defined mono-N_2 complexes of transition metals have been shown to react to give more than a trace of ammonia and/or hydrazine.[4,5] This is to be contrasted with the behavior of (i) the bis-N_2 complexes of molybdenum and tungsten, from which high yields of ammonia and occasionally hydrazine can be obtained,[6-9] and (ii) the bridged-N_2 complexes of titanium[10] and tantalum[11] and the mixed bridged- and terminal-N_2 complex of zirconium,[12] from which high yields of hydrazine were obtained. The mono-N_2 complexes reported in this paper yielded ammonia and hydrazine. Although there are a number of mono-N_2 complexes of molybdenum known, only one similar complex has been reported previously, $Mo(N_2)(PMe_3)_5$.[13]

In this paper we describe in detail the syntheses of the new mono-N_2 complexes and their reactions to afford ammonia and hydrazine, which have been reported in preliminary communications.[2,3] In addition, the replacement of N_2 in **1** by H_2, CO, and C_2H_4, respectively, is reported.

Results

Formation of Mono(dinitrogen) Complexes. Reduction of $MoCl_3$(triphos) with sodium amalgam in the presence of a controlled amount of N_2 and PMe_2Ph (L, 2 mol) or 1 mol of a bidentate ligand (L_2) led to the isolation of a series of mono-N_2 complexes **1**–**5** (eq 1). Reactions were successfully carried out with 4 mol of N_2/mol of Mo in a closed system typically using 4 mmol of $MoCl_3$(triphos) and 0.1 L of N_2-saturated THF in a 0.5 L vessel filled with N_2 (0.4 L, 16 mmol at ambient temperature). In the syntheses of **1** and **3**–**5**, the pressure in the vessel was increased to 75 psi by the addition of argon. Yields of **1** were noticeably higher under these conditions than when the pressure was not increased by adding argon. However, employing these conditions in the preparation of **2** led to the isolation of **2** and **6**, a non-N_2-containing complex, Mo(triphos)(dmpm)(η^1-dmpm) in

Chart I



1 **3A** **5A**

2
4 **3B** **5B**

[†] Dedicated to Professor M. Frederick Hawthorne on the occasion of his 60th birthday.

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which one dmpm ligand is monodentate. The highest yields of **2** were obtained when the synthesis was carried out with a large excess of N_2, under which conditions no **6** was detected.

Complex **1** is very soluble in most solvents. Thoroughly N_2-saturated wet methanol proved to be a better countersolvent for the precipitation of **1** than dry methanol. However, methanol slowly reacted with **1**, so that once collected **1** was rapidly dried in vacuo. This procedure led to the rapid loss of N_2 from solid **1** as evidenced by a rapid color change from bright orange to a progressively darker brown and the subsequent chemistry (vide infra). Reintroduction of N_2 resulted in the rapid restoration of the bright orange color. Of the complexes **1**–**5**, only **1** showed loss of N_2 in vacuo at room temperature. For this reason, during the isolation of **1** solutions were bubbled with N_2 to minimize possible irreversible loss of N_2 and during manipulations of solid **1** on the vacuum line samples were only briefly subjected to vacuum.

The structures of all new complexes were assigned on the basis of their $^{31}P\{^1H\}$ NMR spectra by comparison with those of other [Mo(triphos)] complexes (see Chart I).[14-16] However these spectra were frequently second order, and therefore many of the coupling assignments given in the Experimental Section are best estimates. An important part of determining the structure was to locate any large PP coupling constants. Complex **1**, isolated in 78% yield, gave a spectrum in which four of the phosphorus atoms displayed large trans coupling constants: the PMe_2Ph ligands, the central phosphorus atom P_a, whose chemical shift value is normally downfield of the terminal phosphorus atoms of triphos, and one of the terminal phosphorus atoms P_b. The data clearly show that triphos is facial and P_c is trans to N_2. In previously reported bis-N_2 complexes of molybdenum, triphos adopted a meridional configuration in which it was generally found that within triphos $^2J_{PP} \approx 0$ Hz, a useful guide in assigning the configuration of triphos.

Both **2** and **4** displayed AMM′XX′ spectra. The proposed structures with *fac*-triphos and N_2 trans to P_a are consistent with P_a showing no large J_{PP} coupling. The complex MoBr(triphos)(dmpm) that was prepared from **2** and for which we have an X-ray crystal structure displays this arrangement of phosphorus atoms.[17]

Complex **3** was isolated as a mixture of two isomers. The major isomer (62%) showed two singlets consistent with *mer*-triphos and N_2 trans to an arsenic atom. In the ^{31}P NMR spectrum of the other isomer each phosphorus atom displayed a doublet of doublets consistent with *fac*-triphos and N_2 trans to P_c. The IR spectrum showed one broad $\nu(NN)$ band at 1960 cm^{-1}. No effort was made to separate these isomers.

Complex **5** was also a mixture of isomers. In the ^{31}P NMR spectrum the minor isomer **5B** (41%) exhibited a quintet and a doublet of relative areas 1:4. This can only be accounted for by having *fac*-triphos and all four Ph_2P groups in the equatorial girdle and P_a trans to N_2. The other isomer **5A** displayed a much more complex spectrum interpreted as *fac*-triphos and N_2 trans to P_c. The IR spectrum showed two strong $\nu(NN)$ bands at 2008 and 1955 cm^{-1}, respectively. The vibration at 2008 cm^{-1} is at much higher energy than those of the other mono-N_2 complexes reported here and more intense than the antisymmetric $\nu(NN)$ vibration associated with *trans*-bis(dinitrogen)molybdenum complexes.

Table I. Yields of Dinitrogen, Ammonia, and Hydrazine

	acid		time,	T,	yield		
complex[a]	(amt, mol)[b]	solvent[c]	h	°C	N_2[d,e]	NH_3[d]	N_2H_4[d]
1	HCl (40)	A	64	18	28	32	17
1	HBr (40)	A	36	18	35	51	30
1	HCl (40)	C	39	70	56	36	48
1	HBr (36)	C	15	61	54	51	29
1	HCl (20)	D	63	25	24	12	7
1	HCl (10)	B	38	55	130	10	12
1	HCl (80)	B	38	55	68	8	41
1	HBr (20)	B	96	25	82	8	0
1	HBr (26)	E	39	47	33	7	<1
2	HBr (23)	A	48	25	93	36	32
2	HCl (10)	B	39	55	241[f]	5	0
2	HCl (80)	B	39	55	235[f]	5	0
2	HBr (11)	C	67	25	92	26	10
2	HBr (50)	C	67	25	114	29	16
2	HBr (100)	C	67	25	94	24	10
2	HCl (29)	C	42	48	153	15	4
3	HBr (23)	A	48	25	69	47	18
4	HBr (22)	A	48	25	36	6	39
4	HBr (20)	A	36	38	45	3	35
4	HBr (20)	A	36	38	45	3	35
4	HCl (40)	B	16	25	208	0	0
4	HCl (40)	B	16	45	225	0	0
4	HBr (20)	C	64	25	24	4	15
5	HBr (20)	A	36	38	23	15	19
5	HCl (40)	B	16	45	178	10	0

[a] **1** = $Mo(N_2)(triphos)(PMe_2Ph)_2$; **2** = $Mo(N_2)$(triphos)(dmpm); **3** = $Mo(N_2)$(triphos)(diars); **4** = $Mo(N_2)$(triphos)(dppm); **5** = Mo(N_2)(triphos)(dppe). [b] Per mol of complex. [c] A = CH_2Cl_2; B = THF; C = toluene; D = C_6H_6; E = MeOH. [d] (mol/mol of complex) × 100. [e] H_2 also produced in some cases. [f] H_2 was shown to constitute >50% of the noncondensable gas according to gas chromatography upon comparison with a N_2/H_2 mixture of known composition.

Reactions of Mono-N_2 Complexes with Acid: Ammonia and Hydrazine Formation. In order to investigate the ability of the new mono-N_2 complexes to yield ammonia and hydrazine and to compare the results with those from the bis-N_2–triphos system similar conditions were employed:[8] HBr and HCl in THF, CH_2Cl_2, and toluene solvents (see Table I). Reactions were run (≥15 h) from 18 to 70 °C with different initial concentrations of acid. The amounts of noncondensable gas, ammonia, and hydrazine formed were measured quantitatively. The evolved gas consisted of N_2 and frequently H_2 at higher reaction temperatures (see Table I). Dihydrogen had not been detected in similar studies of **11**.[8] In CH_2Cl_2 solution **1**–**5** all produced ammonia and hydrazine with HBr under similar conditions. Whereas **1**, **2**, **4**, and **5** favored hydrazine over ammonia, **3** favored ammonia. In THF solution with HCl, no hydrazine was detected except for the reaction with **1** and very little or no ammonia was produced. Significant amounts of H_2 were produced in these reactions. The reactions of **1**–**5** in toluene resulted in the immediate formation of an oil. Prolonged reaction with acid, usually at elevated temperature, resulted in varying amounts of ammonia and hydrazine being formed, with **1** showing the highest yields of reduced nitrogen products. Overall, **1** was more reactive toward N_2 reduction than the other complexes that contain a bidentate ligand.

Reactions of Solid 1 with H_2, CO, and C_2H_4. The facile loss of N_2 from solid orange **1** at room temperature under vacuum (to yield a dark brown solid) was in marked contrast to the behavior of **2**–**5**, which showed no such loss. The ^{31}P NMR spectrum of a sample of **1** that had been subjected to vacuum for 48 h revealed a mixture of **1** and a second complex containing five inequivalent phosphorus atoms formulated as [Mo(triphos)$(PMe_2Ph)_2$] (**7**). The IR spectrum of a sample of **1** that had been evacuated and treated with $^{15}N_2$ in the solid state showed that the ratio of **1**($^{14}N_2$) to **1**($^{15}N_2$) was ca. 3:2.

Reactions of **1** (orange) that had been evacuated to yield **7** (brown) were carried out in the solid state with H_2, CO, and C_2H_4, respectively, at room temperature. Reaction of H_2 with **7** caused the solid to become orange immediately. The IR spectrum showed $\nu(MoH)$ at 1869 cm^{-1} and no $\nu(NN)$. The hydride region of the ^1H NMR spectrum showed a doublet of quintets consistent with a stereochemically nonrigid, seven-coordinate dihydride structure for **8**. Each hydride ligand is coupled to four similar ($^2J_{PH}$ = 35.5 Hz) phosphorus atoms and one unique ($^2J_{PH}$ = 19.8 Hz) phos-

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(14) Phosphorus atom assignments: for triphos, P_a central, P_b and P_c terminal; P_{d-g} are other phosphorus atoms arranged in order of decreasing chemical shift.

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phorus atom. The ^{31}P NMR spectrum confirmed the presence of five-coordinated phosphorus atoms with P_b and P_c appearing together as a broad singlet, which contrasts with their inequivalence in **1**. Furthermore there are no large J_{PP} values in contrast to those for **1** and **7**, suggesting a geometric change upon coordination of H_2. The X-ray crystal structure of $MoH_2(PMe_3)_5$[17] revealed a pentagonal-bipyramidal geometry with three phosphines and the two hydrogen atoms constituting the girdle. On the basis of this structure, P_b and P_c would occupy the axial positions and the remaining ligating atoms the five equatorial sites in **8** with P_d and P_e inequivalent. Evacuation of solid **8** resulted in the formation of a dark brown solid, and when **8** was stored under N_2, **1** was formed slowly. The facile loss of H_2 from **8** suggests that one of the tautomeric forms of **8** contains the η^2-H_2 ligand.[18]

Carbon monoxide reacted irreversibly with **7** in the solid state to form *fac*-$Mo(CO)(triphos)(PMe_2Ph)_2$ (**9**), whose ^{31}P NMR spectrum suggested that **9** is isostructural with **1**. The low value of $\nu(CO)$ reflects the electron richness of Mo in the MoP_5 framework. In $Mo(CO)(PMe_3)_5$, $\nu(CO)$ occurred at 1773 cm^{-1}.[19] There was a second weaker absorption in the IR spectrum at 1850 cm^{-1} present in the original solid sample prepared from **1** and in solution. The ^{31}P NMR spectrum showed resonances due to a second complex and free PMe_2Ph. These same resonances together with many others were present after CO had been bubbled (0.1 h) through a solution of **1** in C_6D_6. This minor product was probably *cis*-$Mo(CO)_2(triphos)(PMe_2Ph)$ with the second $\nu(CO)$ hidden under the intense $\nu(CO)$ absorption at 1760 cm^{-1}.[20] Thus even in the solid state CO was able to displace one of the monodentate phosphines from **9** at room temperature.

Ethylene reacted slowly with **7** in the solid state to form unstable *fac*-$Mo(C_2H_4)(triphos)(PMe_2Ph)_2$ (**10**). Reaction with N_2 in the solid state regenerated **1**. In benzene solution, C_2H_4 reacted with **1** with the loss of N_2 and one PMe_2Ph ligand to form a mixture of *mer,trans*-$Mo(C_2H_4)_2(triphos)(PMe_2Ph)$ and *cis,fac*-$Mo(C_2H_4)_2(triphos)(PMe_2Ph)$ according to the ^{31}P NMR spectrum. There was no evidence in the ^{31}P NMR spectrum of the mono(ethylene) complex. When a solution containing the bis(ethylene) complexes was reduced to dryness by bubbling with N_2, the resulting solid displayed $\nu(NN)$ at 1980 cm^{-1}. Although the bis(ethylene) complexes *trans*-$Mo(C_2H_4)_2(PMe_3)_4$ and *trans*-$Mo(C_2H_4)_2(dppe)_2$ are know,[13,24] no mono(ethylene) complex of molybdenum with five phosphorus ligands has been reported previously.

Discussion

Molybdenum complexes in a variety of oxidation states can be readily transformed by reducing agents such as sodium amalgam into molybdenum(0) species. For example, in the presence of organophosphine ligands and under an argon atmosphere the following types of complexes can be formed: (i) $Mo(\eta^6\text{-}C_6H_5PMe_2)(PMe_2Ph)_3$,[25] (ii) $MoH_2(PMe_3)_5$,[26] and (iii) **6**.[27] Under an atmosphere of N_2 (i) mono-,[27-29] (ii) bis-,[30] and (iii) tris-N_2[31] complexes can be prepared.

Within the series of mono-N_2 complexes **1**–**5** a number of different geometric arrangements are observed. In all but one example (**3B**) triphos adopts a facial configuration. Dinitrogen is trans to a terminal phosphorus atom of triphos in **1** but trans to P_a in **2** and **4**. Complexes **3** and **5** both exist as a pair of isomers. All complexes were assayed for their ability to produce ammonia and hydrazine upon treatment with acid and are the first mononuclear, mono-N_2 complexes of any metal to yield more than a trace of ammonia and hydrazine. Overall, the yields of ammonia and hydrazine obtained from **1**–**5** were similar to those from bis-N_2 complexes such as **11**.[8] Complex **1** is unique among these new complexes in losing N_2 so readily. This is probably due to steric reasons. In the formally analogous complexes *fac*-**3A** and *fac*-**5A** the two PMe_2Ph ligands are replaced by constraining bidentate ligands.

Reactions of **1** and **2** with limited amounts of HX have led to the isolation and characterization of new hydrazido(2−) and mono- and dihydride complexes. These results will be reported in detail in a forthcoming paper.[17]

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,[32] 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.

Synthesis of N_2 complexes was performed in a 0.5-L Fischer-Porter pressure bottle. Sodium amalgam for all pressure bottle reactions was made and the reaction was assembled in the drybox.

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

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 and distilled under N_2. Immediately before use solvents were either vigorously bubbled with N_2 for ≥1 h or subjected to five or more 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. For pressurized reactions, dry grade N_2 and prepure Ar were purchased from Linde. Nitrogen-15 (99.89 atom %; nitrogen-14, 0.11 atom %; N_2 99.99 atom %; CO_2, 0.01 mol %) was obtained from Monsanto Research Corporation, Mound Laboratory, Miamisburg, OH 45342, and phosphines and arsine ligands from Strem Chemicals, Inc. $MoCl_3(triphos)$ was prepared by a published method.[8]

Ammonia, Hydrazine, and Dinitrogen Analyses. The general procedure for carrying out the reactions of anhydrous acid with N_2 complexes and the determination of amounts of ammonia, hydrazine, and N_2 produced has been reported.[8] The nitrogen content of some complexes was measured by oxidative decomposition with bromine.

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[14] (80.984 MHz with broad-band decoupling of protons) spectra were obtained 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) and 85% H_3PO_4 (^{31}P) with positive values being to low field.

Synthesis of Compounds. ***fac*-$Mo(N_2)(triphos)(PMe_2Ph)_2$ (1).** Sodium amalgam (0.94 g Na, 100 g Hg) was added to a mixture of $MoCl_3(triphos)$ (5.0 g, 6.8 mmol), PMe_2Ph (2.0 mL, 13.6 mmol), and THF (0.1 L) in a 0.5-L pressure bottle equipped with a magnetic stirbar. The bottle was rapidly sealed (enclosing ca. 16 mmol N_2), cooled (0 °C), and pressurized with Ar (75 psi). The reaction mixture was stirred (5

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h) at 0 °C and at ambient temperature (12 h) before being transferred to a glovebag. The bottle was depressurized and the solution decanted and filtered through Celite on a medium-porosity frit. N_2 was vigorously bubbled through the dark orange filtrate to reduce the volume to ca. 35 mL. The extremely rapid addition of methanol (ca. 0.2 L) with vigorous swirling of the solution resulted in the precipitation of product. N_2 bubbling was maintained (ca. 0.5 h) while additional methanol (0.2 L) was added to complete precipitation. The suspension was filtered and the solid washed with methanol (2 × 10 mL). The wet bright orange powder was rapidly transferred to a Schlenk tube and dried in vacuo for ca. 15 h. Exposure of the solid to vacuum resulted in a slow darkening of color (eventually becoming dark brown). Refilling the tube with N_2 restored the bright orange color within ca. 2 h. Yield of product was 4.9 g (5.3 mmol, 80%). Anal. Calcd for $C_{50}H_{55}MoN_2P_5$: C, 64.24; H, 5.93; N, 3.00; P, 16.56. Found: C, 63.56; H, 5.93; N, 2.87; P, 16.28. ^{31}P NMR [C_6D_6]: δ 85.91 (dd, 1, $^2J_{P_aP_e} = 101.5$ Hz, $^2J_{P_aP_d} = 11.5$ Hz, $^2J_{P_aP_b} \approx {}^2J_{P_aP_c} \approx 0$ Hz, P_a), 66.41 (ddd, 1, $^2J_{P_bP_d} = 93.0$ Hz, $^2J_{P_bP_c} \approx 4$ Hz, $^2J_{P_bP_e} \approx 18$ Hz, P_b), 58.96 (complex t, 1, $^2J_{P_cP_d} \approx {}^2J_{P_cP_e} \approx 18$ Hz, P_c), 1.41 (ddt, 1, P_d), −3.57 (ddt, 1, P_e). IR: ν(NN) 1978 cm^{-1}.

***fac*-Mo(N$_2$)(triphos)(dmpm) (2).** This reaction was carried out as described above with dmpm (0.92 g, 6.8 mmol) substituted for PMe_2Ph *except* the bottle was pressurized with N_2 (75 psi). Following filtration, N_2 was vigorously bubbled through the dark red filtrate to reduce the volume to ca. 35 mL. To the solution was added methanol (ca. 0.3 L), and the solution was vigorously bubbled with N_2 (ca. 1.5 h). A bright orange solid began to form after ca. 0.5 h, and more methanol (ca. 0.2 L) was added during the bubbling stage to complete precipitation. The solid was filtered off and washed with methanol (3 × 10 mL). The wet powder was transferred to a Schlenk tube and dried in vacuo at room temperature for ca. 15 h. The yield was 2.28 g (2.87 mmol, 42%). Recrystallization by layering heptane (2:1) onto a toluene solution of **2** afforded, after allowing the layers to diffuse together, bright red plates. Anal. Calcd for $C_{39}H_{47}MoN_2P_5$: C, 58.95; H, 5.96; N, 3.52; P, 19.49. Found: C, 58.13; H, 6.02; N, 3.53; P, 20.03. ^{31}P NMR [C_6D_6] AMM′XX′: δ 85.92 (t, 1, $^2J_{PP} = 15.5$ Hz, P_a), 63.45 (MM′, 2, P_b, P_c), −22.40 (XX′, 2, P_d, P_e). IR: ν(NN) 1966 cm^{-1}.

Synthesis of **2** under Ar (cf. preparation of **1**) resulted in a mixture of **2** and **6**. Addition of methanol to the initial filtrate resulted in the rapid precipitation of a purple solid, which was filtered off, washed with (2 × 10 mL) methanol, and dried in vacuo. Recrystallization was accomplished by dissolving the solid in toluene and adding an equal volume of methanol while the solution was vigorously bubbled with N_2. A further 0.2 L of methanol was added. From the solution steel gray needles were isolated by filtration. ^{31}P NMR [C_6D_6; Mo(triphos)($Me_2P_dCH_2P_eMe_2$)($Me_2P_fCH_2P_gMe_2$)]: δ 97.53 (complex dt, 1, $^2J_{P_aP_f} = 86.7$ Hz, $^2J_{P_aP_d} = {}^2J_{P_aP_e} = 14.7$ Hz, $^2J_{P_aP_b} \approx {}^2J_{P_aP_c} \approx 4.4$ Hz, P_a), 75.0 (m, 2, $^2J_{P_bP_e} \approx {}^2J_{P_cP_e} \approx 78.5$ Hz, $^2J_{P_bP_f} \approx {}^2J_{P_cP_f} \approx 21.3$ Hz, P_b, P_c), 1.49 (complex dt, 1, $^2J_{P_dP_f} \approx 5.6$ Hz, P_f), −18.13 (m, 2, P_d, P_e), −59.54 (s, 1, P_g).

Mo(N$_2$)(triphos)(diars) (3A and 3B). This synthesis was carried out as per that of **1** by using sodium amalgam (0.5 g Na, 50 g Hg), $MoCl_3$(triphos) (2.3 g, 3.1 mmol), diars (1.0 g, 3.5 mmol), and THF (80 mL). Following filtration, N_2 was vigorously bubbled through the dark orange solution to reduce the volume to ca. 25 mL. To the solution was added methanol (ca. 60 mL), and the vigorous bubbling was continued for ca. 1.5 h. Bright orange solid began to form after ca. 0.5 h. During the bubbling a further 50 mL of methanol was added to complete precipitation. The product was collected by filtration, washed (2 × 10 mL) with methanol, and dried in vacuo for 1 h. The yield of product was 0.81 g (0.86 mmol, 27%). Anal. Calcd for $C_{44}H_{49}As_2MoN_2P_3$: C, 55.95; H, 5.23; As, 15.86; N, 2.97; P, 9.84. Found: C, 55.16, H, 5.25; As, 14.68; N, 2.25; P, 9.48. ^{31}P NMR [C_6D_6]: *fac*-**3A**, δ 100.30 (dd, 1, $^2J_{P_aP_b} = 3.6$ Hz, $^2J_{P_aP_c} = 11.8$ Hz, P_a), 85.91 (dd, 1, $^2J_{P_bP_c} = 11.8$ Hz, P_b), 66.80 (dd, 1, P_c); *mer*-**3B**, δ 91.87 (s, 1, P_a), 63.63 (s, 2, P_b, P_c). IR: ν(NN) 1960 cm^{-1}.

***fac*-Mo(N$_2$)(triphos)(dppm) (4).** This synthesis was carried out as per **1** by using sodium amalgam (0.6 g Na, 60 g Hg), $MoCl_3$(triphos) (3.0 g, 4.1 mmol), dppm (1.0 g, 3.5 mmol), and THF (0.1 L). Following filtration, the filtrate volume was reduced as described previously to ca. 25 mL, after which methanol (60 mL) was added. The solution was bubbled for a further 0.5 h during which time more (50 mL) methanol was added to complete precipitation. The bright orange product was filtered off, washed (2 × 20 mL) with methanol, and dried in vacuo for 1 h. Yield was 2.75 g (2.64 mmol, 65%). Anal. Calcd for $C_{59}H_{55}MoN_2P_5$: C, 67.95; H, 5.32; N, 2.69; P, 14.85. Found: C, 67.36; H, 5.37; N, 2.36; P, 13.43. ^{31}P NMR [THF] AMM′XX′: δ 86.97 (t, 1, $^2J_{PP} = 13.9$ Hz, P_a), 63.81 (MM′, 2, P_b, P_c), 7.25 (XX′, 2, P_d, P_e). IR: ν(NN) 1978 cm^{-1}.

Mo(N$_2$)(triphos)(dppe) (5A and 5B). This synthesis was carried out as per that of **1** by using sodium amalgam (0.6 g Na, 60 g Hg), $MoCl_3$(triphos) (3.0 g, 4.1 mmol), dppe (1.8 g, 4.5 mmol), and THF (0.1 L). Following filtration, the filtrate volume was reduced to ca. 30 mL, after which methanol (ca. 40 mL) was added and bubbling continued for ca. 0.75 h. Bright orange solid began to form after ca. 0.5 h. A further 0.5 mL of methanol was added to complete precipitation. The product was collected by filtration, washed (3 × 15 mL) with methanol, and dried in vacuo for 1 h. The yield of bright orange microcrystals was 2.25 g (2.14 mmol, 52%). Anal. Calcd for $C_{60}H_{57}MoN_2P_5$: C, 68.18; H, 5.44; N, 2.65; P, 14.65. Found: C, 68.69; H, 5.44; N, 2.49; P, 14.05. ^{31}P NMR [THF]: *fac*-**5A**, δ 87.94 (ddd, 1, $^2J_{P_aP_e} = 106.6$ Hz, $^2J_{P_aP_d} = 15.7$ Hz, $^2J_{P_aP_b} = 6.8$ Hz, $^2J_{P_aP_c} = 0$ Hz, P_a), 69.36 (dddd, 1, $^2J_{P_bP_d} = 101.0$ Hz, $^2J_{P_bP_e} = 20.9$ Hz, $^2J_{P_bP_c} = 12.6$ Hz, P_b), 65.91 (dddd, 1, $^2J_{P_dP_e} = 4.0$ Hz, P_d), 64.01 (complex dt, P_e), 58.08 (quin, 1, P_c); *fac*-**5B**, δ 70.74 (quin, 1, $^2J_{P_aP_x} = 5.9$ Hz, P_a), 60.04 (d, 4, $P_{b,c,d,e}$). IR: ν(NN) 2008, 1955 cm^{-1}.

Mo(^{15}N$_2$)(triphos)(PMe$_2$Ph)$_2$. After **1** was evacuated for 19 h at ca. 1.0 × 10^{-5} Torr, an atmosphere of $^{15}N_2$ was introduced, causing the dark brown solid to rapidly turn orange. IR: ν(NN) 1978 ($^{14}N_2$), 1918 ($^{15}N_2$) cm^{-1}.

Mo(triphos)(PMe$_2$Ph)$_2$ (7). Evacuation of solid orange **1** resulted in the rapid formation of a brown color, which became progressively darker with time. A ^{31}P NMR spectrum of the sample run in C_6D_6 indicated a mixture of **1** and **7**. ^{31}P NMR [C_6D_6] for **7**: δ 93.49 (complex m, P_a), 88.61 (dd, $^2J_{P_bP_d} = 108.1$ Hz, $^2J_{PP} = 13.4$ Hz, P_b), 60.67 (dd, $^2J_{PP} = 22.9$ Hz, $^2J_{PP} = 7.5$ Hz, P_c), 17.84 (m, P_d), 6.09 (dquin, $^2J_{P_aP_e} = 105.3$ Hz, $^2J_{PP} = 16.3$ Hz, P_e).

MoH$_2$(triphos)(PMe$_2$Ph)$_2$ (8). After **1** was evacuated for ca. 15 h, an atmosphere of H_2 was introduced causing a rapid color change to bright orange. The solid was reevacuated to give a brown solid again. Readdition of H_2 afforded the orange solid. ^{31}P NMR [H_2-saturated C_6D_6]: δ 110.66 (m, 1, P_a), 90.53 (broad s (width at half-height = 20 Hz), 2, P_b, P_c), 14.92 (broad m (width at half-height = 73 Hz), 1, P_d), 6.51 (broad m (cf. P_d), 1, P_e). ^{1}H NMR [H_2-saturated C_6D_6]: δ 8.3–6.9 (m, Ph), 3.6–0.8 (m, CH), −4.31 (dquin, 2, $J_{PH} = 35.3$, 19.8 Hz, hydride). IR: ν(MoH) 1869 (vw) cm^{-1}. After the sample was allowed to stand in the drybox (N_2) for a few days, the IR spectrum showed a strong ν(NN) at 1978 cm^{-1}.

***fac*-Mo(CO)(triphos)(PMe$_2$Ph)$_2$ (9).** A solid sample of **1** was evacuated for 1 h. One atmosphere of CO was admitted at room temperature. This operation was repeated four times, and the solid was then allowed to sit under CO for 15 h. ^{31}P NMR [C_6D_6]: δ 84.89 (ddd, $^2J_{P_aP_d} = 84.9$ Hz, $^2J_{P_aP_e} = 9.8$ Hz, $^2J_{P_aP_b} \approx {}^2J_{P_aP_c} \approx 4$ Hz, P_a), 73.93 (dt, $^2J_{P_bP_e} = 74.1$ Hz, $^2J_{P_bP_d} = 19.7$ Hz, $^2J_{P_bP_c} \approx 4$ Hz, P_b), 40.76 (complex m, P_c), 0.61 (ddt, $^2J_{P_dP_e} = 24.4$ Hz, P_d), −2.28 (dddt, $^2J_{P_cP_e} \approx 4$ Hz, P_e). ^{1}H NMR [C_6D_6]: δ 7.7–6.2 (m, Ph), 2.8–1.2 (m, CH_2), 1.69 (d, $J_{PH} = 4.1$ Hz, Me), 1.58 (d, $J_{PH} = 3.8$ Hz, Me), 1.13 (d, $J_{PH} = 5.5$ Hz, Me), 0.92 (d, $J_{PH} = 3.8$ Hz, Me). IR: ν(CO) 1850 (w), 1760 (vs) cm^{-1}.

***fac*-Mo(C$_2$H$_4$)(triphos)(PMe$_2$Ph)$_2$ (10).** A sample of **1** (0.19 g) was evacuated (19 h). One atmosphere of C_2H_4 was admitted. Over a 15 h period of time the solid became pinkish brown. ^{31}P NMR [Ar-saturated C_6D_6]: δ 106.90 (dd, $^2J_{P_aP_d} = 61.3$ Hz, $^2J_{P_aP_e} = 16.2$ Hz, P_a), 67.00 (dm, $^2J_{P_bP_e} = 87.3$ Hz, P_b), 65.90 (d, $^2J_{P_cP_d} \approx {}^2J_{P_cP_e} \approx 21.9$ Hz, P_c), 3.89 (ddd, $^2J_{P_dP_e} = 33.3$ Hz, P_d), 1.99 (dm, P_e).

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