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Spectroscopic and Chemical Properties of Nitrogen-15-Enriched Molybdenum Dinitrogen Complexes *trans,mer*-$Mo(N_2)_2(L)(PMePh_2)_3$

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Grignard Mg reduction of 0.5 equiv of Mo_2Cl_{10} and 4 equiv of $PMePh_2$ in THF at 0 °C under 1 atm of N_2 gives *trans*-$Mo(N_2)_2(PMePh_2)_4$ (**1**), which is isolated in 82% yield without contamination by $Mo(\eta^6\text{-PhPMePh})(PMePh_2)_3$. Substitution of a $PMePh_2$ ligand in **1** by L gives stable complexes *trans,mer*-$Mo(N_2)_2(L)(PMePh_2)_3$ when L is a phosphorus or nitrogen donor ligand with a Tolman cone angle that falls in the approximate range $100 < \theta_L < 136°$: $P(OMe)_3$, PMe_3, *N*-methylimidazole (*N*-$CH_3C_3H_3N_2$), pyridine, or 4-Me-, 4-*t*-Bu-, 3-Me-, 3-Cl-, 3-F-, or 3-PPh_2-pyridine. The last coordinates only via the nitrogen donor. The substituted pyridine complexes display intense MLCT absorptions. The chelating ligands $PPh_2(CH_2)_nSMe$ (n = 2 or 3) substitute for two $PMePh_2$ ligands to give *trans*-$Mo(N_2)_2$(chelate)$(PMePh_2)_2$ complexes. The dinitrogen ligands of these complexes and also of $Mo(N_2)(\eta^6\text{-PhPPh}_2)(PPh_2(CH_2)_2PPh_2)$ exchange with $^{15}N_2$ gas at 22 °C. Force constants k_{NN} are calculated from the IR spectra of the various $^{14}N_2/^{15}N_2$ isotopomers. There is a poor linear correlation (r = 0.85) of k_{NN} with the $E_{1/2}^{ox}$ (Mo(0) $\rightleftarrows$ Mo(I)) values for these and all other N_2 complexes of molybdenum(0): $k_{NN} = 2.25E_{1/2}^{ox} + 16.75$. The k_{NN} value is sensitive to the other ligands in the complex, especially the one trans to N_2. Couplings $|^1J(N_\alpha,N_\beta)|$ as determined by ^{15}N NMR decrease as constants k_{NN} increase for the trans N_2 complexes, which implies that this one-bond coupling is negative and that nonbonding s electron density on N_β is decreasing as the bond strength increases. The ^{15}N NMR spectra show that the N_2 ligands in the complexes *trans,mer*-$Mo(N_2)_2(3\text{-}RC_5H_4N)(PMePh_2)_3$ (R = Me, F, PPh_2) are inequivalent due to hindrance to rotation about the Mo–heterocycle bond as a result of steric crowding and possibly Mo–N(heterocycle) multiple bonding. The A_1 mode of $\nu(N_2)$ is observed in the IR spectra of these complexes because of this reduction in symmetry. Complexes *trans,mer*-$Mo(N_2)_2(L)(PMePh_2)_3$, where L = *N*-$CH_3C_3H_3N_2$, $PMePh_2$, and $P(OMe)_3$, react with H_2SO_4 in MeOH to give ammonia. The yield of ammonia is highest (0.70 NH_3/Mo) for the most reducing complex with L = *N*-$CH_3C_3H_3N_2$ and lowest for the most electron-poor complex with L = $P(OMe)_3$ (0.22 NH_3/Mo) although there is not a linear relationship between the yield of ammonia and k_{NN} or $E_{1/2}^{ox}$ values.

Introduction

The complex *trans*-$Mo(N_2)_2(PMePh_2)_4$ (**1**) is an unusual dinitrogen complex in that it allows a variety of substitution reactions cis to the N_2 ligands without loss of the N_2 ligands. These reactions have provided complexes with novel properties: $Mo(N_2)_2$(N-donor)$(PMePh_2)_3$, N-donor = *N*-methylimidazole (**2a**), 4-methylpyridine (**2b**), 3-methylpyridine (**2c**), and pyridine (**2d**);[2] $Mo(N_2)_2$(chelate)$(PMePh_2)_2$, chelate = $PPh_2CH_2CH_2SMe$ (**3**)[3] and $PPh_2CH_2CH_2PPh_2$.[4,5] The pyridine derivatives undergo an interesting $\sigma \rightarrow \pi$ rearrangement with loss of 2 mol of N_2 to give compounds $Mo(\eta^6\text{-py})(PMePh_2)_3$.[2] Complex **3** is a rare molybdenum dinitrogen complex containing a sulfur donor ligand that gives ammonia when treated with sulfuric acid.[3] This paper presents relationships between spectroscopic and chemical properties of a series of complexes derived from **1** that span a range of oxidation potentials. The other dinitrogen complexes that are known to undergo similar substitution reactions with pyridine or phosphine ligands where dinitrogen is retained are *trans*-$W(N_2)_2(PMePh_2)_4$[4] and *trans*-$ReCl(N_2)(PMe_2Ph)_4$,[6] and some properties of these complexes have already been reported.[4,6,7]

Although complex **1** has been prepared by several methods,[8-11] it was not realized until recently that contamination of the product by $Mo(\eta^6\text{-PhPMePh})(PMePh_2)_3$ was a problem.[11,12] We report here an efficient, one-pot synthesis involving commercially available reagents for the useful starting complex **1**.

The characterization of dinitrogen complexes by ^{15}N NMR has become an established technique.[13-15] This study of ^{15}N-enriched complexes demonstrates that a combination of both ^{15}N NMR data and vibrational data yield interesting steric and electronic information about these dinitrogen complexes.

The six new dinitrogen complexes reported here bring the total number of different, known molybdenum dinitrogen complexes that are stable under ambient conditions to about 75.[6,16,17] Of these only about 9 are known to yield ammonia when reacted with strong acid at 22 °C.[3,16-19] In this study the yield of ammonia is determined for the most easily and least easily oxidized complexes of the series. The reactions of such complexes could have relevance to the reactions of nitrogenase.[17]

Discussion

Preparation and Properties of the Complex *trans*-$Mo(N_2)_2(PMePh_2)_4$. The direct reduction of 0.5 mol of Mo_2Cl_{10} with magnesium in the presence of 4 mol of $PMePh_2$ under 1 atm of N_2 in THF at 0 °C provides an efficient route to *trans*-$Mo(N_2)_2(PMePh_2)_4$ (**1**).[8,10,11] Keeping the reduction reaction temperature near 0 °C and using a large volume of solvent saturated with N_2 improves the yield. However methanol should not be added to precipitate **1** as previously suggested since the side product, $Mo(\eta^6\text{-PhPMePh})(PMePh_2)_3$, will coprecipitate.[11,12] Instead, THF is removed and **1** is crystallized from concentrated

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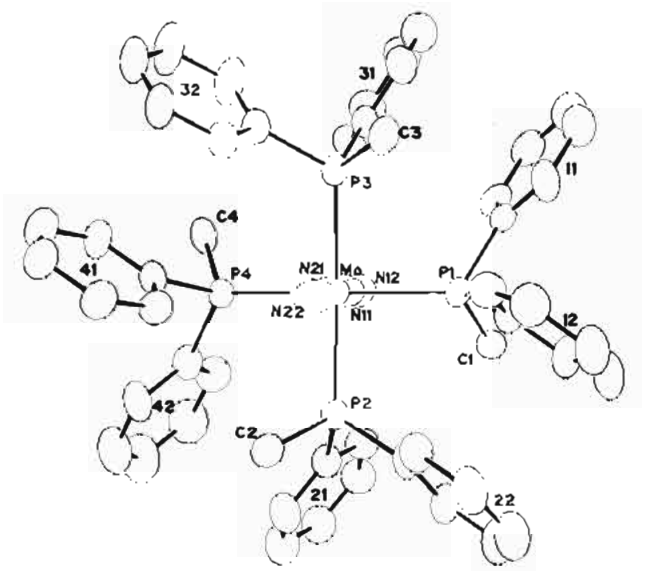

Figure 1. Structure by X-ray diffraction of the complex $Mo(N_2)_2(PMePh_2)_4$, (**1**). Reprinted with permission from ref 20. Copyright 1985 Munksgaard.

Table I. ^{31}P NMR, λ_{max}, and Equilibrium Constant (K_1) Data

ligand	complex	^{31}P NMR data[a] $\delta(P_{trans})$	$\delta(P_{cis})$	$^2J_{P-P}$, Hz	λ_{max}, nm	K_1
		Mo Complexes				
N-$MeN_2C_3H_3$	**2a**	37.9	26.4	9.8	524	2
4-$MeNC_5H_4$	**2b**	36.9	25.9	9.8	531	7
3-$MeNC_5H_4$	**2c**	36.3	25.9	9.5	547	4
		34.8[b]	24.2[b]			
NC_5H_5	**2d**	36.4	25.9	9.8	555	4
4-*t*-$BuNC_5H_4$	**2e**	36.4	25.8	9.3		7
3-$PPh_2NC_5H_4$[c]	**2f**	35.6	25.3	9.7	611	7
3-$ClNC_5H_4$	**2g**	35.2	25.1	10		
3-FNC_5H_4	**2h**	35.5	25.1	10	587	3
$PMePh_2$	**1**	18.6	18.6	...	...	
$P(OMe)_3$[d]	**4a**	15.7	22.0	15.5		
PMe_3[e]	**4b**	19.5	20.3	13		
		W Complexes[f]				
4-$MeNC_5H_4$		2.9[g]	3.3[h]	<2	red[f]	
NC_5H_5		2.7[g]	2.5[h]	<2	purple	
$PMePh_2$		−10.5	−10.5	...		

[a] THF solvent. [b] −50 °C. [c] $\delta(3\text{-}PPh_2) = -10.0$. [d] $\delta(P(OMe)_3) = 160.7$; $^2J_{PP} = 30.5$, 173.4 Hz. [e] $\delta(PMe_3) = -6.23$; $^2J_{PP} = 16$, 103 Hz. [f] Reference 4. [g] $^1J(^{31}P,^{183}W) = 192$ Hz. [h] $^1J(^{31}P,^{183}W) = 168$ Hz.

benzene solution as a benzene solvate in up to 82% yield; the complex $Mo(\eta^6\text{-}PhPMePh)(PMePh_2)_3$ is much more soluble and remains in solution. The presence of as yet unidentified molybdenum complexes in intermediate oxidation states is signalled during the reduction by several solution color changes involving brown, red, green, yellow, and then brown compounds or mixtures. Gas uptake studies indicate that dinitrogen uptake takes place during the final brown stage; there is indirect evidence that this last intermediate is $Mo(PMePh_2)_4(THF)_n$ ($n = 1$ or 2).[12]

The crystal structure of **1** demonstrates the trans stereochemistry and reveals a spectacular stacking of phenyl groups of neighboring $PMePh_2$ ligands in an array with local D_{2d} symmetry (Figure 1).[20] The four equivalent Mo–P distances (2.496 (2) Å) are longer than those of less crowded molybdenum phosphine compounds,[20] and this is consistent with the lability of the $PMePh_2$ ligands in **1**, as discussed below.

The dinitrogen ligands remain trans in solution. The ^{31}P and ^1H NMR spectra corroborate the trans structure (see Experimental section). The IR spectrum of **1** as a concentrated Nujol mull shows both the commonly observed $A_{2u}N_2$ vibration at 1927 cm^{-1} along with a weak A_{1g} mode at 1993 cm^{-1}.

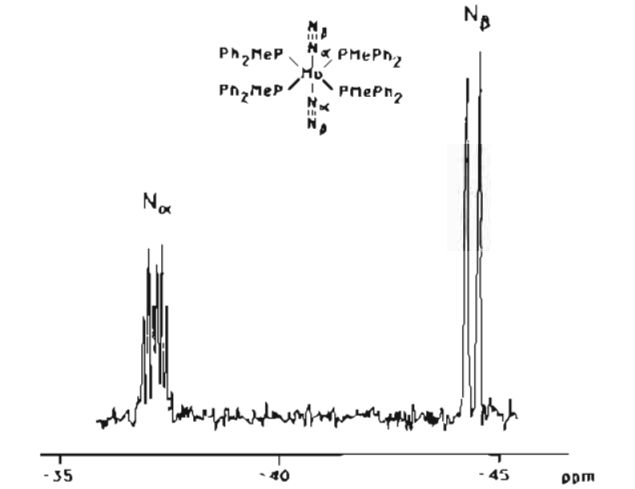

Figure 2. ^{15}N NMR spectrum at 20.28 MHz of the complex $Mo(N_2)_2(PMePh_2)_4$.

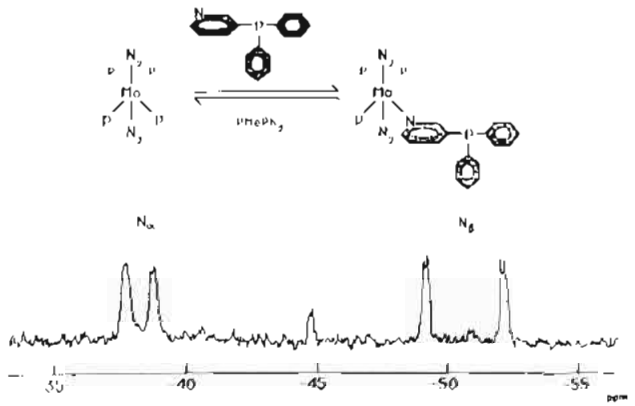

Figure 3. ^{15}N NMR spectrum at 20.28 MHz of the complex $Mo(N_2)_2(3\text{-}(PPh_2)C_5H_4N)(PMePh_2)_3$ and the coordination mode of the Ligand 3-$PPh_2C_5H_4N$.

Preparation of the Complexes *trans,mer*-$Mo(N_2)_2(L)(PMePh_2)_3$. The complexes are prepared according to eq 1. A

$$Mo(N_2)_2(PMePh_2)_4 + L \underset{}{\overset{K_1}{\rightleftharpoons}} Mo(N_2)_2(L)(PMePh_2)_3 + PMePh_2 \quad (1)$$

L: *N*-methylimidazole, **2a**; 4-methylpyridine, **2b**; 3-methylpyridine, **2c**; pyridine, **2d**; 4-*tert*-butylpyridine, **2e**; 3-(diphenylphosphino)pyridine, **2f**; 3-chloropyridine, **2g**; 3-fluoropyridine, **2h**; trimethyl phosphite, **4a**; trimethylphosphine, **4b**

large excess of the nitrogen donors (L) is required to drive equilibrium 1 to the right;[2] no loss of dinitrogen or further substitution is observed over a period of hours for solutions under 1 atm of N_2 although 3-fluoro- and 3-(diphenylphosphino)-substituted pyridines undergo a $\sigma \rightarrow \pi$ rearrangement over longer reaction times (see below). No reaction of **1** with 2-picoline occurs because of steric hindrance. The equilibrium constants, K_1, for THF solutions at 30 °C are insensitive to the nature of the nitrogen donor ligands and all have values of 4 ± 3 as determined via integration of ^{31}P NMR spectra (Table I). Solid samples of complexes **2a-h** can be isolated by reaction **1** with excess L in a pentane slurry, but they are always contaminated with starting material.[2]

In contrast to the nitrogen donors, the small phosphorus donors $P(OMe)_3$ and PMe_3 react irreversibly with complex **1** to give the new complexes **4a** and **4b**; further substitution occurs if more than 1 equiv is added. Only solution data are reported for complex

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Table II. Infrared and ^{15}N NMR Data

ligand	complex	mode	infrared data $\nu(N_2)$,[a] (cm^{-1}) $(^{14}N_2)_2$ obsd	$(^{14}N_2)_2$ calcd	$(^{14}N_2)(^{15}N_2)$ obsd	$(^{14}N_2)(^{15}N_2)$ calcd	$(^{15}N_2)_2$ obsd	$(^{15}N_2)_2$ calcd	^{15}N NMR data[b] $\delta(N_\alpha)$	$\delta(N_\beta)$	$^1J(N_\alpha,N_\beta)$, Hz	$\lvert^2J(N_\alpha,P)\rvert$, Hz
N-$MeN_2C_3H_3$	**2a**	B_1	1911, s	1913	1869, s	1868	1850, sh	1848	−37.4, dq	−50.3, d	−6.7	2.6
		A_1	1988, w	1985	1966, mb	1965	...	1918				
4-$MeNC_5H_4$	**2b**	B_1	1914, s	1915	1867, s	1870	1851, s	1850	−37.7, dq	−51.7, d	−6.5	2.2
		A_1	...	1992	1968, wb	1970	...	1924				
3-$MeNC_5H_4$	**2c**	B_1	1912, s	1914	1870, s	1869	1851, s	1850	−36.0, b[c]	−50.8, bd[c]	−5.8[c]	...
		A_1	1977, w	1984	1970, wb	1964	1917, m	1917	−38.4, b[c]	−55.2 bd[c]	−6.0[c]	...
3-$PPh_2NC_5H_4$	**2f**	B_1	1916, s	1916	...	1871	1854, s	1851	−37.6, b	−49.2, bd	−6.3	...
		A_1	1995, w	1995	...	1973	...	1928	−38.7, b	−52.2, bd	−7.0	...
3-FNC_5H_4	**2h**	B_1	1915, s	1918	1868, s	1873	1851, s	1853	−37.4, b	−50.1, b	...	...
		A_1	...	1994	1971, wb	1973	...	1927	−38.2	−51.8, b	...	...
$PMePh_2$	**1**	A_{2u}	1929, s	1929	1883, s	1882	1866, s	1863	−37.6, dqu	−44.7, d	−5.8	2.2
		A_{1g}	1993, vw[d]	1996	1977, wb	1976	...	1928				
$P(OMe)_3$	**4a**	B_1	1959, s	1960	1919, s	1911	1885, s	1893	−42.9, m	−45.1, d	−5.0	2.1
		A_1	...	2019	2008, wb	2000	...	1951				
$PPh_2CH_2CH_2SMe$	**3**	B	1942, s	1942	...		...		−42.7, dq	−46,8, d	−5.7	2.2
		A	2014, w	2014	...		...					
cis-$Mo(N_2)_2(PMe_2Ph)_4$	**11**	B_2	1932, s	1934	1887, s	1889	1869, sh	1868				
		A_1	2019, s	2019	2002, w	1996	1951	1951				

[a] Solvent: THF/C_6D_6; 10/1 v/v. Key: s = strong, m = medium, w = weak, vw = very weak, sh = shoulder, b = broad. [b] Solvent: THF/C_6D_6; 10/1 v/v. Key: b = broad, d = doublet, q = quartet, qu = quintet, m = multiplet. [c] −50 °C, coupling not well resolved. [d] Nujol mull.

4b since it is difficult to isolate it as a pure solid.

No reaction is observed with large cone angle phosphines $P(C_6H_{11})_3$ ($\theta = 170°$) and PPh_3 ($\theta = 145°$), suggesting a steric limitation to eq 1. This explains why the ligand 3-$PPh_2C_5H_4N$ coordinates only via the small N-donor end (Figure 3). Both donor sites of the ligand $PPh_2CH_2CH_2SMe$ are small enough to coordinate. The molecular structure and properties of the complex formed, $Mo(N_2)_2(PPh_2CH_2CH_2SMe)(PMePh_2)_2$ (**3**), have been described elsewhere.[3] The complex $Mo(N_2)_2(PPh_2(CH_2)_3SMe)(PMePh_2)_2$ has also been generated in solution in equilibrium with excess sulfur ligand and **1**, but it decomposes in a few hours to paramagnetic products that do not contain N_2.[21] Complex **3** also decomposes in solution in a few days; the reaction may involve S–C bond cleavage to give a thiolate ligand and radical species, but further study is required. This would explain why thioethers $RSCH_2CH_2SR$ (R = Me, Et) and *cis*-$PhCH_2SCH{=}CHSCH_2Ph$ react with loss of N_2. Carbon monoxide,[22] MeCN, PhCN and *tert*-butyl isocyanide, which are small cone angle ligands ($\theta < 100°$), have access to the N_2 binding site and rapidly cause N_2 displacement at 25 °C.

Equilibrium 1 is established in less than 15 min at 22 °C in THF. It is not known whether the reaction proceeds via initial dissociation of phosphine or dinitrogen ligand. Phosphine dissociation is feasible since N_2 can substitute for a ligand $P(n\text{-}Pr)_2Ph$ in the complex *trans*-$Mo(N_2)_2(P(n\text{-}Pr)_2Ph)_4$, which is a little more crowded than complex **1**, to give *mer*-$Mo(N_2)_3(P(n\text{-}Pr)_2Ph)_3$.[23] No tris(dinitrogen) complex has been observed for reaction 1 at 1 atm of N_2.

The ^{31}P NMR data (see Table II for the N-donor complexes, the Experimental Section for the others) and IR data (Table II) are consistent in all cases with the *mer,trans* stereochemistry. Complexes **2b–h** range in color from intense red, through deep purple, to intense green. The color is due to the charge-transfer transition d(Mo) → π*(pyridine).[24] The increase of λ_{max} values (Table I) with increasing electron-withdrawing ability of the substituent on the pyridine reflects the increasing stabilization by the substituent of the π*(pyridine) level. The similar range of colors that was reported for corresponding tungsten complexes can also be explained in this way.[4] The trend in ^{31}P chemical shifts for **2b–h** is a decrease in shielding of both cis and trans P nuclei in the $PMePh_2$ ligands with an increase in electron-donating ability of substituents on the pyridine ligands. This is not in the direction expected by using shielding arguments, and so the ^{31}P chemical shifts are likely influenced by the ΔE parameter in the paramagnetic circulation term of the Ramsey equation.[25,26] The ^{31}P chemical shift of the $PMePh_2$ ligands cis to L is upfield of that of the ligand trans to L when L is an N-donor ligand. We have found that for the complexes $W(N_2)_2(PMePh_2)_3(L)$ (L = pyridine, 4-picoline) this ordering is reversed (Table I).

Preparation of ^{15}N-Enriched Complexes. The dinitrogen ligands in all the complexes are labile and exchange with $^{15}N_2$ at 22 °C. With our experimental conditions (~1 atm of $^{15}N_2$), the rate of the exchange reaction for *trans*-$Mo(N_2)_2(PMePh_2)_4$ (**1**) ($t_{1/2} \sim$ 60 min for first-order loss of N_2 at 22 °C; see Experimental Section) is comparable to that of *trans*-$Mo(N_2)_2((p\text{-}ClC_6H_4)_2PCH_2CH_2P(p\text{-}ClC_6H_4)_2)_2$ ($t_{1/2}$ = 68 min at 22 °C[27]) but slower than *cis*-$Mo(N_2)_2(PMe_2Ph)_4$ ($t_{1/2} \sim$ 30 s) where N_2 appears to be labilized by a trans-phosphine ligand.[27] Conversion to the $^{15}N_2$-enriched complexes was qualitatively slower for the substituted complexes containing the more electron-donating substituents, *N*-methylimidazole and 3- or 4-methylpyridine, than for those containing $P(OMe)_3$ and 3-fluoropyridine. A similar trend in rate of first-order N_2 loss from complexes *trans*-$M(N_2)_2(R_2PCH_2CH_2PR_2)_2$ (M = Mo, W) as a function of the donor properties of R has been reported.[27] In both cases the trend is explained by a strengthening of the Mo–N_2 interaction by electron-donating ligands. The spectroscopic data for the complexes that were enriched with $^{15}N_2$ are listed in Table II.

Vibrational Data. The *trans*-$(^{14}N_2)_2$ and -$(^{15}N_2)_2$ complexes of local D_{4h} or C_{2v} symmetry give the expected intense asymmetric A_{2u} or B_1 $\nu(N_2)$ absorption, respectively. A weak symmetric mode (A_{1g} in D_{4h}, A_1 in C_{2v}) is observed in the solid state (Nujol mull) for the $(^{14}N_2)_2$ complexes but the corresponding mode for the $(^{15}N_2)_2$ complexes was hidden under other absorptions. The A_1 mode is also observed in solution for the $(^{14}N_2)_2$ complexes of the 3-substituted pyridines and *N*-methylimidazole where the symmetry of the complex is lowered by restricted rotation of the ligand (vide infra). Complex **3** containing $PPh_2CH_2CH_2SMe$ also shows this mode. The $(^{14}N_2)(^{15}N_2)$ complexes give two broad $\nu(N_2)$ stretches.

Force constants k_{NN} and $k_{NN\text{-}NN}$ that generate these frequencies within ±2 cm^{-1} can be calculated for each complex and are listed

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Table III. Force Constant, Coupling Constant, and Electrochemical Data

no.	complex[a]	$^1J(N_\alpha,N_\beta)$, Hz	K_{NN}, mdyn/Å	K_{NN-NN}, mdyn/Å	$E_{1/2}^{ox}$,[b] V	ref
2a	L = *N*-$MeN_2C_3H_3$	−6.7	15.67	0.58	−0.65	*g*
2b	L = 4-$MeNC_5H_4$	−6.5	15.74	0.62	−0.48	*g*
1	L = $PMePh_2$	−5.8	15.88	0.54	−0.17	*g*
6	$Mo(N_2)_2(DEPE)_2$	−5.7	15.78	0.51	−0.43	13, 17
3	$Mo(N_2)_2(PMePh_2)_2(PS)$	−5.7	16.1	0.6	−0.31	*g*, 3
7	$W(N_2)_2(DPPE)_2$	−5.4	16.11	0.52	−0.15	6, 13, 33
4a	L = $P(OMe)_3$	−5.0	16.32	0.49	−0.11	*g*
8	$Mo(N_2)_2(DPPE)_2$	−4.4	16.58	0.57	−0.16	6, 13, 33
9	$[Mo(N_2)_2H(DEPE)_2]^+$	−4 ± 1	16.7[c]	0.55[c]		6, 34
10	$[W(N_2)_2H(DPPE)_2]^+$	−4 ± 1	16.9[c]	0.55[c]		38, 45
		Data Used in Figure 5 but Not in Figure 4				
2c	L = 3-$MeNC_5H_4$	−5.8, −6.0[d]	15.67	0.56	−0.46	*g*
2d	L = NC_5H_5				−0.45	*g*
2f	L = 3-$PPh_2NC_5H_4$	−6.3, −7.0[d]	15.77	0.64	−0.42	*g*
2h	L = 3-FNC_5H_4		15.78	0.62	−0.40	*g*
5	$Mo(N_2)(\eta^6\text{-}PhPPh_2)(DPPE)$	−4.6[e]	17.0		−0.04	*g*
11	*cis*-$Mo(N_2)_2(PMe_2Ph)_4$	−6.3	16.14	0.64	−0.23[f]	*g*, 13, 27

[a] DEPE = $PEt_2CH_2CH_2PEt_2$; PS = $PPh_2CH_2CH_2SMe$; DPPE = $PPh_2CH_2CH_2PPh_2$. [b] Vs. SCE; solvent, THF/0.2 M $(NBu_4)(BF_4)$. [c] Assumption: k_{NN-NN} = 0.55 mdyn/Å. [d] Obtained from poorly resolved peaks of the spectra obtained at −50 °C. [e] $\delta(N_\alpha)$ = −48.1, $\delta(N_\beta)$ = −19.5, $^2J_{NP}$ = 3.5 Hz in THF. [f] E_p^{ox}. [g] This work.

in Table III. This treatment assumes that interactions with other modes are negligible.[28] The k_{NN} values indicate the following order of increasing electron-donor ability for the ligands: $P(OMe)_3$ < $PMePh_2$ ~ $PPh_2CH_2CH_2SMe$ < 3-fluoropyridine ~ 3-methylpyridine ~ 4-methylpyridine < *N*-methylimidazole.

^{15}N NMR Data. The spectra of the complexes as mixtures of $(^{14}N_2)(^{15}N_2)$ and $(^{15}N_2)_2$ isotopomers show well-resolved peaks at 22 °C except for those of the 3-substituted pyridine derivatives, which show temperature-dependent broadening. The chemical shifts fall in the range identified previously for molybdenum dinitrogen complexes.[13] The spectrum of complex **1** (Figure 2) gives one intense doublet for N_β and a doublet quintet for N_α with typical couplings[13] $|^1J(^{15}N,^{15}N)| \sim 5.8$ Hz and $|^2J(^{31}P,^{15}N_\alpha)| \sim 2.2$ Hz. Chemical shift differences between isotopomers are not resolved at 40.56 MHz. The N_α and N_β chemical shifts are relatively insensitive to changes in the cis ligand (Table II).

The broad N_α and N_β resonances for the 3-methylpyridine derivative resolve into two sets at −50 °C, corresponding to two inequivalent $^{15}N_2$ ligands. This suggests that interactions of the 3-methyl group with the bulky cis-phosphine ligands hinder rotation about the Mo–N(pyridine) bond. The spectrum of the more crowded 3-(diphenylphosphino)pyridine derivative (Figure 3), which shows two distinct sets of resonances *at room temperature*, supports this hypothesis. The spectrum of complex **2h** also indicates this hindrance to rotation. *N*-Methylimidazole must have a lower barrier to rotation in its complex since no line broadening is observed at room temperature. These observations do not rule out the possibility that multiple bonding involving d(Mo)–π^*(N) overlap as indicated by the charge-transfer absorptions contributes to the restricted rotation for the pyridine ligands.

The spectrum of $Mo(^{15}N_2)(\eta^6\text{-}PhPPh_2)(PPh_2CH_2CH_2PPh_2)$ (**5**),[29] which was also recorded (Table III), shows that N_α is shielded relative to N_β, unlike complexes **1**–**4** but like complexes *cis*-$Mo(N_2)_2(PMe_2Ph)_4$ and *trans*-$Mo(N_2)_2(PPh_2CH_2CH_2PPh_2)_2$.[13] This crossover of $\delta(N_\alpha)$ and $\delta(N_\beta)$ has only been observed for dinitrogen complexes of molybdenum.[13]

This work has revealed an interesting correlation between ^1J(N,N) and k_{NN} (Table III, Figure 4), which supports the idea that the sign of this ^1J coupling is actually negative. The absolute value of ^1J(N,N) decreases monotonically as k_{NN} increases. This is consistent with the observed couplings for N_2O, $^1J_{NN}$ = −9.2 Hz,[30] and ethyl diazoacetate, $^1J_{NN}$ = −5.62 Hz,[31,32] where again

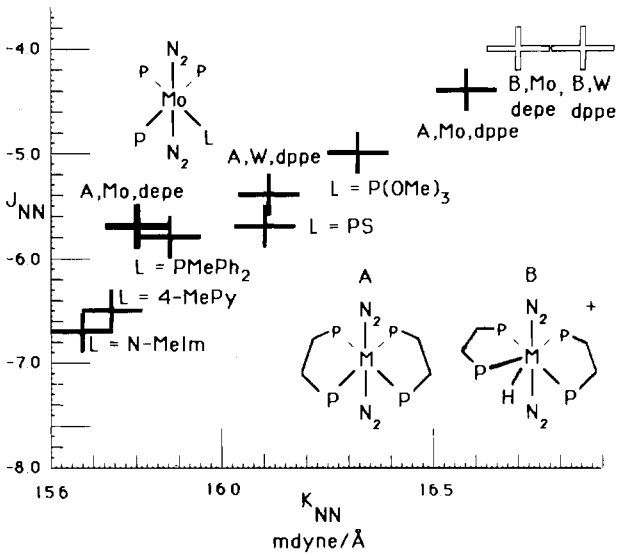

Figure 4. Correlation between $^1J_{NN}$ and k_{NN} data from Table III. The white crosses indicate that k_{NN} was calculated by assuming that k_{NN-NN} is 0.55 kdyn/Å.

the magnitude of the coupling decreases as the bond order increases. The negative sign for the latter compound was assigned on the basis of the calculation of a large negative Fermi contact term in the coupling equation, which results from nonbonding s electron density on N_β.[31,32] Thus nonbonding s electron density on N_β appears to decrease as the N_2 bond strength increases. All literature values to date for *trans*-bis(dinitrogen) complexes appear to obey this correlation. Figure 4 includes the coupling and force constant values for $Mo(N_2)_2(DEPE)_2$ (**6**),[13] $W(N_2)_2(DPPE)_2$ (**7**),[13,33] $Mo(N_2)_2(DPPE)_2$ (**8**),[13,33] $[Mo(N_2)_2H(DEPE)_2]^+$ (**9**),[34] and $[W(N_2)_2H(DPPE)_2]^+$ (**10**).[13] Thus these values of ^1J(N,N) are likely to be negative. Data for **2f**–**h** are not plotted in Figure 4 because of uncertainty in the *J* values because of the line broadening due to the restricted rotation of the pyridine ligands. The data in Table III for the cis complexes $M(N_2)_2(PMe_2Ph)_4$ (M = Mo, W), as well as data for other complexes that contain ligands other than N_2 trans to N_2, are not expected to fall on the curve defined in Figure 4.

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Table IV. Force Constant and Electrochemical Data Derived from the Literature

no.	complex	$E_{1/2}^{ox}$,[a] V	K_{NN}, mdyn/Å	ref
12	$Mo(N_2)_2[(p\text{-}CF_3C_6H_4)_2PCH_2CH_2P(p\text{-}CF_3C_6H_4)_2]_2$	0.22	~16.8[b]	27
13	$Mo(N_2)_2[(p\text{-}ClC_6H_4)_2PCH_2CH_2P(p\text{-}ClC_6H_4)_2]_2$	0.05	~16.6[b]	27
14	$Mo(N_2)(\eta^6\text{-}PhPhMe)(PMePh_2)_2$	−0.13	16.2	47
15	$Mo(N_2)(CO)(PPh_2CH_2CH_2PPh_2)_2$	−0.13	18.1	35, 48
16	$Mo(N_2)_2[(p\text{-}MeC_6H_4)_2PCH_2CH_2P(p\text{-}MeC_6H_4)_2]_2$	−0.25	~16.5[d]	27
17	$Mo(N_2)_2[(p\text{-}MeOC_6H_4)_2PCH_2CH_2P(p\text{-}MeOC_6H_4)_2]_2$	−0.30	16.31[c]	27
18	$Mo(N_2)(PhCN)(PPh_2CH_2CH_2PPh_2)_2$	−0.48	15.59	35, 49, 50
19	$Mo(N_2)(MeCN)(PPh_2CH_2CH_2PPh_2)_2$	−0.58	15.04	35, 49, 50
20	$Mo(N_2)(SCN^-)(PPh_2CH_2CH_2PPh_2)_2$	−0.87	14.27	35
21	$Mo(N_2)(N_3^-)(PPh_2CH_2CH_2PPh_2)_2$	−1.19	14.11	35

[a] Vs. SCE; solvent, THF/0.2 M $(NBu_4)(BF_4)$. [b] $k_{NN\text{-}NN}$ = 0.55 mdyn/Å assumed. [c] $k_{NN\text{-}NN}$ = 0.54 mdyn/Å.

Table V. Yields of Ammonia from Reactions of Selected Complexes with H_2SO_4

complex	$E_{1/2}^{ox}$,[a] V	k_{NN}, mdyn/Å	NH_3/Mo	N_2/Mo	H_2/Mo	N balance, mol	ref
			$Mo(N_2)_2(L)(PMePh_2)_3$				
L = *N*-$MeC_3H_3N_2$	−0.65	15.67	0.70	1.50	0.01	1.84	*b*
L = $PMePh_2$	−0.17	15.88	0.66	1.64		1.97	18
L = $P(OMe)_3$	−0.11	16.32	0.23	1.60	0.08	1.72	*b*
			$Mo(N_2)_2(L)(PMePh_2)_2$				
L = $PPh_2CH_2CH_2SMe$	−0.31	16.1	0.3	1.4	0.7	1.55	3
L = $PPh_2CH_2CH_2PPh_2$	−0.16	15.6	0.56	1.2	0.2	1.48	18

[a] This work; vs. SCE. [b] This work.

Electrochemical Data. Complexes **1–4** undergo reversible one-electron oxidations at 25 °C in THF solutions under N_2. The $E_{1/2}^{ox}$ values fall in the range −0.65 V for the most electron-donating ligand, *N*-methylimidazole, to −0.11 V vs. S.C.E. for the least electron donating ligand, trimethyl phosphite. The ordering of the ligand donor strengths parallels that given by the k_{NN} values although the methyldiphenylphosphine ligand in complex **1** appears out of place. This is seen in Figure 5, where the force constants k_{NN} are plotted against the $E_{1/2}^{ox}$ values.

Included in Figure 5 and Table IV are literature values for all other molybdenum dinitrogen complexes where both properties have been measured. The electrochemical data were all obtained under similar conditions (THF solvent, 0.2 M $(NBu_4)(BF_4)$ electrolyte and SCE reference) and are all believed to represent reversible oxidations, and so the uncertainties should be less than ±0.1 V. Errors in the force constant estimates are due to IR data obtained under different conditions (solid state vs. solution), interactions of $\nu(N_2)$ with other vibrational modes, and a lack of isotopic substitution data for many of the complexes; these errors could amount to ±0.15 mdyn/Å. The trend expected is an increase in k_{NN} as the redox potential becomes more positive. In other words there is less back-bonding to the dinitrogen ligand as the complex becomes less reducing and the electrons in the dπ orbitals on the metal become more difficult to remove or ionize. This trend is indeed apparent although for a given redox potential a wide range of force constants can be observed. For example at −0.1 V the force constants range from 16.2 to 18.1 mdyn/Å corresponding to complexes $Mo(N_2)(\eta^6\text{-}PhPMePh)(PMePh_2)_2$ (**14**) ($\nu(N_2)$ = 1980 cm^{-1}), and *trans*-$Mo(N_2)(CO)(dppe)_2$ (**15**) ($\nu(N_2)$ = 2100 cm^{-1}), respectively. Clearly the σ and π influences of the ligands trans and probably of the ligands cis to N_2 are very important. The equation for the line of least-squares deviations for Figure 5 is

$$k_{NN} = 2.25E_{1/2}^{ox} + 16.75$$

The correlation is poor with r = 0.85 if no correction is made to account for trans-ligand and cis-ligand effects. The largest deviation from this line occurs when N_2 is trans to CO (complex **15**). It can be argued that CO is competing with N_2 for dπ electrons so that k_{NN} is higher than expected.

If this trend holds true and if it can be modeled by use of ligand parameters, then redox potentials can be more accurately predicted from the force constant for the dinitrogen ligand. Ligand parameters P_L have been derived for ligands trans to dinitrogen that are linearly related to $E_{1/2}^{ox}$ and to $\nu(N_2)$ for dinitrogen binding sites $M(L)(dppe)_2^{n+}$ (M = Mo, W, Fe, and Ru).[35] However ligands cis to N_2 in the complexes *trans*-$M(N_2)_2((p\text{-}XC_6H_4)_2PCH_2CH_2P(p\text{-}XC_6H_4)_2)_2$ (M = Mo, W)[27a] and $Re(N_2)Cl(R_2PCH_2CH_2PR_2)_2$[36] have been shown to influence $E_{1/2}^{ox}$ and $\nu(N_2)$ in different ways so that plots of $E_{1/2}^{ox}$ vs. $\nu(N_2)(A_{2u})$ are nonlinear. In these cases the cis phosphine ligands influence the HOMO inductively, but they conjugate directly with the dπ-system involved in bonding to the N_2.[27a] Further work is required to determine whether simple ligand parameters can be derived to accurately describe these subtle cis and trans effects.

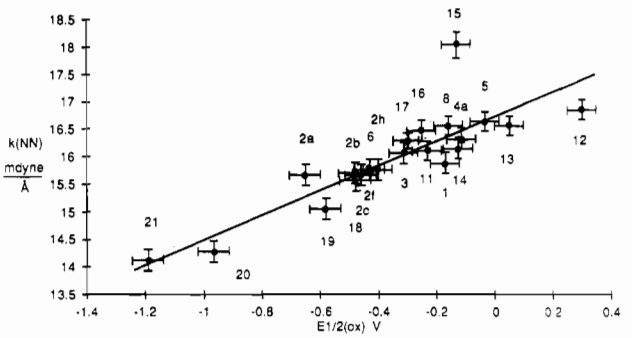

Figure 5. Correlation between k_{NN} and $E_{1/2}^{ox}$ data for the complexes numbered in Tables III and IV.

Reactions of the Complexes with Sulfuric Acid To Give Ammonia. Reaction of concentrated sulfuric acid with the complexes $Mo(N_2)_2(PMePh_2)_3(L)$ (L = *N*-methylimidazole (**2a**), $PMePh_2$ (**1**), and $P(OMe)_3$ (**4a**)) suspended in methanol yielded ammonia but no hydrazine (Table V). Reaction conditions were kept as close as possible to those reported by Chatt, et al. for the reaction of **1** with sulfuric acid[18] and comparable yields of NH_3 and a similar nitrogen balance were obtained (Table V).

The yield of ammonia produced by **2a**, the most reducing complex according to $E_{1/2}^{ox}$ and k_{NN} values, is higher than that

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for **4a**, the most electron-poor complex, as might be expected if electron richness at the metal favors protonation at the N_2 as opposed to other reactions that result in loss of the N_2 ligands. However the yield of ammonia from **1**, despite its more positive potential, is similar to that of **2a**. A uniform relationship between $E_{1/2}^{ox}$ and yields of ammonia might not be expected considering the multistep nature of the protonation/reduction process. The complexes $Mo(N_2)_2(chelate)(PMePh_2)_2$ (chelate = $PPh_2CH_2CH_2SMe$ (**3**) and $PPh_2CH_2CH_2PPh_2$)[18] also yield intermediate amounts of ammonia but also significant yields of dihydrogen; different reaction pathways must be available here.

Other Reactions of the Complexes. The complexes **2b–h** containing σ-bonded pyridine ligands are unstable in solution under argon and rearrange to π-bonded pyridine complexes.[2,37] The complexes rearrange more slowly in THF than in benzene, presumably because of the ability of THF to better solvate reactive species generated by loss of a dinitrogen ligand from **2b–h**. Complexes **2f–h** rearrange to π-complexes over a period of days at 22 °C in THF under N_2 whereas the other complexes are stable for weeks in THF under N_2. Thus electron-withdrawing groups and bulky groups on the pyridine ligand favor the rearrangement. The corresponding tungsten σ-pyridine complexes are less stable than those of molybdenum, but they do not appear to rearrange to π-complexes.[37] The decomposition of thioether-containing complexes like **3** is suspected to involve S–C bond cleavage, but further study is required.

Summary. *trans*-$Mo(N_2)_2(PMePh_2)_4$ (**1**) can be synthesized directly from Mo_2Cl_{10} in 82% yield without contamination by $Mo(\eta^6\text{-}PhPMePh)(PMePh_2)_3$. Complex **1** undergoes substitution reactions to give the stable complexes *trans,mer*-$Mo(N_2)_2(L)(PMePh_2)_3$ when L is a nitrogen or phosphorus donor ligand with Tolman's cone angles that fall in the approximate range $100 < \theta_L < 136°$. Thus 3-$PPh_2C_5H_4N$ coordinates only via the nitrogen donor. The substituted pyridine complexes display intense MLCT absorptions. The chelating ligands $PPh_2CH_2CH_2PPh_2$ and $PPh_2(CH_2)_nSMe$ (n = 2 or 3) substitute for two $PMePh_2$ ligands to give complexes *trans*-$Mo(N_2)_2(chelate)(PMePh_2)_2$.

The dinitrogen ligands of these complexes and also $Mo(N_2)(\eta^6\text{-}PhPPh_2)(PPh_2(CH_2)_2PPh_2)$ are labile and exchange with $^{15}N_2$ gas. Force constants k_{NN} can be calculated from the IR spectra of the various $^{14}N_2/^{15}N_2$ isotopomers. These correlate roughly with the $E_{1/2}^{ox}$ values corresponding to the reversible one-electron oxidation of the complexes in this study. The trend of increasing k_{NN} with more positive $E_{1/2}^{ox}$ applies to all available literature values for molybdenum dinitrogen complexes although the k_{NN} value is sensitive to trans- and probably cis-ligand effects. The force constants for the trans N_2 complexes increase as the couplings $|^1J(N_\alpha N_\beta)|$ (as determined by ^{15}N NMR) decrease, suggesting that this one-bond coupling is negative and that nonbonding s electron density on N_β is decreasing. The ^{15}N NMR spectra show that the dinitrogen ligands in the complexes *trans,mer*-$Mo(N_2)_3(3\text{-}RC_5H_4N)(PMePh_2)_3$, (R = Me, F, and PPh_2) are inequivalent. The appearance in the IR spectra of these complexes of a moderately strong A_1 $\nu(N_2)$ mode is consistent with this reduction in symmetry. There must be a hindrance to rotation about the Mo–heterocycle bond as a result of steric crowding and possibly Mo–N multiple bonding.

Complexes *trans,mer*-$Mo(N_2)_2(L)(PMePh_2)_3$ (L = N-methylimidazole, $PMePh_2$, and $P(OMe)_3$) react with H_2SO_4 in MeOH to give ammonia. The yield of ammonia is highest (0.70 NH_3/Mo) for the most reducing complex with L = methylimidazole and lowest for the most electron-poor complex with L = $P(OMe)_3$ (0.22 NH_3/Mo) although there is not a uniform relationship between the yield of ammonia and k_{NN} or $E_{1/2}^{ox}$ values.

Experimental Section

All operations were conducted under a purified nitrogen or argon atmosphere by using vacuum-line and glovebox techniques. The preparations of complexes **1**,[8,10,11] **2b,d**,[2] and $Mo(N_2)_2(PMePh_2)_2(PPh_2CH_2CH_2PPh_2)$[4,5] have been described. However a reliable, detailed preparation of **1** is provided below. Solvents other than alcohols were dried over sodium benzophenone ketyl and were degassed before use. Tetrahydrofuran (THF) was further dried over and vacuum distilled from $LiAlH_4$. Alcohols were distilled from their magnesium alkoxides. $^{15}N_2$ gas was used as obtained from Merck, Sharp and Dohme Canada, Ltd.

Tetrahydrofuran/benzene-d_6 solutions (90/10:v/v) of the complexes (~0.05 M) to be enriched in $^{15}N_2$ were vacuum-degassed by three freeze–pump–thaw cycles in a 10-mm NMR tube that was attached to a 100-mL $^{15}N_2$ reservoir bulb via a stopcock and ground-glass joint. Dead volume was minimized. The degassed solution was then exposed to the $^{15}N_2$ gas (approximately 700 Torr), usually for 12–14 h and then the NMR tube was sealed off.

The NMR spectra were recorded by use of a Varian XL200 instrument operating at 20.28 MHz for ^{15}N and 80.98 MHz for ^{31}P or a Bruker WH400 instrument (40.56 and 161.98 MHz, respectively). We have found that addition of $Cr(acac)_3$ was not required to obtain reasonable relaxation times for the $^{15}N_2$ spectra.[38] Typically about 12000 transients were collected over a 17-h period with a relaxation delay of 4–5 s for a 12-μs pulse at 20.28 MHz. ^{15}N chemical shifts were referenced to external CH_3NO_2. Free $^{15}N_2$ (δ −69.8 to −74.9 ppm) was observed in all spectra. ^{31}P chemical shifts were referenced to 1% $P(OMe)_3$ in a coaxial capillary but are reported here vs. 85% H_3PO_4 by use of $\delta(P(OMe)_3)$ = 140.4 for the XL200 or WH400.

After the NMR spectra were recorded, the tubes were broken open in a glovebag filled with argon and the solutions were transferred to 0.1-mm KBr solution cells. The infrared spectra were obtained by use of a Nicolet 5DX FTIR spectrometer (±2 cm^{-1}).

The redox potentials of 1.31×10^{-3} M solutions of substituted complexes of *trans*-$Mo(N_2)_2(PMePh_2)_4$ in 0.2 M $(NBu_4)(BF_4)$ in THF were determined by cyclic voltammetry by use of a BAS CV 1B instrument and a Houston instruments 100 recorder. All measurements were carried out at 22 °C by using a glassy-carbon working electrode, a Ag/AgCl reference electrode and a platinum auxiliary electrode. Complexes **3** and **4a** were added directly to the electrolyte-containing solution. The other complexes were generated in the electrolyte solution by adding 5 equiv of each heterocycle or 0.5 equiv of PMe_3 to 1.31 mM solutions of *trans*-$Mo(N_2)_2(PMePh_2)_4$. The waves for the redox process Mo(O) ⇄ Mo(I) showed peak to peak separations of about 100 mV at scan rates of 75 mV/s. A small wave due to the starting complex *trans*-$Mo(N_2)_2(PMePh_2)_4$ was usually also present because of equilibrium 1.

Microanalyses were performed by Microanalysis Laboratories Ltd., Markham, Ontario, Canada, and by Canadian Microanalytical Service Ltd., Vancouver, B.C., Canada. All phosphines used, with the exception of 3-$PPh_2C_5H_4N$ and $PPh_2CH_2CH_2SMe$ were obtained from the Strem Chemical Co. The nitrogen donor ligands were obtained from Aldrich Chemical Co. and were distilled from CaH_2 before use.

Preparation of 3-$PPh_2C_5H_4N$. The method was based on the synthesis of 2-$PPh_2C_5H_4N$.[39] *n*-Butyl lithium (12.93 mL of 1.664 M, 21 mmol) was diluted to 35 mL with diethyl ether, and then added dropwise with stirring to a solution of 4.0 g of $HPPh_2$ (21 mmol) in 65 mL of diethyl ether over the course of 45 min. To this red solution 2.05 mL (2.44 g, 21.5 mmol) of 3-ClC_5H_4N in 15 mL of diethyl ether was added dropwise. The reaction was exothermic, and the solution became progressively deeper red. The resulting solution turned yellow after stirring for 5 h. After the solution was allowed to stir overnight, ethanol was added and the mixture was stirred for 30 min and then pumped to dryness. Hexanes and then activated charcoal were added, and the mixture was stirred for 60 min and then filtered through Celite. Vacuum removal of hexanes yielded a flaky white solid. Yield: 3.08 g (55%). MS, selected m/e (relative intensity): 263 (M, 100%), 264 (19), 262 (18), 186 (14), 185 (27), 184 (14), 183 (24), 109 (11), 108 (22), 107 (14). ^{31}P NMR (THF): δ −12.5. ^1H NMR (C_6D_6): δ 8.8 (m, 1 H, 6-$C_5H_4NPPh_2$), 8.4 (m, 1 H, 2-$C_5H_4NPPh_2$), 7.3 (m, 1 H, 5-$C_5H_4NPPh_2$), 6.6 (m, 1 H, 4-$C_5H_4NPPh_2$), 7.3–7.0 (m, 10 H, $P(C_6H_5)_2$).

Preparation of $Mo(N_2)_2(PMePh_2)_4$. Tetrahydrofuran (600 mL) in a 2-L flask under N_2 was cooled with an ice bath. $PMePh_2$ (6.48 g, 32.3 mmol) and then $MoCl_5$ (2.28 g, 8.3 mmol) were added with stirring. Magnesium (activated with I_2 vapor) (3.0 g, 123 mmol) was added with very vigorous stirring. The solution changes from the initial brown color to red rapidly and to green after 25 min, then to yellow after 55 min, and finally to golden brown after 90 min. The ice bath was removed and the solution stirred for a further 45 min. The solution was separated from

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the remaining magnesium turnings by canulation and then stripped to dryness under vacuum. The solid was taken into solution in ca. 500 mL of benzene and filtered through Celite. The filtered solution was reduced in volume under vacuum to 10 mL. The resulting slurry was filtered through a medium sintered glass frit and the filtered solid was washed with 200 mL of methanol. The resulting bright orange solid was dried under vacuum for 30 min. Yield: 6.3 g (82%). The filtrate contains impure $Mo(\eta^6\text{-}PhPMePh)(PMePh_2)_3$.[12] Complex **1** can be recrystallized by adding methanol to a filtered, concentrated benzene solution (75%). The crystals occlude various amounts of solvating benzene, which can be removed by prolonged evacuation. The X-ray structure sample contained 1.5 C_6H_6 per Mo.[20] Anal. Calcd for $C_{52}H_{52}MoN_4P_4$: C, 65.55; H, 5.50; N, 5.88. Found: C, 65.0; H, 5.5; N, 5.2. ^{31}P NMR (THF): δ 18.6 (s). ^1H NMR (C_6D_6): δ 7.6–6.8 (m, 40 H, $P(C_6H_5)_2$) 1.85 (br s, 12 H, PCH_3).

Preparation of *trans,mer*-$Mo(N_2)_2(L)(PMePh_2)_3$ (2a–f), L = N-Donor. The complexes were prepared as intensely colored solids contaminated with 5–15% of starting complex **1** by stirring a suspension of **1** with a 5-fold excess of the ligand, L, in pentane under dinitrogen at 22 °C for 5 h, filtering the product, and then equilibrating it again and again with excess ligand in pentane until acceptable purity was attained. Attempted recrystallization of the complexes in the presence of excess ligand resulted in increased contamination of the product by compound **1**. **2a**: L = *N*-methylimidazole, 50% yield, red solid; see Table II for $\nu(N_2)$ for sample in THF. **2b**: 4-picoline, 30%, purple; see Table II. **2c**: 3-picoline, 25%, purple; see Table II. **2d**: pyridine, 50%, purple, $\nu(N_2)$ = 1914 cm^{-1}. **2e**: 4-*tert*-butylpyridine, 5%, purple, $\nu(N_2)$ = 1914 cm^{-1}. **2f**: 3-(diphenylphosphino)pyridine, 28%, black-green; see Table II. **2g**: 3-chloropyridine, 20%, green, $\nu(N_2)$ = 1915 cm^{-1}. **2h**: 3-fluoropyridine, observed in solution, blue-green; see Table II.

Preparation of $Mo(N_2)_2(PMePh_2)_2(PPh_2CH_2CH_2SMe)$ (3). $Mo(N_2)_2(PMePh_2)_4$ (0.50 g, 0.52 mmol) was suspended in a mixture of diethyl ether/benzene (50 mL/10 mL) under nitrogen. Solid $PPh_2CH_2CH_2SMe$[40] (0.165 g, 0.63 mmol) was added and stirred for 2 h to give a dark red-brown solution. This was filtered and concentrated to 10 mL, and 5 mL of diethyl ether was added. When the mixture was cooled to 5 °C, red-purple crystals formed. These were collected, washed with diethyl ether, and dried in vacuo (0.17 g, 40%). The single-crystal X-ray structure and spectra of **3** have been reported.[3]

Preparation of *trans,mer*-$Mo(N_2)_2(P(OMe)_3)(PMePh_2)_3$ (4a). $Mo(N_2)_2(PMePh_2)_4$ (1.0 g, 1.0 mmol) and $P(OMe)_3$ (0.130 g, 1.0 mmol) were suspended in 30 mL of benzene. The orange slurry was stirred for 2.5 h. The resulting yellow solution was reduced under vacuum to 10 mL and cooled. The bright yellow precipitate was filtered off. Yield: 0.205 g (22.3%); however yields were very variable (0–30%). This complex appears to be >95% pure according to NMR and cyclic voltammetry measurements apart from contamination by free $PMePh_2$ and traces of complexes containing more than one phosphite ligand, which are very difficult to remove. Correct elemental analyses have not yet been obtained. ^1H NMR (C_6D_6): δ 6.85–7.55 (m, 30 H, $PCH_3(C_6H_5)_2$), 2.97 (d, $^3J_{HP}$ = 10.0 Hz, 9 H, $P(OCH_3)_3$), 2.02 (m, 6 H, $PCH_3(C_6H_5)_2$), 1.66 (d, $^2J_{HP}$ = 4.2 Hz, 3 H, $PCH_3(C_6H_5)_2$).

Observation of *trans,mer*-$Mo(N_2)_2(PMe_3)(PMePh_2)_3$ (4b). Trimethylphosphine (0.039 g, 0.51 mmol) in 1.0 mL of THF was added to a solution of *trans*-$Mo(N_2)_2(PMePh_2)_4$ (0.567 g, 0.59 mmol) in 20 mL of THF to give an orange-yellow solution. ^1H NMR (C_6D_6): δ 6.87–7.54 (multiplets, 30 H, $PCH_3(C_6H_5)_2$), 1.67 (d, $^2J_{HP}$ = 4.0 Hz, 3 H, $PCH_3(C_6H_5)_2$), 1.39 (d, $^2J_{HP}$ = 6.6, 6 H, $PCH_3(C_6H_5)_2$), 1.36 (d, $^2J_{HP}$ = 4.0 Hz, 9 H, $P(CH_3)_3$).

Reactions of the Complexes with Sulfuric Acid. Complexes **2a** and **4a** were suspended in methanol and treated with concentrated sulfuric acid according to the method of Richards et al.[18] The amount of gas evolved was collected and measured by use of a Toepler pump. The ratio of N_2 to H_2 was determined by using gas chromatography. A 6-ft by $^1/_8$-in. column packed with 5A molecular sieves was used in a Varian 920A instrument. The injection temperature was 50 °C; the detector was at 80 °C, and the column was at 40 °C. The carrier gas was argon flowing at 20 mL/min. The response of the thermal conductivity detector to N_2 and H_2 was calibrated by using mixtures of the two gases. Yields of ammonia and hydrazine were determined by using the indophenol and *p*-(dimethylamino)benzaldehyde reagents, respectively.[41,42]

Calculation of the Rate of Exchange of 1 with $^{15}N_2$. Integrated peak intensities for the $(^{14}N_2)_2$, $(^{15}N_2)_2$, and $(^{14}N_2)(^{15}N_2)$ isotopomers were obtained from spectra of **1** in THF exchanged with $^{15}N_2$ (~1 atm) for 3.0 h at 22 °C. These were converted into relative concentrations by use of relative intensities calculated[43] for the various stretching modes of the isotopomers. The reaction can be described as two consecutive first-order reactions since $^{15}N_2$ is in great excess:

$$Mo(^{14}N_2)_2 \xrightarrow{k_1} Mo(^{14}N_2)(^{15}N_2) \xrightarrow{k_1/2} Mo(^{15}N_2)_2$$

The value $k_1 = 2 \pm 1 \times 10^{-4}$ s^{-1} at 22 °C gave the best match of observed and calculated[44] relative concentrations. The value is approximate because of extensive overlap of the broad IR peaks.

Calculation of Force Constants. Assuming that no other modes interact with the dinitrogen modes in the range 2100–1800 cm^{-1},[28] then equations can be derived by using the **F**, **G** matrix method and the equation $\mathbf{F \cdot G - E\lambda = 0}$. The diagonalized **F** matrix for the *trans*-bis(dinitrogen) complexes has the diagonal elements $(k_{NN} + k_{NN\text{-}NN})$ and $(k_{NN} - k_{NN\text{-}NN})$. The diagonalized **G** matrix has the elements $2\mu_1$ and $2\mu_2$ where for the $(^{14}N_2)_2$ complexes $\mu_1 = \mu_2 = {}^1/_{14}$, for the $(^{15}N_2)_2$ complexes $\mu_1 = \mu_2 = {}^1/_{15}$, and for the $(^{14}N_2)(^{15}N_2)$ complexes $\mu_1 = {}^1/_{14}$ and $\mu_2 = {}^1/_{15}$. The following equations can then be derived with ν values in cm^{-1} and k values in mdyn/Å.

For the $(^{14}N_2)_2$ and $(^{15}N_2)_2$ complexes of local D_{4h} symmetry

$$k_{NN} = (1.47225 \times 10^{-7})(\nu(A_{1g})^2 + \nu(A_{2u})^2)/\mu_1$$

$$k_{NN\text{-}NN} = (1.47225 \times 10^{-7})(\nu(A_{1g})^2 - \nu(A_{2u})^2)/\mu_1$$

For the $(^{14}N_2)_2$ and $(^{15}N_2)_2$ complexes of local C_{2v} symmetry

$$k_{NN} = (1.47225 \times 10^{-7})(\nu(A_1)^2 + \nu(B_1)^2)/\mu_1$$

$$k_{NN\text{-}NN} = (1.47225 \times 10^{-7})(\nu(A_1)^2 - \nu(B_1)^2)/\mu_1$$

For the $(^{14}N_2)(^{15}N_2)$ complexes

$$\nu = ((8.4904 \times 10^5)(2\mu_1 k_{NN} + 2\mu_2 k_{NN} + D))^{0.5}$$

$$\nu' = ((8.4904 \times 10^5)(2\mu_1 k_{NN} + 2\mu_2 k_{NN} - D))^{0.5}$$

where $D = ((2\mu_1 k_{NN} + 2\mu_2 k_{NN})^2 - 16\mu_1\mu_2(k_{NN}^2 - k_{NN\text{-}NN}^2))^{0.5}$ and ν is the high-energy mode and ν' is the low-energy mode. Values of k_{NN} and $k_{NN\text{-}NN}$ that give the best fit to the observed ν values can be obtained iteratively.

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Registry No. **1**, 33248-03-2; **1**$(^{14}N_2)(^{15}N_2)$, 104115-09-5; **1**$(^{15}N_2)_2$, 104115-10-8; **2a**, 104114-93-4; **2a**$(^{14}N_2)(^{15}N_2)$, 104115-00-6; **2a**$(^{15}N_2)_2$, 104115-01-7; **2b**, 87890-80-0; **2b**$(^{14}N_2)(^{15}N_2)$, 104115-02-8; **2b**$(^{15}N_2)_2$, 104115-03-9; **2c**, 104114-94-5; **2c**$(^{14}N_2)(^{15}N_2)$, 104115-04-0; **2c**$(^{15}N_2)_2$, 104115-05-1; **2d**, 87890-79-7; **2e**, 104114-95-6; **2f**, 104114-96-7; **2f**$(^{15}N_2)_2$, 104115-06-2; **2g**, 104114-97-8; **2h**, 104114-98-9; **2h**$(^{14}N_2)(^{15}N_2)$, 104115-07-3; **2h**$(^{15}N_2)_2$, 104115-08-4; **3**, 89958-79-2; **4a**, 104130-04-3; **4a**$(^{14}N_2)(^{15}N_2)$, 104115-11-9; **4a**$(^{15}N_2)_2$, 104115-12-0; **4b**, 104130-05-4; **5**, 98703-49-2; **11**, 32457-67-3; **11**$(^{14}N_2)(^{15}N_2)$, 104115-13-1; **11**$(^{15}N_2)_2$, 104115-14-2; $3\text{-}PPh_2C_5H_4N$, 104114-99-0; ^{15}N, 14390-96-6; NH_3, 7664-41-7; N_2, 7727-37-9; $HPPh_2$, 829-85-6; $3\text{-}ClC_5H_4N$, 626-60-8; Mo_2Cl_{10}, 26814-39-1.

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