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Chemistry of Coordinated Dinitrogen. I. Preparation and Characterization of Bis(dinitrogen) Complexes of Molybdenum

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The compounds $\text{Mo}(\text{N}_2)_2\text{L}_4$ and $\text{Mo}(\text{N}_2)_2(\text{LL})_2$ [$\text{L} = \text{PPh}_2\text{Me}$, PMe_2Ph ; $\text{LL} = 1,2$ -bis(diphenylphosphino)ethane (dppe), 1-diphenylarsino-2-diphenylphosphinoethane (arphos), 1,2-bis(diphenylarsino)ethane (dpae), *o*-phenylenebis(dimethylarsine) (diars)] were prepared by reducing either MoCl_4L_2 , $\text{MoCl}_4(\text{LL})$, or $\text{MoCl}_3(\text{THF})_3$ (THF = tetrahydrofuran) with sodium amalgam in the presence of the appropriate amount of the ligand in THF, under a dinitrogen atmosphere. All the complexes have a trans configuration with the exception of *cis*- $\text{Mo}(\text{N}_2)_2(\text{PMe}_2\text{Ph})_4$. Phosphorus-31 nmr spectral data and differential scanning calorimetry and thermogravimetric analysis studies are reported for some of the complexes.

A wide variety of dinitrogen complexes of molybdenum have been prepared since the initial report of $\text{Mo}(\text{N}_2)(\text{PPh}_3)_2 \cdot \text{C}_6\text{H}_5\text{CH}_3$.^{1,2} Among the bis(dinitrogen) complexes of molybdenum that have been isolated are $\text{Mo}(\text{N}_2)_2(\text{LL})_2$, where $\text{L} = \text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 1, 2, 3$,³⁻⁶ and 3^2), *cis*- $[\text{Ph}_2\text{PCH}=\text{CHPPH}_2]$,⁵ $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{PPh}_2$,⁷ $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2$,⁷ and $\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2$,⁸ and $\text{Mo}(\text{N}_2)_2\text{L}_4$, where $\text{L} = \text{PPh}_2\text{Me}$ ⁶ and PMe_2Ph .⁶ A mono(dinitrogen)molybdenum complex has also been reported, $\text{MoCl}(\text{N}_2)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2$.⁴ All of these complexes were obtained by the reduction of an appropriate molybdenum complex in the +2 to +5 oxidation state with trialkylaluminum,¹⁻³ sodium amalgam,⁴⁻⁷ or zinc dust⁴ in toluene or tetrahydrofuran with an excess of the appropriate organophosphine or -arsine, under an atmosphere of molecular nitrogen. However, the interesting binuclear dinitrogen complex $[\text{C}_6\text{H}_6\text{-Mo}(\text{Ph}_3\text{P})_2]_2\text{N}_2$ was prepared⁹ by treating $\text{MoH}_2(\text{C}_6\text{H}_6)(\text{PPh}_3)_2$ with dinitrogen in benzene at room temperature. This reaction is reversible. A molybdenum-dinitrogen-rhenium bonding framework is believed to be present in the following complexes: $(\text{PhMe}_2\text{P})_4\text{ReCl}(\text{N}_2)\text{MoOCl}_3\text{L}$ and $(\text{PhMe}_2\text{P})_4\text{ReCl}(\text{N}_2)\text{Mo}_2\text{OCl}_5\text{L}$, where $\text{L} = \text{Et}_2\text{O}$, THF, or PPh_2Et .¹⁰ Iodine, in methanol, oxidizes $\text{Mo}(\text{N}_2)_2(\text{LL})_2$, where $\text{LL} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{AsPh}_2$, to give the new bis(dinitrogen) cationic complexes $[\text{Mo}(\text{N}_2)_2(\text{LL})_2]^+$.¹¹ A few dinitrogen complexes of molybdenum remain to be more thoroughly characterized, namely, $\text{Mo}(\text{N}_2)(\text{PPh}_3)_2\text{C}_6\text{H}_5\text{CH}_3$,^{1,2} $\text{Mo}(\text{N}_2)(\text{PPh}_3)_2$,² and $\text{Mo}(\text{N}_2)(\text{C}_5\text{Me}_5)_2$.¹²

This paper elaborates upon the preparation of a series of

bis(dinitrogen) complexes of molybdenum that have already received preliminary communication.^{6,7}

Experimental Section

General Data. All reactions, work-up, and storage of products were carried out in an oxygen-free argon or dinitrogen atmosphere using standard inert-atmosphere techniques. Air- and moisture-sensitive solids were stored in a Vacuum Atmospheres Corp. Dri-lab. All reduction reactions were carried out in a flat-bottomed Schlenk tube and dinitrogen was slowly bubbled through the stirred suspension.

Reagents. All solvents were freshly distilled under an argon or dinitrogen atmosphere immediately before use. THF and diethyl ether were distilled from lithium aluminum hydride. Benzene, toluene, and diglyme were distilled from calcium hydride. Methanol was distilled from magnesium turnings. Acetonitrile, carbon tetrachloride, and dichloromethane were distilled from phosphorus(V) oxide.

Chemicals were purchased from the following sources and used without further purification: molybdenum(V) chloride and molybdenum(0) hexacarbonyl (Alfa); $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$, PPh_2Me , PMe_2Ph , and 1,2- $\text{C}_6\text{H}_4[\text{AsMe}_2]_2$ (ROC/RIC); $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{PPh}_2$ and $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2$ (Pressure Chemical Co.); $\text{P}(\text{C}_6\text{H}_5)_3$ (Orgmet); $\text{P}(n\text{-Bu})_3$ (Baker); PPh_3 (Matheson Coleman and Bell); AsPh_3 (Eastman); 2,2-bipyridyl and 1,10-phenanthroline (G. F. Smith).

The following compounds were prepared by published procedures: $\text{MoCl}_4(\text{MeCN})_2$,¹³ $\text{MoCl}_4(\text{dppe})$,¹⁴ $\text{MoCl}_4(\text{PPh}_2\text{Me})_2$,¹⁴ $\text{MoCl}_4(\text{PMe}_2\text{Ph})_2$,¹⁵ $\text{MoCl}_4(\text{P}(n\text{-Bu})_3)_2$,¹⁵ and $\text{MoCl}_3(\text{THF})_3$.⁵

Physical Measurements. Infrared spectra were run on a Perkin-Elmer Model 621 spectrophotometer. Solid samples were run as Nujol mulls or as pellets in CsBr or KBr. All solution spectra were run in deoxygenated reagent grade solvents, the samples were prepared, and the cells were filled and sealed in an inert atmosphere. Phosphorus-31 nmr spectra were run at 40.5 MHz on a Varian XL-100 spectrometer assisted by a Varian 620-I computer. The samples were 3% by weight solutions in 12-mm o.d. nmr tubes with benzene- d_6 as the solvent. The chemical shift values (γ (ppm), x (Hz)) with reference to 85% H_3PO_4 were calculated by reference to the value of $\text{P}(\text{OCH}_3)_3$ (-144 ppm, 95,626 Hz) in benzene- d_6 using the following conversion: $\gamma(\text{ppm}) = \{[95,626 - x(\text{Hz})]/40.5\} - 144$. The differential scanning calorimetry was measured on a Perkin-Elmer scanning calorimeter (PE DSC 1B) with a dinitrogen flush. The temperature was calibrated with indium (402°K), tin (406°K), and lead (494°K). The thermal gravimetric analysis was kindly run by Dr. Carracher, University of South Dakota, Vermillion, S. D. Melting points were determined in capillaries sealed under dinitrogen with a Mel-Temp apparatus and were uncorrected.

Analyses were performed by Schwarzkopf Analytical Laboratories, Woodside, N. Y.

Syntheses. $\text{Mo}(\text{N}_2)_2(\text{dppe})_2$. (1) To 2.5 g (3.9 mmol) of $\text{MoCl}_4(\text{dppe})$ was added 1.25 g (3.1 mmol) of dppe in THF (30 ml) and 40 g (17 mmol of Na) of 1% Na-Hg. The mixture was stirred magnetically under dinitrogen for 6 hr. The orange-brown suspension was poured off the mercury and filtered through a medium

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frit. The THF was removed under vacuum. The remaining oil was dissolved in benzene (5 ml) and chilled methanol (50 ml, 0°) was added to precipitate the product. The orange crystals were recrystallized from benzene-methanol (1:10) and dried *in vacuo* to yield 1.3 g (36%) of pure product, mp 165° dec. *Anal.* Calcd for $C_{52}H_{48}MoN_4P_4$: C, 65.8; H, 5.06; N, 5.90. Found: C, 65.8; H, 5.08; N, 5.46.

(2) A solution of 3.8 g (9.5 mmol) of dppe in THF (40 ml) was added to 2.0 g (4.8 mmol) of $MoCl_3(THF)_3$ and 40 g (17 mmol of Na) of 1% Na-Hg. After the mixture was stirred for 6 hr, the suspension was allowed to settle for 30 min. The orange-brown solution was filtered and the residue extracted with additional THF (50 ml). Solvent was removed under vacuum. The tacky solid was dissolved in benzene (10 ml) and filtered. Chilled methanol (60 ml, 4°) was added to precipitate orange crystals. The product was recrystallized from benzene-methanol (1:10) and dried *in vacuo*, to yield 2.5 g (60%) of pure product.

$Mo(N_2)_2(arphos)_2$. A mixture of $MoCl_3(THF)_3$ (1.0 g, 2.4 mmol), arphos (2.1 g, 4.8 mmol), and 1% Na-Hg (25 g, 11 mmol of Na) in THF (40 ml) was stirred magnetically for 4 hr under dinitrogen. The rich yellow-brown solution was poured off the mercury and filtered through a medium frit. The filtrate was taken to dryness under vacuum to give an orange-brown amorphous mass. The solid was dissolved in benzene (20 ml) and the solution filtered. Methanol (80 ml) was added and the solution cooled (0°) to precipitate fine orange-yellow crystals. The crystals were filtered, washed with methanol, and dried *in vacuo* to yield 1.0 g (40%) of pure product, mp 105° dec. *Anal.* Calcd for $C_{52}H_{48}As_2MoN_4P_2$: C, 60.2; H, 4.63; N, 5.41; Mo, 9.27. Found: C, 60.5; H, 5.07; N, 5.34; Mo, 7.83.

$Mo(N_2)_2(PPh_2Me)_4$. (1) A solution of PPh_2Me (0.5 g, 2.5 mmol) in THF (40 ml) was added to 0.8 g (1.2 mmol) of $MoCl_4(PPh_2Me)_2$ and 25 g (11 mmol of Na) of 1% Na-Hg. The mixture was stirred magnetically for 8 hr. After settling, the solution was filtered to give an orange filtrate. The solvent was removed under vacuum leaving an oil. The oil was dissolved in benzene (4 ml) and chilled methanol (*ca.* 50 ml, 4°) was added to precipitate a yellow powder. The material was recrystallized from benzene-methanol (5 ml:50 ml). The orange crystals were dried *in vacuo* to yield 0.52 g (45%) of pure product, mp 105° dec. *Anal.* Calcd for $C_{52}H_{52}MoN_4P_4$: C, 65.5; H, 5.46; N, 5.88; Mo, 10.1. Found: C, 64.2; H, 5.35; N, 5.80; Mo, 9.92.

(2) $MoCl_3(THF)_3$ (1.2 g, 2.9 mmol) was added to 2.5 g (12.5 mmol) of PPh_2Me in THF (40 ml) and 25 g (11 mmol of Na) of 1% Na-Hg. The mixture was stirred magnetically for 8 hr. The solution was filtered and solvent removed under vacuum. The oil was crystallized from benzene-methanol (5 ml:50 ml) to yield 1.0 g (26%) of orange product.

$Mo(N_2)_2(PMe_2Ph)_4$. (1) A solution of 1.0 g (1.9 mmol) of $MoCl_4(PMe_2Ph)_2$ and 0.5 g (3.6 mmol) of PMe_2Ph in THF (40 ml) was stirred magnetically with 50 g (22 mmol of Na) of 1% Na-Hg for 8 hr. The resulting brown solution was poured from the mercury and filtered. Solvent was removed under vacuum. The oily solid was dissolved in benzene (5 ml). Heptane (50 ml) was added and the solution cooled to give a yellow-brown precipitate. The solid was filtered off, redissolved in diethyl ether (75 ml), and re-filtered. The yellow solution was slowly concentrated (0.1 mm) at room temperature to give fine yellow crystals that were filtered off and dried *in vacuo*. The yield of pure product, mp 110° dec, was 0.2 g (15%). *Anal.* Calcd for $C_{32}H_{44}MoN_4P_4$: C, 54.5; H, 6.25; N, 7.95; Mo, 13.6. Found: C, 53.0; H, 6.38; N, 4.89; Mo, 13.3.

(2) To 25 g (11 mmol of Na) of 1% Na-Hg was added 1.0 g (2.4 mmol) of $MoCl_3(THF)_3$ and 1.2 g (8.7 mmol) of PMe_2Ph in THF (40 ml). The mixture was stirred magnetically for 8 hr. The yellow-brown solution was filtered and THF removed under vacuum. The resulting oil was dissolved in benzene (5 ml) and then treated with methanol (50 ml). The solvent was removed slowly (0.1 mm) until fine yellow-green crystals began to precipitate. The crystals were recrystallized from diethyl ether to give 0.2 g (10%) of pure product.

$Mo(N_2)_2(dpae)_2$. A solution containing dpae (1.0 g, 2.1 mol) and $MoCl_3(THF)_3$ (0.5 g, 1.2 mmol) in THF (40 ml) was stirred magnetically with 25 g (11 mmol of Na) of 1% Na-Hg for 10 hr. The resulting mixture was sealed and transferred to a Dri-Lab. The yellow-brown solution was decanted and filtered through a medium frit. Solvent was removed under vacuum at room temperature. The tacky solid was dissolved in benzene (*ca.* 5 ml). Addition of hexane (50 ml) precipitated a brown-green material that contained no dinitrogen. The filtrate was taken to dryness. The solid

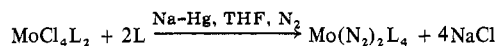
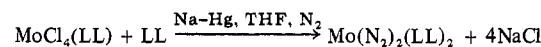
was dissolved in dichloromethane (*ca.* 3 ml). Addition of hexane (30 ml) precipitated a yellow-brown solid, which was filtered and dried under a stream of dinitrogen. The yield of this light-sensitive, yellow-brown solid, mp 101° dec, was *ca.* 10%. *Anal.* Calcd for $C_{22}H_{18}As_2MoN_4$: C, 55.5; H, 4.27; N, 4.98; Mo, 8.54. Found: C, 52.4; H, 4.35; N, 3.11; Mo, 7.65.

$Mo(N_2)_2(diars)_2$. A solution containing $MoCl_3(THF)_3$ (1.0 g, 2.4 mmol) and diars (1.3 g, 4.5 mmol) in THF (40 ml) was stirred magnetically with 40 g (17 mmol Na) of 1% Na-Hg for 8 hr under dinitrogen. The rich brown solution was filtered through a medium frit. The filtrate was taken to dryness under vacuum. The tacky solid was dissolved in benzene (*ca.* 3 ml). Addition of cold (0°) methanol (75 ml) precipitated an orange-brown powder that was dried *in vacuo*. The yield of this extremely air-sensitive material was very low. *Anal.* Calcd for $C_{20}H_{32}As_4MoN_4$: C, 33.2; H, 4.56. Found: C, 33.7; H, 5.75.

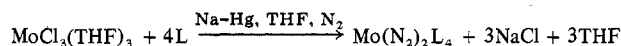
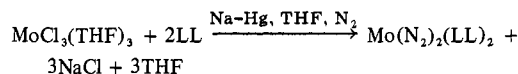
$Mo(N_2)_2(P(n-Bu)_3)_4$. A solution of 0.3 g (1.5 mmol) of $P(n-Bu)_3$ in THF (40 ml) and 1.0 g (1.7 mmol) of $MoCl_4(P(n-Bu)_3)_2$ was stirred magnetically with 25 g (11 mmol of Na) of 1% Na-Hg for 8 hr under dinitrogen. The yellow-brown solution was poured off the mercury and filtered. Solvent was removed under vacuum. Despite repeated attempts, the oil would not crystallize from either benzene-pentane or diethyl ether-pentane. However, during the crystallization efforts no decomposition appeared to occur (see Results and Discussion).

Results and Discussion

Preparation and Characterization of $Mo(N_2)_2(LL)_2$ and $Mo(N_2)_2L_4$. All the dinitrogen complexes were prepared by the reduction of an appropriate molybdenum complex with sodium amalgam in THF under a dinitrogen atmosphere. Initially, phosphine complexes of molybdenum(IV) chloride were selected as starting materials. They were prepared either by replacing the organonitrile ligands of $MoCl_4(NCR)_2$ (R = Me and *n*-Pr) by the appropriate phosphine¹⁴ (LL = dppe and arphos; L = PPh_2Me) or by the chlorination of $Mo(CO)_4L_2$ (L = PMe_2Ph and $P(n-Bu)_3$).¹⁵ The tetrachloro complexes were reduced in the presence of 1 equiv of LL or 2 equiv of L. The presence of an excess of PPh_2Me or



PMe_2Ph adversely affected the ease of work-up and the yield of pure product. All the above compounds can also be prepared from $MoCl_3(THF)_3$ according to the published procedure of Chatt and Wedd,⁵ although an excess of added ligand was avoided in this work. Both methods give comparable



yields of pure product. However, the latter method was found to be superior for the preparation of the very unstable arsine complexes, $Mo(N_2)_2(dpae)_2$ and $Mo(N_2)_2(diars)_2$.

The reductions were carried out using a slight excess of 1% sodium amalgam for up to 10 hr with steady stirring. Dinitrogen was bubbled slowly through the THF solution during this time. When the reaction was judged to be complete (solution infrared spectrum), the solid was allowed to settle and the solution was decanted. The solid was washed with THF and solvent was removed *in vacuo* from the combined solution. The resulting oil or solid was then crystallized and further recrystallized to provide analytically pure samples. A benzene-methanol solvent system was very successful for the crystallization of all the products with the exception of $Mo(N_2)_2(PMe_2Ph)_4$ and $Mo(N_2)_2(dpae)_2$, when

Table I. Infrared Data for the Bis(dinitrogen) Complexes of Molybdenum

Compd	$\nu_{N\equiv N}$, cm^{-1}			
	Nujol	KBr	CH_2Cl_2 soln	C_6H_6 soln
$\text{Mo}(\text{N}_2)_2(\text{dppe})_2$	2020 vw, 1975 vs	2030 vw, 1975 vs	2040 vw, 1971 vs	..., 1979 s
$\text{Mo}(\text{N}_2)_2(\text{arphos})_2$	2032 vw, 1964 vs	2027 vw, 1962 vs	2044 vw, 1968 vs	
$\text{Mo}(\text{N}_2)_2(\text{PPh}_2\text{Me})_4$	1925 vs	1926 vs		1925 vs
$\text{Mo}(\text{N}_2)_2(\text{PMe}_2\text{Ph})_4$	2025 s, 1940 s	2020 s, 1937 s ^a		2018 s, 1939 s
$\text{Mo}(\text{N}_2)_2(\text{dpae})_2$	2031 vw, 1964 vs		2041 vw, 1970 vs	
$\text{Mo}(\text{N}_2)_2(\text{diars})_2$	2020 vw, 1960 vs		2044 vw, 1950 vs	
$\text{Mo}(\text{N}_2)_2(\text{P}(n\text{-Bu})_3)_4$ ^b	2065 m, 1980 s, 1940 m			

^a CsBr pellet. ^b Film, NaCl plates; purity doubtful (see Experimental Section and Discussion).

diethyl ether and dichloromethane-hexane, respectively, were used.

As already reported,²⁻⁶ $\text{Mo}(\text{N}_2)_2(\text{dppe})_2$ is an orange-yellow solid that can be stored in a desiccator for several months without decomposition. In solution the complex is sensitive to oxygen and moisture. The complex is soluble in benzene and dichloromethane but is insoluble in methanol and petroleum ether. It reacts with chloroform and carbon tetrachloride with the evolution of dinitrogen. The complex was recovered quantitatively after refluxing a benzene solution of the complex for 24 hr, under a dinitrogen atmosphere. However, all dinitrogen was lost when argon was bubbled through a benzene solution of the complex for 24 hr at room temperature. The complex is stable in acetonitrile (24 hr) and pyridine (2 hr) at room temperature, but dinitrogen was lost rapidly upon heating these solutions.

The orange-yellow $\text{Mo}(\text{N}_2)_2(\text{arphos})_2$ complex is essentially identical with $\text{Mo}(\text{N}_2)_2(\text{dppe})_2$ in its chemical and physical properties.

The complex $\text{Mo}(\text{N}_2)_2(\text{PPh}_2\text{Me})_4$ is an orange solid that is stable in dry air. However, it readily decomposes in solution in the presence of oxygen and moisture. It is soluble in benzene but is insoluble in methanol and petroleum ether and reacts with dichloromethane and chloroform with the liberation of dinitrogen.

The complex $\text{Mo}(\text{N}_2)_2(\text{PMe}_2\text{Ph})_4$ is a solid that is stable in dry air. It decomposes rapidly in solution in the presence of oxygen and moisture and slowly even in the absence of oxygen and moisture.

The arsine complexes $\text{Mo}(\text{N}_2)_2(\text{dpae})_2$ and $\text{Mo}(\text{N}_2)_2(\text{diars})_2$ are very unstable in the solid state and in solution, and their synthesis was very difficult. The yellow-brown $\text{Mo}(\text{N}_2)_2(\text{dpae})_2$ complex is also light sensitive.

The general stability of these bis(dinitrogen) complexes of molybdenum appears to vary in the following order: $\text{dppe} \approx \text{arphos} > \text{PPh}_2\text{Me} > \text{PMe}_2\text{Ph} > \text{dpae} \approx \text{diars}$. It is surprising and interesting that while dppe and arphos appear to impart similar stability to the $\text{Mo}(\text{N}_2)_2$ moiety, the presence of two arsenic atoms per ligand dramatically reduces the stability of the $\text{Mo}(\text{N}_2)_2$ unit.

Attempts were made to prepare many other bis(dinitrogen) complexes of molybdenum by the above routes, e.g., where LL = bipyridyl, *o*-phenanthroline, and 8-aminoquinoline; L = PPh_3 , AsPh_3 , $\text{P}(\text{cyclohexyl})_3$, and $\text{P}(n\text{-Bu})_3$. Only the reaction mixture employing $\text{P}(n\text{-Bu})_3$ showed a peak in the 2000- cm^{-1} region of the infrared spectrum. Repeated attempts to crystallize the oil failed. However, the three infrared bands at 2065 (m), 1980 (m), and 1940 (m) cm^{-1} persisted throughout all attempts of purification, suggesting that it may be a low-melting material [$\text{Mo}(\text{CO})_4(\text{P}(n\text{-Bu})_3)_2$ is an oil at room temperature].

In an effort to find a simpler method of synthesizing dinitrogen complexes of molybdenum, $\text{MoCl}_4(\text{NCR})_2$ was reduced in the presence of the appropriate equivalents of

phosphine ligand. In no case, however, was any dinitrogen complex formed. Since the more stable dinitrogen complexes do not react with organonitriles at room temperature, the nitrile must be inhibiting the uptake of dinitrogen. No nitrile-molybdenum complex was isolated or inferred from the infrared spectrum.

The original proposal,³ based upon the infrared spectrum, that the dinitrogen ligands in $\text{Mo}(\text{N}_2)_2(\text{dppe})_2$ were mutually trans has been supported by the recent crystal structure reported¹⁶ for this complex. The $\nu(\text{N}_2)$ data, under various conditions, are reported in Table I. All the complexes with bidentate ligands show two bands in the 2100-1900- cm^{-1} region of their infrared spectra and appear to have a trans configuration by analogy with $\text{Mo}(\text{N}_2)_2(\text{dppe})_2$. The more intense band (1979-1950 cm^{-1}) is assigned to the A_{2u} mode based on D_{4h} symmetry. However, the crystal structure of $\text{Mo}(\text{N}_2)_2(\text{dppe})_2$ reveals that in the solid state the Mo-N-N unit is slightly bent¹⁶ therefore distorting the local symmetry about molybdenum from D_{4h} . The weak band (2044-2020 cm^{-1}) is assigned to the symmetry-forbidden A_{1g} mode.^{2,17} $\text{Mo}(\text{N}_2)_2(\text{PPh}_2\text{Me})_4$ shows only one strong band in the 2100-1900- cm^{-1} region, at 1925 cm^{-1} (Nujol), but is assigned a trans configuration. The infrared spectrum of $\text{Mo}(\text{N}_2)_2(\text{PMe}_2\text{Ph})_4$ shows two bands, at 2025 and 1940 cm^{-1} (Nujol). This complex is assigned a cis configuration since it shows the two stretching modes ($A_1 + B_1$) predicted for *cis*- $\text{Mo}(\text{N}_2)_2(\text{PMe}_2\text{Ph})_4$ based upon C_{2v} symmetry.¹⁸ The change in stereochemistry appears to reflect the greater basicity of PMe_2Ph as compared to the other ligands. It is tempting to interpret the infrared spectrum of $\text{Mo}(\text{N}_2)_2(\text{P}(n\text{-Bu})_3)_4$ as arising from a mixture of cis and trans isomers.

For the trans compounds, the A_{2u} $\nu(\text{N}_2)$ value decreases as the basicity of the other ligands increases.² On the other hand, the A_{2u} $\nu(\text{N}_2)$ values bear no obvious relationship¹⁹ to the general stability of these complexes.

The proton-decoupled phosphorus-31 nmr spectral data of the dinitrogen complexes are presented in Table II. Included in the table are the data for *cis*- $\text{Mo}(\text{CO})_2(\text{dppe})_2$, for comparison purposes. A sharp singlet is observed for the four equivalent phosphorus nuclei in *trans*- $\text{Mo}(\text{N}_2)_2(\text{dppe})_2$ at -69 ppm (relative to 85% H_3PO_4). This represents a coordination shift of 78 ppm downfield from uncomplexed dppe. A sharp singlet at -31 ppm and a multiplet at -12 ppm are observed in the ³¹P nmr spectrum of *cis*- $\text{Mo}(\text{N}_2)_2(\text{PMe}_2\text{Ph})_4$. The singlet appears 78 ppm downfield from uncomplexed PMe_2Ph , which absorbs at 47 ppm. The multiplet appears 59 ppm downfield from uncomplexed

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Table II. Phosphorus-31 Nmr Data^a

Compd	δ^b		Δ^c
	Ligand	Complex	
Mo(N ₂) ₂ (dppe) ₂	9	-69 s	78
Mo(N ₂) ₂ (PPh ₂ Me) ₄	24	27 s	0
		24 s	
		21 s	
		-23 s	
		-38 s	
Mo(N ₂) ₂ (PMe ₂ Ph) ₄	47	-31 s	78
		-12 m	59
		-50 m	59

^a Proton-decoupled spectra. ^b Ppm relative to 85% H₃PO₄ (see Experimental Section for this calculation); benzene-*d*₆ solution; s = singlet, m = multiplet. ^c Coordination shift = $\delta(\text{complex}) - \delta(\text{ligand})$. ^d Cis isomer.

PMe₂Ph. However, *cis*-Mo(CO)₂(dppe)₂ exhibits a multiplet at -50 ppm which is 59 ppm downfield from free dppe. The data suggest that in solution Mo(N₂)₂(PMe₂Ph)₄ exists as a mixture of *cis* and *trans* isomers. Eventually, the sample decomposes in solution.

The ³¹P nmr spectrum of Mo(N₂)₂(PPh₂Me)₄ is complex, showing the following resonances: 27 ppm (singlet), 24 ppm (singlet), 21 ppm (singlet), -23 ppm (singlet), and -38 ppm (singlet). The most intense peaks are those at 24 and -38 ppm. The former peak may be assigned to uncomplexed PPh₂Me, which absorbs at 24 ppm, and the latter is at -38 ppm, assigned to *trans*-Mo(N₂)₂(PPh₂Me)₄. However, none of the remaining signals can be assigned with any certainty. After the nmr spectrum was run, pure Mo(N₂)₂(PPh₂Me)₄ was recovered by removing the solvent. No evidence for decomposition was apparent. Over extended periods of time the compound does decompose in solution.

A characteristic feature of metal-dinitrogen complexes is their relatively low thermal stability. The melting points of the dinitrogen complexes of molybdenum are not sharp and the compounds visually appear to undergo decomposition. Differential scanning calorimetric (dsc) studies are shown in Table III. The scans were run from 300 to 500°K at a heating rate of 10°/min in a dinitrogen atmosphere. The curves were quite broad, beginning soon after the visual

Table III. Differential Scanning Calorimetry Data^a

Compd	Visual mp, ^b °K	Dsc curve, ^c °K
Mo(N ₂) ₂ (dppe) ₂	438	450-480
Mo(N ₂) ₂ (arphos) ₂	378	400-435
Mo(N ₂) ₂ (PPh ₂ Me) ₄	378	388-412

^a Heating rate of 10°/min. ^b Determined in a capillary tube, sealed under dinitrogen. ^c The temperature range covered by the endothermic transition.

melting point (determined in a capillary tube sealed under dinitrogen). The data show that the thermal stabilities of the three compounds studied vary in the following order: Mo(N₂)₂(dppe)₂ > Mo(N₂)₂(arphos)₂ > Mo(N₂)₂(PPh₂Me)₄. The thermogravimetric analysis (tga) of *trans*-Mo(N₂)₂(dppe)₂ was run to study the loss of dinitrogen. At a heating rate of 20°/min, there was a 9% weight loss between 478 and 498°K. From 518 to 728°K there was an additional loss of 45% weight. The initial transition is assigned to the complete loss of dinitrogen, which would correspond to a theoretical weight loss of 6%. There was no evidence for the stepwise loss of dinitrogen. The dsc and tga data indicate that dinitrogen is lost from *trans*-Mo(N₂)₂(dppe)₂ at a higher temperature than previously reported by Hidai, *et al.*³

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Registry No. *trans*-(N₂)₂(dppe)₂, 25145-64-6; Mo(N₂)₂(arphos)₂, 37138-36-6; *trans*-Mo(N₂)₂(PPh₂Me)₄, 33248-03-2; *cis*-Mo(N₂)₂(PMe₂Ph)₄, 32457-67-3; *trans*-Mo(N₂)₂(dpae)₂, 37041-96-6; *trans*-Mo(N₂)₂(diars)₂, 41371-99-7; Mo(N₂)₂[P(*n*-Bu)₃]₄, 33792-03-9.