adenosine moiety compared with that of the adenosine residue is expected to be overruled to some extent by the even greater affinities of the di- and triphosphate groups.

Predictions for mixed ligand complexes (section 5) are more difficult, as certain groups may be released from the coordination sphere of a metal ion due to the participation of an additional ligand. This could often mean that ternary complexes with ε-adenine nucleotides are of relatively low stability compared with their binary parent complexes (eq 7 and 8). However, in cases where an intramolecular ligand–ligand interaction is possible[32–34,82] between aromatic-ring systems, or a hydrophobic interaction with an alkyl residue, the ε-adenine moiety is expected to be about as effective as the adenine group itself.

Overall one may conclude that in systems which involve metal ions and ε-adenine nucleotides, the structural arrangements will often be altered, mainly due to the increased metal ion affinity of the modified base residue, so that conclusions reached with ε-adenosine derivatives should be transferred to the unaltered nucleotide system with reservations.

Acknowledgment. We thank K. Aegerter of the Institute for Organic Chemistry for recording the 90-MHz NMR spectra and R. Baumbusch for the skillful performance of the potentiometric pH titrations, which were evaluated on a computer Univac 1100/81 made available by the Rechenzentrum der Universität Basel. This support, a research grant from the Swiss National Science Foundation, and grants toward the costs of the ε-adenine derivatives from the CIBA-Stiftung Basel and the Stiftung der Portlandcementfabrik Laufen are also gratefully acknowledged.

Registry No. Mg, 7439-95-4; Mn, 7439-96-5; Co, 7440-48-4; Ni, 7440-02-0; Cu, 7440-50-8; Zn, 7440-66-6; Cd, 7440-43-9; 1,N^6-ethenoadenosine, 39007-51-7; ε-adenosine L-tryptophan adduct, 85048-85-7.

Preparation and Properties of Dinitrogen Trimethylphosphine Complexes of Molybdenum and Tungsten. 4. Synthesis, Chemical Properties, and X-ray Structure of *cis*-$[Mo(N_2)_2(PMe_3)_4]$. The Crystal and Molecular Structures of *trans*-$[Mo(C_2H_4)_2(PMe_3)_4]$ and *trans,mer*-$[Mo(C_2H_4)_2(CO)(PMe_3)_3]$

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Contribution from the Departamento de Quimica Inorgânica, Facultad de Quimica, Universidad de Sevilla, Sevilla, Spain, the Department of Chemistry, University of Alabama, University, Alabama 35486, and the Department of Chemistry, Northern Illinois University, Dekalb, Illinois 60115. Received October 4, 1982

Abstract: The complex *cis*-$[Mo(N_2)_2(PMe_3)_4]$ (**1**) has been prepared by reduction of $[MoCl_2(PMe_3)_4]$ with dispersed sodium under dinitrogen. Loss of ligating dinitrogen in **1** readily occurs by oxidation with alkyl halides, RX (X = Cl, R = Me_3SiCH_2; X = Br, R = Et; X = I, R = Me), to yield the monomeric Mo(II) halo derivatives *trans*-$[MoX_2(PMe_3)_4]$ (X = Cl, Br, and I) or by substitution with (i) carbon monoxide to give $[Mo(CO)_x(PMe_3)_{6-x}]$ complexes (x = 2,3), (ii) trimethylphosphine under argon to afford $[Mo(N_2)(PMe_3)_5]$ (**2**), or (iii) ethylene to yield *trans*-$[Mo(C_2H_4)_2(PMe_3)_4]$ (**3**). One of the phosphine ligands in **3** can be easily exchanged by CO to form *trans,mer*-$[Mo(C_2H_4)_2(CO)(PMe_3)_3]$ (**4**). The structures of complexes **1**, **3**, and **4** have been determined by X-ray crystallography. **1** crystallizes in the monoclinic space group $P2_1/c$ with unit cell parameters a = 9.371 (4) Å, b = 15.890 (6) Å, c = 16.692 (7) Å, β = 106.58 (4)°, and D_c = 1.27 g cm^{-3} for Z = 4. Least-squares refinement based on 1720 independent observed reflections led to a final R value of 0.038. Complex **3** belongs to the monoclinic space group $P2_1/n$ with a = 10.165 (3) Å, b = 13.683 (3) Å, c = 17.139 (4) Å, β = 98.84 (3)°, and D_c = 1.29 g cm^{-3} for Z = 4. The final R value based on 2715 observed reflections was 0.043. **4** is also monoclinic, crystallizing in the space group $P2_1/n$ with a = 10.637 (3) Å, b = 13.069 (3) Å, c = 15.201 (4) Å, β = 98.45 (2)°, and D_c = 1.30 g cm^{-3} for Z = 4. It was refined to a final R value of 0.037 on the basis of 2764 independent observed reflections. In **1** the cis N ligands are coordinated to the molybdenum atom at a Mo–N bond distance of 1.97 (1) Å. In **3** and **4** the planes formed by the two carbons of each of the trans ethylene ligands and the Mo atom are perpendicular and eclipse the trans P–Mo–P bonds. The average Mo–C(ethylene) distance is 2.270 (5) Å in **3** and 2.29 (3) Å in **4**.

Molecular dinitrogen complexes of molybdenum have received considerable attention in the past few years in the hope of finding model systems for the binding of N_2 and subsequent transformation into ammonia and amines.[1,2] The complexes studied generally contain tertiary phosphine as coligands, particular attention having been devoted to *trans*-$[Mo(N_2)_2(dppe)_2]$ (dppe = 1,2-bis(diphenylphosphine)ethane). Although up to four groups of dinitrogen complexes of molybdenum can be envisaged,[3] for zerovalent molybdenum they are basically of two types,[4] $[M(N_2)_2P_4]$ and $[M(arene)P_2]_nN_2$ (n = 1, 2) (P = phosphorus donor, either mono- or bidentate phosphine). The range of complexes

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(1) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589–625.

(2) "New Trends in the Chemistry of Nitrogen Fixation"; Chatt, J., da Camara Pina, L. M., Richards, R. L., Eds.; Academic Press: New York, 1980.

(3) Stiefel, E. I. *Prog. Inorg. Chem.* **1977**, *22*, 1–223.

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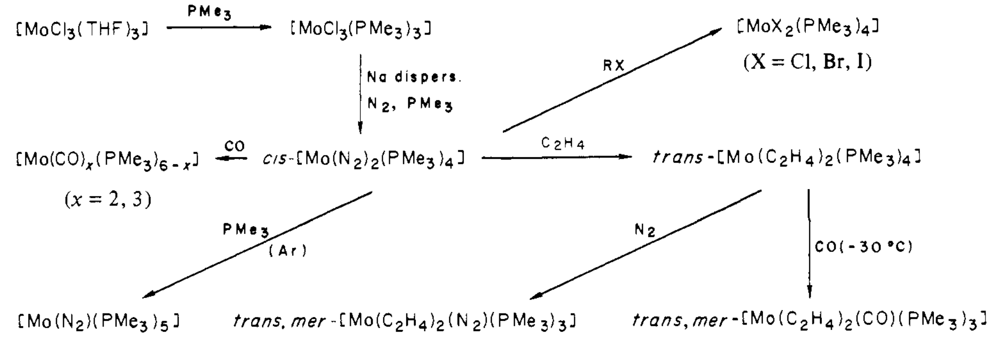
0002-7863/83/1505-3014$01.50/0

Scheme I



that can be prepared is however limited, and prior to our work,[5,6] there were no reports on bis(dinitrogen) complexes of molybdenum with monodentate trialkylphosphines as coligands. We have recently shown[5] that the reduction of $[MoCl_3(PMe_3)_3]$ with sodium amalgam yields a compound of composition $[MoCl(N_2)(PMe_3)_4]$, which behaves as a mixture of *trans*-$[Mo(N_2)_2(PMe_3)_4]$ and *trans*-$[MoCl_2(PMe_3)_4]$. In this paper we report the preparation of *cis*-$[Mo(N_2)_2(PMe_3)_4]$ (**1**) from the dispersed sodium reduction of $[MoCl_3(PMe_3)_3]$, under dinitrogen, and some of its chemical properties, particularly its smooth and essentially quantitative transformation into $[Mo(N_2)(PMe_3)_5]$ (**2**) and its reaction with ethylene under mild conditions to afford *trans*-$[Mo(C_2H_4)_2(PMe_3)_4]$ (**3**). This latter complex binds N_2 to give a species formulated as *trans,mer*-$[Mo(C_2H_4)_2(N_2)(PMe_3)_3]$ (which in turn can be converted into **3** by interaction with PMe_3) and reacts with CO to yield *trans,mer*-$[Mo(C_2H_4)_2CO(PMe_3)_3]$ (**4**). These and other reactions summarized in Scheme I are discussed together with the X-ray structures of complexes **1**, **3**, and **4**. Part of this work has been briefly communicated.[6] When this work was essentially finished, a preliminary communication dealing with **2** and **3** appeared.[7]

Results and Discussion

Synthesis of *cis*-$[Mo(N_2)_2(PMe_3)_4]$ (1). The new dinitrogen complex was first prepared, in ca. 30–40% yield by the two-step sequence of eq 1. The addition of a tetrahydrofuran solution of

$$[MoCl_3(THF)_3] \xrightarrow[THF]{PMe_3} [MoCl_3(PMe_3)_3] \xrightarrow[THF]{Na\ dispers,\ N_2} cis\text{-}[Mo(N_2)_2(PMe_3)_4] \quad (1)$$

freshly prepared $[MoCl_3(PMe_3)_3]$ to a vigorously stirred suspension of finely divided sodium metal in tetrahydrofuran produces a change in color from yellow to deep green. The green color persists for relatively long periods of time (30–45 min), then darkens, and finally turns dark yellow-brown. The formation of a green solution is also observed in the early stages of the preparations[5] of $[MCl(N_2)(PMe_3)_4]$ (M = Mo, W), but attempts to isolate this intermediate species have been unsuccessful. The choice of the precursor is of the greatest importance; as found in other related systems,[1,5] no dinitrogen species being formed from the reduction of either $[MoCl_3(THF)_3]$ or $[MoCl_3(PMe_3)_3]$ in the presence of an excess of phosphine or from $[MoCl_2(PMe_3)_4]$. The yield of reaction 1 can be substantially improved (50–60%) by addition of ca. 80% of the required amount of phosphine approximately 20 min after the appearance of the green color. On the other hand, the nature of the reducing agent used is also of importance not only in determining the composition of the reduced dinitrogen complex (as indicated earlier, the use of sodium amalgam produces[5] $[MoCl(N_2)(PMe_3)_4]$ and only small amounts of *cis*-$[Mo(N_2)(PMe_3)_4]$) but also in making workup and hence isolation of the final product easier. Thus, we have found that the time the green solution lasts, depends on the active surface of the sodium used (see Experimental Section). If the phosphine is added too soon, the yield of complex **1** diminishes drastically, *trans*-$[MoCl_2(PMe_3)_4]$ being formed in considerable amounts. All the above clearly shows that, as pointed out by Chatt,[1] the preparation of dinitrogen complexes of transition metals is still in an essentially empirical state.

Properties and X-ray Structure of *cis*-$[Mo(N_2)_2(PMe_3)_4]$ (1). The pure dinitrogen complex **1** is a yellow crystalline solid, which becomes opaque or crumbles into a yellow powder when dried in vacuo. This has made the preparation of crystals suitable for X-ray studies difficult. The complex is very soluble in most common organic solvents; crystallization from petroleum can only be achieved at −78 °C or at −20 °C with very concentrated solutions. It is very air sensitive, both in solution and in the solid state, decomposing immediately upon exposure to air. Complex **1** is only moderately thermally stable. Although it can be stored indefinitely at 0 °C, both as a solid or in petroleum ether solutions, it decomposes rapidly at 40–50 °C. Thermal decomposition is probably initiated by loss of one of the dinitrogen ligands to yield a 5-coordinate intermediate species $[Mo(N_2)(PMe_3)_4]$. This is in accord with the easy substitution of one of the dinitrogen molecules in **1** by PMe_3 to give $[Mo(N_2)(PMe_3)_5]$ (**2**) and by other neutral ligands (see below). It is also noteworthy in this respect, that while petroleum ether solution of **1** decompose rapidly upon heating at 40–50 °C, no decomposition is apparently observed at 50–60 °C, for several hours, under 50 psi of N_2. The dissociative activation of one of the Mo–N_2 ligands has been shown to be the rate-controlling step in a number of reactions of bis(dinitrogen) complexes of molybdenum.[2,8]

IR and NMR spectroscopic data for **1** are in accord with the proposed formulation as a cis bis(dinitrogen) complex. The IR spectrum shows two strong absorptions at 2010 and 1965 cm^{-1} (hexane), as expected for the two NN stretching modes (A_1,B_1) in the C_{2v} symmetry characteristic of the $Mo(N_2)_2P_4$ coordination sphere of this complex. The cis distribution of the dinitrogen ligands leaves the four remaining coordination sites of an octahedral configuration to the four trimethylphosphine ligands, and this situation is easily recognized both in the ^1H and in the $^{31}P\{^1H\}$ NMR spectrum. Thus, the proton NMR spectrum shows two sets of signals of equal intensity, each consisting of three lines with the central ones at δ 1.4 and 1.2, while the ^{31}P NMR spectrum shows two slightly distorted triplets that can be approximately interpreted in terms of an A_2X_2 system with δ_{P_A} −4.85, δ_{P_X} −6.90, and $^2J(P_AP_X)$ = 18 Hz. This compares well with data reported[9] for *cis*-$[Cr(N_2)_2(PMe_3)_4]$.

The molecular structure and atom labeling scheme for *cis*-$[Mo(N_2)_2(PMe_3)_4]$ (**1**) are presented in Figure 1. The relative thermal instability of complex **1** is apparently reflected in the high thermal motion of the atoms. The only resolvable disorder, however, involved the rotational disorder of the carbons bonded

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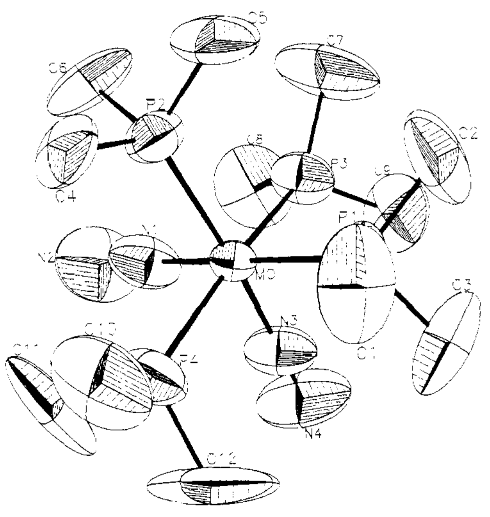

Figure 1. Molecular structure of *cis*-$[Mo(N_2)_2(PMe_3)_4]$ (**1**) with the atoms represented by their 50% probability ellipsoids for thermal motion. The disorder of atoms C(4)–C(6) is not shown.

to P(2) (see Experimental Section). As a result of the high thermal motion the standard deviations associated with most of the bond distances and angles are somewhat high as can be seen in Table I. Comparison with other structures should bear this in mind.

cis-$[Mo(N_2)_2(PMe_3)_4]$ (**1**) is essentially octahedral. The four phosphine ligands are coordinated to the molybdenum atom at an average Mo–P separation of 2.451 (8) Å. There is no significant difference between the Mo–P distances trans to the N_2 ligands and the remaining two Mo–P lengths. In $[Mo(N_2)(PMe_3)_5]$[6b] the Mo–P distance trans to the dinitrogen ligand is longer at 2.483 (7) Å than the average of the three different Mo–P lengths (2.460 (5) Å). The 2.451 (8) Å value in **1** is comparable to the Mo–P length of 2.461 (1) Å in *trans*-$[MoCl(N_2)(PMe_3)_4]$[5] but considerably shorter than in *trans*-$[MoCl_2(PMe_3)_4]$[5] (2.496 (3) Å). Although Mo–P bond lengths have been found to cluster around ca. 2.47 Å, the range is wide (2.3–2.6 Å) and thus the Mo–P lengths in **1** should be considered normal.

The two Mo–N distances are equal at 1.97 (1) Å. These values are considerably shorter than the corresponding Mo–N distances of 2.014 Å in *trans*-$[Mo(N_2)_2(dppe)_2]$[10] and 2.07 (1) Å in *trans*-$[Mo(CO)(N_2)(dppe)_2]\cdot 0.5C_6H_6$.[11] An expected increase is observed in the corresponding N–N distances, 1.14 (1) Å average in **1** vs. 1.118 and 1.087 Å for the N–N distances in *trans*-$[Mo(N_2)(dppe)_2]$ and *trans*-$[Mo(CO)(N_2)(dppe)_2]\cdot 0.5C_6H_6$, respectively.

Reactions of *cis*-$[Mo(N_2)_2(PMe_3)_4]$ (1) with Alkyl Halides, CO, and PMe_3. The preparation of complex (**1**) provided an opportunity to study its chemical behavior and to compare it with that of other known dinitrogen complexes of group 6 metals. In this paper, we shall mainly concentrate on the substitution reactions of bound dinitrogen by some neutral ligands which are isoelectronic or similar to dinitrogen, although some oxidation reactions by alkyl halides will also be discussed (Scheme I). Other characteristic reactions will be reported in subsequent publications.

The interaction of alkyl halides and other similar molecules with *trans*-$[M(N_2)_2(dppe)_2]$ (M = Mo, W) complexes has received considerable attention, and both the nature of the products and the reaction mechanism are now well established.[1,12] In contrast, the similar reactions of complexes $[M(N_2)_2(PR_3)_4]$ (PR_3 = monotertiary phosphine) are less well studied and lead to general decomposition and loss of all dinitrogen as N_2.[12] These reactions have been reported to yield only uncharacterizable products.[13]

Table I. Bond Distances (Å) and Angles (deg) for *cis*-$[Mo(N_2)_2(PMe_3)_4]$ (1)

	Distances		
Mo–P(1)	2.441 (3)	Mo–P(2)	2.459 (3)
Mo–P(3)	2.449 (3)	Mo–P(4)	2.456 (3)
Mo–N(1)	1.97 (1)	Mo–N(3)	1.97 (1)
P(1)–C(1)	1.84 (1)	P(1)–C(2)	1.85 (2)
P(1)–C(3)	1.87 (2)	P(2)–C(4)	1.87 (2)
P(2)–C(5)	1.83 (3)	P(2)–C(6)	1.81 (2)
P(2)–C(4)	1.87 (2)	P(2)–C(5)	1.81 (3)
P(2)–C(6)	1.80 (3)	P(3)–C(7)	1.85 (1)
P(3)–C(8)	1.89 (2)	P(3)–C(9)	1.84 (2)
P(4)–C(10)	1.84 (3)	P(4)–C(11)	1.85 (2)
P(4)–C(12)	1.81 (2)	N(1)–N(2)	1.15 (1)
N(3)–N(4)	1.14 (1)		
	Angles		
P(1)–Mo–P(2)	93.9 (1)	P(1)–Mo–P(3)	92.9 (1)
P(2)–Mo–P(3)	95.3 (1)	P(1)–Mo–P(4)	93.0 (1)
P(2)–Mo–P(4)	94.4 (1)	P(3)–Mo–P(4)	168.3 (1)
P(1)–Mo–N(1)	178.4 (4)	P(2)–Mo–N(1)	87.2 (4)
P(3)–Mo–N(1)	85.8 (4)	P(4)–Mo–N(1)	88.2 (3)
P(1)–Mo–N(3)	91.9 (3)	P(2)–Mo–N(3)	174.2 (3)
P(3)–Mo–N(3)	84.6 (3)	P(4)–Mo–N(3)	85.1 (3)
N(1)–Mo–N(3)	87.0 (5)	Mo–P(1)–C(1)	121.7 (5)
Mo–P(1)–C(2)	121.9 (6)	C(1)–P(1)–C(2)	99.0 (8)
Mo–P(1)–C(3)	113.9 (6)	C(1)–P(1)–C(3)	98.4 (8)
C(2)–P(1)–C(3)	98.8 (9)	Mo–P(2)–C(4)	120.1 (8)
Mo–P(2)–C(5)	121.4 (9)	C(4)–P(2)–C(5)	94 (1)
Mo–P(2)–C(6)	115.4 (9)	C(4)–P(2)–C(6)	101 (1)
C(5)–P(2)–C(6)	101 (1)	Mo–P(2)–C(4)	119 (1)
Mo–P(2)–C(5)	122 (1)	C(4)–P(2)–C(5)	89 (2)
Mo–P(2)–C(6)	114 (1)	C(4)–P(2)–C(6)	97 (2)
C(5)–P(2)–C(6)	110 (2)	Mo–P(3)–C(7)	125.8 (6)
Mo–P(3)–C(8)	112.7 (6)	C(7)–P(3)–C(8)	102.6 (9)
Mo–P(3)–C(9)	116.5 (5)	C(7)–P(3)–C(9)	98.3 (9)
C(8)–P(3)–C(9)	96.2 (9)	Mo–P(4)–C(10)	127.6 (6)
Mo–P(4)–C(11)	113.4 (6)	C(10)–P(4)–C(11)	97.6 (9)
Mo–P(4)–C(12)	115.7 (6)	C(10)–P(4)–C(12)	96 (1)
C(11)–P(4)–C(12)	102 (1)	Mo–N(1)–N(2)	179 (1)
Mo–N(3)–N(4)	177 (1)		

Complex **1** reacts with RX (X = Br, R = Et; X = I, R = Me) at room temperature, during 15–30 min. to give the complexes *trans*-$[MoX_2(PMe_3)_4]$ (X = Br, I) in high yields.[14] A similar reaction takes place with I_2. While alkyl chlorides do not react with $[M(N_2)_2(dppe)_2]$ (M = Mo, W) complexes at room temperature[10] (the reactions requiring thermal stimulation) complex **1** interacts with Me_3SiCH_2Cl, at 20 °C, over a period of ca. 2 h to yield *trans*-$[MoCl_2(PMe_3)_4]$[5] also in high yields. The reactions with Me_3SiCl and *n*-BuCl are more complex. The former gives, besides *trans*-$[MoCl_2(PMe_3)_4]$, a mixture of still unidentified products, with IR bands in the region characteristic for alkyldiazenido species,[15] while the latter yields an unstable violet solid with a strong IR absorption at 1920 cm^{-1}, which readily transforms into *trans*-$[MoCl_2(PMe_3)_4]$.

Interaction of petroleum ether solutions of **1** with CO, between 0 and −10 °C, results in the substitution of the two dinitrogen ligands with formation of *cis*-$[Mo(CO)_2(PMe_3)_4]$.[16] Since no change in stereochemistry is observed, it is clear that in these $[MoL_2(PMe_3)_4]$ (L = N_2, CO) complexes N_2 and CO have the same stereochemical preferences.[17] It is worth noting that the fractional lowerings of N_2 and CO frequencies in *cis*-$[MoL_2(PMe_3)_4]$ are nearly identical (14.6%, L = N_2; 14.0%, L = CO), in accord with the general observation that N_2 is weaker in both its σ-donor and π-acceptor capabilities.[18] If the reaction between

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[17] This constitutes a further example of the tendency shown by π-acceptor ligands to avoid sharing the same central atom orbital. See, for instance: Burdett, J. K.; Albright, T. A. *Inorg. Chem.* **1979**, *18*, 2112–2120.

1 and carbon monoxide is carried out at room temperature, partial substitution of the phosphine ligands also takes place, and a mixture of carbonyl complexes[16] $[Mo(CO)_x(PMe_3)_{6-x}]$ (x = 2, 3) is obtained. A similar behavior has been observed for *cis*-$[Cr(N_2)_2(PMe_3)_4]$[9] and for other related complexes.[1]

When complex **1** is dissolved in petroleum ether, under helium or argon, in the presence of an excess of PMe_3, $[Mo(N_2)(PMe_3)_5]$ (**2**) is formed according to eq 2. The reaction can be monitored

$$cis\text{-}[Mo(N_2)_2(PMe_3)_4] + PMe_3 \xrightarrow{Ar} [Mo(N_2)(PMe_3)_5] + N_2 \tag{2}$$

by IR spectroscopy, following the disappearance of the two characteristic solution bands of **1** at 2010 and 1965 cm^{-1} and the formation of a new, strong absorption at 1950 cm^{-1}, characteristic of the mono(dinitrogen) species. From the resulting solution, **2** can be collected in very high yields. As with the parent bis(dinitrogen) complex, **2** is a yellow crystalline solid which becomes opaque upon drying in vacuo. It is also very air sensitive both in solution and in the solid state, decomposing immediately upon exposure to air. Although very soluble in most common organic solvents, its solubility in petroleum ether is significantly lower than that of **1** making its isolation and purification easier. Complex **2** has been independently reported[7] and together with the tungsten analogue, $[W(N_2)(PMe_3)_5]$[6b] constitutes the first example of dinitrogen complexes of group 6 metals having a single dinitrogen molecule and five tertiary phosphine ligands coordinated to the central atom.

Compound **2** can be converted into the cis parent complex by reaction with dinitrogen at room temperature. Although the conversion is very slow if **2** is stirred under a dinitrogen atmosphere, it can be accelerated if the displaced PMe_3 ligand is removed from the equilibrium by bubbling nitrogen through the solution. It is worht pointing out that the trans derivative, *trans*-$[Mo(N_2)_2(PMe_3)_4]$, cannot be detected during this process. This and other observations[5] seem to indicate that the cis bis(dinitrogen) complex is the thermodynamically more stable form.

^1H and ^{31}P NMR data for **2** are in agreement with the proposed formulation. The ^1H NMR spectrum shows a somewhat broad singlet, centered at δ = 1.5, with some fine structure on both sides resembling an unresolved triplet, and a doublet at δ 1.3 ($^2J(HP)$ = 4 Hz), with intensity ratio ca. 4:1, which correspond respectively to the four equatorial and the axial phosphine ligands. The ^{31}P NMR spectrum is characteristic of an AX_4 spin system with δ_{P_A} 1.46 δ_{P_X} 5.33, and $^2J(P_AP_X)$ = 18.8 Hz. X-ray studies[6b] show **2** to be essentially octahedral, with Mo–N = 2.02 (3) Å and N–N = 1.12 (3) Å. The Mo–P distance trans to the dinitrogen ligand is longer at 2.483 (7) Å than the other four Mo–P bond lengths (2.460 (5) Å).

Reaction of *cis*-$[Mo(N_2)_2(PMe_3)_4]$ (1) with Ethylene. X-ray Structures of *trans*-$[Mo(C_2H_4)_2(PMe_3)_4]$ (3) and *trans,mer*-$[Mo(C_2H_4)_2(CO)(PMe_3)_3]$ (5). When ethylene is bubbled at room temperature and pressure through a petroleum solution of **1**, *trans*-$[Mo(C_2H_4)_2(PMe_3)_4]$ (**3**) is formed in good yields (eq 3).

$$cis\text{-}[Mo(N_2)_2(PMe_3)_4] + 2C_2H_4 \rightarrow trans\text{-}[Mo(C_2H_4)_2(PMe_3)_4] + 2N_2 \tag{3}$$

Complex **3** is also formed, albeit in lower yields, by reduction of $[MoCl_3(PMe_3)_3]$ with dispersed sodium in ethylene-saturated THF. A trans configuration is proposed since the PMe_3 ligands give rise to a single broad resonance, both in the ^1H (δ 1.0) and in the ^{31}P (2.62 ppm) NMR spectra (see below). The ethylene protons appear as a broad unresolved signal centered at δ 1.4.

Table II. Bond Distances (Å) and Angles (deg) for *trans*-$[Mo(C_2H_4)_2(PMe_3)_4]$ (3)

	Distances		
Mo–P(1)	2.485 (2)	Mo–P(2)	2.488 (2)
Mo–P(3)	2.506 (2)	Mo–P(4)	2.487 (2)
Mo–C(1)	2.276 (6)	Mo–C(2)	2.269 (6)
Mo–C(3)	2.265 (7)	Mo–C(4)	2.271 (6)
P(1)–C(5)	1.849 (8)	P(1)–C(6)	1.852 (8)
P(1)–C(7)	1.849 (8)	P(2)–C(8)	1.856 (9)
P(2)–C(9)	1.853 (8)	P(2)–C(10)	1.844 (8)
P(3)–C(11)	1.831 (9)	P(3)–C(12)	1.828 (9)
P(3)–C(13)	1.843 (8)	P(4)–C(14)	1.843 (9)
P(4)–C(15)	1.850 (9)	P(4)–C(16)	1.833 (8)
C(1)–C(2)	1.841 (7)	C(3)–C(4)	1.41 (1)
	1.39 (1)		
	Angles		
P(1)–Mo–P(2)	90.97 (7)	P(1)–Mo–P(3)	164.43 (6)
P(2)–Mo–P(3)	91.73 (7)	P(1)–Mo–P(4)	90.47 (7)
P(2)–Mo–P(4)	164.31 (7)	P(3)–Mo–P(4)	91.06 (7)
P(1)–Mo–C(1)	79.8 (2)	P(2)–Mo–C(1)	80.3 (2)
P(3)–Mo–C(1)	85.6 (2)	P(4)–Mo–C(1)	115.3 (2)
P(1)–Mo–C(2)	85.8 (2)	P(2)–Mo–C(2)	115.5 (2)
P(3)–Mo–C(2)	79.2 (2)	P(4)–Mo–C(2)	80.2 (2)
C(1)–Mo–C(2)	35.7 (3)	P(1)–Mo–C(3)	115.5 (2)
P(2)–Mo–C(3)	79.7 (2)	P(3)–Mo–C(3)	80.1 (2)
P(4)–Mo–C(3)	85.6 (2)	C(1)–Mo–C(3)	154.9 (3)
C(2)–Mo–C(3)	154.6 (3)	P(1)–Mo–C(4)	79.7 (2)
P(2)–Mo–C(4)	85.9 (2)	P(3)–Mo–C(4)	115.8 (2)
P(4)–Mo–C(4)	79.0 (2)	C(1)–Mo–C(4)	155.0 (3)
C(2)–Mo–C(4)	154.4 (3)	C(3)–Mo–C(4)	36.3 (3)
Mo–P(1)–C(5)	122.7 (3)	Mo–P(1)–C(6)	120.1 (3)
C(5)–P(1)–C(6)	96.5 (4)	Mo–P(1)–C(7)	117.9 (3)
C(5)–P(1)–C(7)	99.1 (4)	C(6)–P(1)–C(7)	94.7 (4)
Mo–P(2)–C(8)	120.8 (3)	Mo–P(2)–C(9)	121.8 (3)
C(8)–P(2)–C(9)	96.0 (5)	Mo–P(2)–C(10)	118.0 (3)
C(8)–P(2)–C(10)	95.5 (5)	C(9)–P(2)–C(10)	99.4 (4)
Mo–P(3)–C(11)	120.3 (3)	Mo–P(3)–C(12)	118.4 (3)
C(11)–P(3)–C(12)	96.1 (4)	Mo–P(3)–C(13)	121.6 (3)
C(11)–P(3)–C(13)	95.9 (4)	C(12)–P(3)–C(13)	99.2 (5)
Mo–P(4)–C(14)	117.9 (3)	Mo–P(4)–C(15)	121.4 (3)
C(14)–P(4)–C(15)	99.5 (4)	Mo–P(4)–C(16)	120.6 (3)
C(14)–P(4)–C(16)	96.0 (4)	C(15)–P(4)–C(16)	96.0 (4)
Mo–C(1)–C(2)	71.9 (4)	Mo–C(2)–C(1)	72.4 (4)
Mo–C(3)–C(4)	72.0 (4)	Mo–C(4)–C(3)	71.6 (4)

The bonding, rotational barriers and conformational preferences in transition-metal ethylene complexes have been the subject of a number of theoretical studies.[17,19,20] Particularly, Veillard[20] has discussed the relative energies of the different conformations for the model complex *trans*-$[Mo(C_2H_4)_2(PH_3)_4]$ on the basis of ab initio LCAO–MO–SCF calculations. Of the four conformations considered, the staggered-eclipsed (the first term applies to the relative orientation of the olefinic ligands while the second defines the position of the axial olefinic molecules relative to the *trans* P–Mo–P vectors[20]) was found to be the most stable on the basis of the metal ligand electronic interactions and of steric effects. Veillard's calculations and a consideration of Tolman's electronic (ν) and steric (θ) parameters[21] for PH_3 and PMe_3 (2081, 2064 cm^{-1} and 87 and 118°, respectively) suggest that the staggered-eclipsed geometry, also proposed by Osborn[22] for *trans*-$[Mo(C_2H_4)_2(dppe)_2]$ on the basis of ^1H and ^{31}P NMR studies, should also be the most stable conformation for *trans*-$[Mo(C_2H_4)_2(PMe_3)_4]$, and this has been confirmed by X-ray crystallographic studies. The ORTEP perspective (Figure 2) shows that the complex is essentially octahedral with the ethylene and phosphine ligands in the expected orientations. Both ethylene molecules are symmetrically bound to the molybdenum atom, the mean distance for the C=C bonds being 1.40 (1) Å (0.06 Å longer than in free ethylene). The four phosphorus atoms lie almost in the same plane and are on the average 2.49 (1) Å from Mo (Table II). This distance is longer than the longest Mo–P bond length in $[Mo(N_2)(PMe_3)_5]$ (2.483(7) Å[6b]) and considerably longer than the average Mo–P bond lengths of 2.451 (8) Å in *cis*-$[Mo(N_2)_2(PMe_3)_4]$ (**1**) and the 2.467 (2) Å found for the recently described $[Mo(PMe_3)_6]$. This is probably due to steric interactions caused

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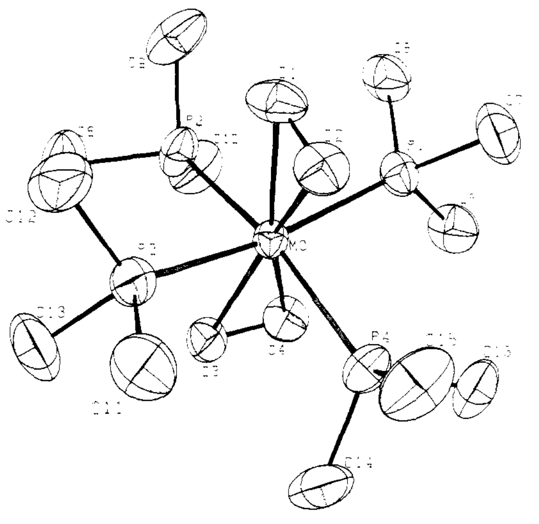

Figure 2. Molecular structure of *trans*-[Mo(C_2H_4)$_2$(PMe_3)$_4$] (**3**).

by the phosphine and ethylene ligands. The long Mo–P distances suggest the phosphine ligands are labile and indeed complex **3** dissociates phosphine in solution, at room temperature, as inferred from the following observations: (i) the appearance of the phosphine methyl proton resonance as a broad singlet and that of the ethylene protons also as a broad unresolved band; (ii) the ^{31}P NMR spectrum shows in addition to the broad singlet at δ 2.62, a small broad band at δ −62.3 due to free PMe_3; exchange between free and coordinated phosphine is slow on the NMR time scale; (iii) molecular weight determinations for complex **3**, cryoscopically in benzene, both under nitrogen and under helium give average values of 265 and 370, respectively (expected, 456). The very low values found when the determinations are carried out under dinitrogen and the fact that hydrocarbon solutions of **3**, prepared under N_2, always show a medium-intensity IR absorption at 2070 cm^{-1} that disappears upon addition of PMe_3 suggest that one of the phosphine molecules in **3** is easily exchanged by N_2 to yield [Mo(C_2H_4)$_2$$N_2$($PMe_3$)$_3$] (A) according to the equilibrium shown in eq 4. Although we have not been able to isolate complex A as a crystalline material, solutions of this compound can be prepared by bubbling N_2 through petroleum solutions of **3** for several hours. Reduction in volume in vacuo leads to the precipitation of a bright yellow crystalline solid, B, which redissolves on admission of N_2. This sequence can be repeated several times, although partial decomposition takes place and the solution darkens considerably. The same solid can be obtained by removing the solvent with a stream of N_2 until saturation is achieved, and cooling at 0 °C. B is an exceedingly air-sensitive material that dissolves slowly in petroleum or diethyl ether, under N_2, to yield A, while under He or Ar extensive decomposition takes place. Interaction with neat PMe_3 occurs instantly with gas evolution and formation of **3**. The IR spectrum of B (Nujol) shows in addition to absorptions due to the ethylene and phosphine ligands, a medium-intensity band at 2070 cm^{-1} and a very weak one at 1975 cm^{-1}. This latter absorption is clearly observed in the solid Raman spectrum, but it is not present in the solution IR spectrum. The ^1H NMR spectrum (35 °C) of benzene solutions of B under N_2 is very similar to that of **3**, consisting of a very broad singlet at δ 0.9, due to the phosphine protons, and a broad band centered at δ 1.5 (a small peak is superimposed at δ 1.4). At 20 °C (200 MHz) the PMe_3 ligands give rise to a slightly broad singlet at δ 0.90 and a well-defined doublet at δ 0.72 ($^2J(PH)$ = 5 Hz). Thus phosphine exchange seems to be faster for the two mutually trans PMe_3 molecules. The $^{31}P\{^1H\}$ NMR spectrum shows a small resonance at δ −62.3 due to free PMe_3, a triplet at δ 6.0, and a doublet at δ 0.6 ($^2J(PP)$ = 21 Hz) with intensity ratio 1:2. The above data supports formulation of A as *trans,mer*-[Mo(C_2H_4)$_2$(N_2)(PMe_3)$_3$]. As for B, although chemical and spectroscopic evidence suggest formulation as a bridged dinitrogen complex,[6a] an unambiguous proposal cannot be given with the present data.

$$[Mo(C_2H_4)_2(PMe_3)_4] + N_2 \rightleftarrows [Mo(C_2H_4)_2N_2(PMe_3)_3] + PMe_3 \quad (4)$$

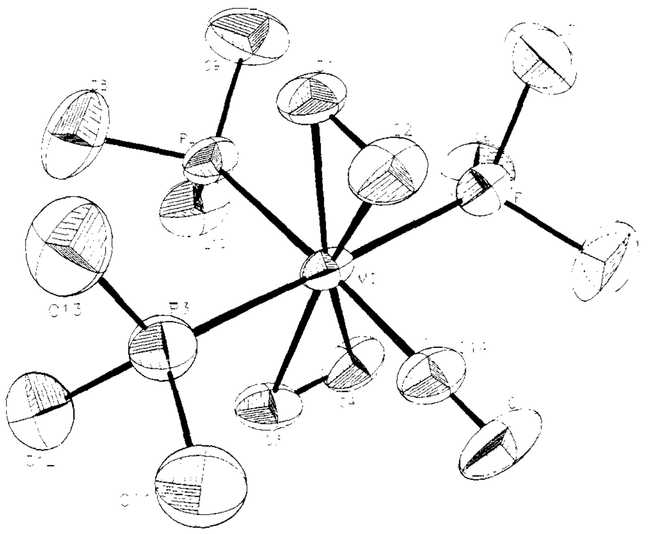

Figure 3. Molecular structure of *trans,mer*-[Mo(C_2H_4)$_2$(CO)(PMe_3)$_3$] (**4**).

The ease of the dissociation of one of the PMe_3 ligands in **3** is also shown by its facile displacement by carbon monoxide to yield *trans,mer*-[Mo(C_2H_4)$_2$(CO)(PMe_3)$_3$] (**4**) (eq 5). A

$$trans\text{-}[Mo(C_2H_4)_2(PMe_3)_4] + CO \xrightarrow[-30\ ^\circ C]{petrol} trans,mer\text{-}[Mo(C_2H_4)_2CO(PMe_3)_3] + PMe_3 \quad (5)$$

trans,mer configuration is assumed since the PMe_3 ligands give rise to a virtually coupled triplet and a doublet (intensity ratio 2:1) at δ 0.93 and 0.71 in the ^1H NMR spectrum (C_7D_8, 35 °C) and an AX_2 pattern in the $^{31}P\{^1H\}$ NMR spectrum (see Experimental Section). On the other hand, only a single although very broad resonance is observed for the ethylene protons at δ 1.6[23] that becomes a sharp quartet at 87 °C (observed J(PH) = 5.2 Hz). At lower temperatures (−54 °C) the ethylene proton resonance spreads out giving several broad unresolved bands (approximately between δ 2.3 and 0.8) that cannot be resolved any further by cooling down to −80 °C.

Complex **4** is a colorless crystalline solid, soluble in most common organic solvents. No evidence for PMe_3 dissociation is found by NMR and chemical studies, in contrast with the situation already described for the dinitrogen species A. Complex **4** is also appreciably more stable, both thermally and toward oxygen, than A. Since the steric requirements of the CO and N_2 ligands are essentially identical,[21] the enhanced stability of **4** with respect to A must be ascribed to electronic effects. The strong interaction between the metal center and the carbonyl group is clearly shown by the low value of ν (C=O) at 1870 cm^{-1} and by the short Mo–C(carbonyl) bond length shown in Table III of 1.952 (6) Å (Mo–C(carbonyl) = 1.973 (16) Å in *trans*-[Mo(CO)(N_2)(dppe)$_2$][11]) and the long Mo–P bond length trans to the carbonyl ligand (2.561 (1) Å). The latter is longer than the average of Mo–P lengths in **3** (2.49 (1) Å). The two remaining Mo–P bond distances in **4** average 2.486 (3) Å, almost identical with the average found for **3**.

As can be seen in the ORTEP illustration of **4** (Figure 3), the ethylene ligands adopt the same staggered-eclipsed conformation as found for **3**, again in excellent agreement with Veillard's studies[20] on model complexes [Mo(C_2H_4)$_2$(PH_3)$_4$] and [Mo(C_2H_4)$_2$(CO)$_4$]. The Mo–C(ethylene) distances average 2.29 (3)

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[23] The downfield shift of the ethylene proton resonance from δ 1.4 in **3** to 1.6 in **4** is to be expected on electronic grounds. CO being a better π-acceptor than PMe_3, the extent of π-back-donation from the metal to the ethylene π^* orbitals is decreased upon substitution of one PMe_3 ligand by CO. See, for example: Jones, K.; Kruger, C. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 520–537.

Table III. Bond Distances (Å) and Angles (deg) for *trans,mer*-[Mo(C$_2$H$_4$)$_2$(CO)(PMe$_3$)$_3$] (4)

Distances			
Mo-P(1)	2.489 (2)	Mo-P(2)	2.561 (1)
Mo-P(3)	2.484 (2)	Mo-C(1)	2.297 (5)
Mo-C(2)	2.325 (5)	Mo-C(3)	2.280 (5)
Mo-C(4)	2.267 (5)	Mo-C(14)	1.952 (6)
P(1)-C(5)	1.804 (7)	P(1)-C(6)	1.834 (7)
P(1)-C(7)	1.837 (7)	P(2)-C(8)	1.807 (8)
P(2)-C(9)	1.808 (7)	P(2)-C(10)	1.824 (7)
P(3)-C(11)	1.852 (7)	P(3)-C(12)	1.828 (8)
P(3)-C(13)	1.853 (7)	O-C(14)	1.162 (6)
C(1)-C(2)	1.417 (8)	C(3)-C(4)	1.404 (9)
Angles			
P(1)-Mo-P(2)	92.04 (5)	P(1)-Mo-P(3)	168.45 (6)
P(2)-Mo-P(3)	94.55 (6)	P(1)-Mo-C(1)	86.0 (2)
P(2)-Mo-C(1)	77.8 (2)	P(3)-Mo-C(1)	86.1 (2)
P(1)-Mo-C(2)	85.9 (2)	P(2)-Mo-C(2)	113.5 (1)
P(3)-Mo-C(2)	82.7 (2)	C(1)-Mo-C(2)	35.7 (2)
P(1)-Mo-C(3)	113.0 (2)	P(2)-Mo-C(3)	86.9 (2)
P(3)-Mo-C(3)	76.8 (2)	C(1)-Mo-C(3)	156.1 (2)
C(2)-Mo-C(3)	152.3 (2)	P(1)-Mo-C(4)	77.1 (2)
P(2)-Mo-C(4)	87.6 (1)	P(3)-Mo-C(4)	112.6 (2)
C(1)-Mo-C(4)	157.3 (2)	C(2)-Mo-C(4)	153.5 (2)
C(3)-Mo-C(4)	36.0 (2)	P(1)-Mo-C(14)	87.0 (2)
P(2)-Mo-C(14)	173.6 (2)	P(3)-Mo-C(14)	87.4 (2)
C(1)-Mo-C(14)	108.4 (2)	C(2)-Mo-C(14)	72.8 (2)
C(3)-Mo-C(14)	87.7 (2)	C(4)-Mo-C(14)	86.0 (2)
Mo-P(1)-C(5)	115.2 (3)	Mo-P(1)-C(6)	121.9 (3)
C(5)-P(1)-C(6)	98.3 (4)	Mo-P(1)-C(7)	120.4 (3)
C(5)-P(1)-C(7)	97.5 (4)	C(6)-P(1)-C(7)	98.7 (4)
Mo-P(2)-C(8)	118.4 (2)	Mo-P(2)-C(9)	118.4 (3)
C(8)-P(2)-C(9)	99.0 (4)	Mo-P(2)-C(10)	118.9 (2)
C(8)-P(2)-C(10)	98.9 (4)	C(9)-P(2)-C(10)	99.1 (4)
Mo-P(3)-C(11)	113.9 (3)	Mo-P(3)-C(12)	123.0 (3)
C(11)-P(3)-C(12)	98.9 (4)	Mo-P(3)-C(13)	120.1 (3)
C(11)-P(3)-C(13)	98.6 (4)	C(12)-P(3)-C(13)	97.8 (4)
Mo-C(1)-C(2)	73.2 (3)	Mo-C(2)-C(1)	71.1 (3)
Mo-C(3)-C(4)	71.5 (3)	Mo-C(4)-C(3)	72.6 (3)
Mo-C(14)-O	179.6 (4)		

Å (2.270 (5) Å in **3**) and the C–C distances 1.410 (9) Å (1.40 (1) Å in **3**).

Concluding Remarks

The range of stable dinitrogen complexes of molybdenum has been enlarged with the synthesis and characterization of two new derivatives *cis*-[Mo(N$_2$)$_2$(PMe$_3$)$_4$] (**1**) and [Mo(N$_2$)(PMe$_3$)$_5$] (**2**), which so far constitute the only known examples of complexes of this type, stabilized by trialkylphosphine ligands. We have also extended this work to the tungsten analogues,[6b] *cis*-[W(N$_2$)$_2$(PMe$_3$)$_4$] and [W(N$_2$)(PMe$_3$)$_5$], which have similarly proved to be readily isolable, although very reactive species. Efforts are being made to synthesize complexes with other trialkylphosphine ligands, particularly PEt$_3$.

Finally, it is hoped that the synthesis and characterization of **1** and **2** can eventually lead to some interesting results in several aspects of nitrogen fixation which have been the subject of a large number of studies in the last ten years. This would include both reactions of coordinated dinitrogen, particularly protonation and alkylation of bound N$_2$, and other reactions leading to nitrogen analogues on dinitrogen binding sites. Some of these expectations have already been fulfilled and will be the subject of future publication from our laboratories.

Experimental Section

Microanalyses were by Butterworth Microanalytical Consultancy, Ltd., Middlesex, and Pascher Microanalytical Laboratory, Bonn. Molecular weights were measured cryoscopically, in benzene, under nitrogen or helium. Infrared spectra were recorded on a Perkin-Elmer Model 577. ^{1}H NMR spectra were run on a Perkin-Elmer R12A (35 °C) or on a Nicolet NT-200. This latter instrument was used for the ^{31}P{^{1}H} NMR studies. ^{31}P NMR shifts are reported in ppm, referenced to external 85% H$_3$PO$_4$.

All preparations and other operations were carried out under oxygen-free nitrogen or argon, following conventional Schlenk techniques. Solvents were rigorously dried under nitrogen by standard techniques and degassed before use. The light petroleum had bp 40–60 °C. The sodium used was purchased from Alfa as 40% dispersion in mineral oil, and after weighing, it was transferred to the deoxygenated reaction flask, washed with 2 × 25 mL of dry ether and then vigorously stirred for ca. 0.5 h with 2 × 25 mL of dry THF. [MoCl$_3$(THF)$_3$][24] and PMe$_3$[25] were prepared by published methods.

Preparations. ***cis*-[Mo(N$_2$)$_2$(PMe$_3$)$_4$]** (1). To a suspension of [MoCl$_3$(THF)$_3$] (4.18 g, ca. 10 mmol) in 80 mL of THF was added 4 mL (ca. 40 mmol) of PMe$_3$, and the mixture was stirred at room temperature overnight. The solvent was evaporated almost to dryness and precipitation of [MoCl$_3$(PMe$_3$)$_3$] (yield ca. 90%) achieved by the successive addition of 30 mL of Et$_2$O and 30 mL of petroleum. The yellow solid was filtered off, washed twice with 30 mL of a 1:1 mixture of Et$_2$O:petroleum and dissolved in 60 mL of THF. The resulting solution was filtered into a 500-mL flask containing an excess of sodium metal (ca. 1.38 g, 60 mmol, prepared from commercial 40% dispersion in mineral oil as indicated above) in 30 mL of THF. After stirring at room temperature for ca. 10 min, the solution turned deep green. PMe$_3$ (0.7 mL, ca. 7 mmol) was slowly added over a period of ca. 5 min (in two portions) approximately 20 min after the appearance of the green color. The stirring was continued for 3–4 h at room temperature, yielding a yellow-brown suspension which was evaporated to dryness and extracted with 80 mL of petroleum ether. This suspension was centrifuged at 1500–2000 rpm for ca. 15 min to give a clear yellow-orange solution which is usually pure enough to be used without any further purification. Yellow *cis*-[Mo(N$_2$)$_2$(PMe$_3$)$_4$] can be crystallized from these solutions by partial removal of the solvent in vacuo and cooling at −78 °C. Additional amounts of complex **1** can be obtained by concentrating the mother liquor resulting from the first crystallization, making a total yield of ca. 55%, referred to PMe$_3$. As indicated above, the yellow-orange solution, obtained after centrifugation, is useful for synthetic purposes. In some preparations, obtaining a clear solution of **1** required two or three filtrations or centrifugations. In some cases small amounts of [MoCl(N$_2$)(PMe$_3$)$_4$][5] were formed too, but this complex is sparingly soluble in petroleum and can therefore be easily separated. The concentration of the solutions can be roughly estimated by weighing the crude solid or by converting an aliquot into [MoI$_2$(PMe$_3$)$_4$] (see below): IR (hexane) 2010, 1965 cm^{-1}, ν(N≡N); ^{1}H NMR (C$_6$H$_6$) δ 1.4 and 1.2 (18 H:18 H, distorted triplets). ^{31}P {^{1}H} NMR (THF–C$_6$D$_6$) A$_2$X$_2$ spin system, δ_{P_A} −4.85, δ_{P_X} −6.90, $^2J(P_AP_X)$ = 18 Hz. Anal. Calcd for MoC$_{12}$H$_{36}$N$_4$P$_4$: C, 31.58; H, 7.89; N, 12.28. Found: C, 31.91; H, 7.75; N, 12.24.

[Mo(N$_2$)(PMe$_3$)$_5$] (2). Complex **1** (0.63 g, ca. 1.5 mmol) was dissolved in 10 mL of petroleum, under argon, and PMe$_3$ (0.4 mL, ca. 4 mmol) was quickly added. The mixture was stirred overnight, the solvent removed in vacuo and the residue extracted with 10 mL of petroleum ether. Centrifugation, partial evaporation of the solvent, and cooling at −20 °C induced crystallization (90% yield). This compound can be recrystallized from the above solvent. In solution under a dinitrogen atmosphere it slowly converts into the cis bis(dinitrogen) derivative, but the reaction is slow. It can be accelerated by removing the displaced PMe$_3$ with a stream of N$_2$, and by heating at 30–40 °C, although some decomposition takes place under these conditions. IR (hexane) 1950 cm^{-1}, ν(N≡N); ^{1}H NMR (C$_6$H$_6$) δ 1.5 (br s, 36), 1.3 (d, 9, ^2J(HP) = 4 Hz). ^{31}P {^{1}H} NMR (THF–C$_6$D$_6$) AX$_4$ spin system, δ_{P_A} 1.46, δ_{P_X} 5.33, $^2J(P_AP_X)$ = 18.8 Hz. Anal. Calcd for MoC$_{15}$H$_{45}$N$_2$P$_5$: C, 35.72; H, 8.93; N, 5.65. Found: C, 35.80; H, 8.90; N, 5.47.

***trans*-[Mo(C$_2$H$_4$)$_2$(PMe$_3$)$_4$] (3).** 1 (0.91 g, 2 mmol) was dissolved in 60 mL of petroleum ether under nitrogen. A slow stream of C$_2$H$_4$ was bubbled through this solution, with stirring at room temperature until the characteristic IR solution bands of 1 at 2010 and 1965 cm^{-1} were not observed (ca. 8 h). Some decomposition took place and a black, very finely divided solid, formed during the reaction, was separated by centrifugation. A slightly cloudy solution was obtained that was evaporated to dryness. The white solid that precipitated was redissolved in 30 mL of petroleum, the suspension centrifuged, and the solvent evaporated under vacuum, until the final volume was ca. 10 mL. Cooling at −30 °C overnight afforded white crystals of **3** in 50% yield. Anal. Calcd for MoC$_{16}$H$_{44}$P$_4$: C, 42.11; H, 9.65. Found: C, 42.10; H, 9.54. IR (C$_6$D$_6$, matched cells) 3020, ν (=C—H). Some weak absorptions in the region 1480–1460 cm^{-1} that could be due to ν(C=C) were observed, but they were too weak even for very concentrated solutions of **3** for any definite assignment to be made. ^{1}H NMR (C$_6$H$_6$) δ 1.4 (br, C$_2$H$_4$), 1.0 (s, br, PMe$_3$). ^{31}P {^{1}H} NMR (THF–C$_6$D$_6$) δ 2.62 (s, br, Mo–PMe$_3$), −62.35 (br, free PMe$_3$). As already discussed (see Results and Discussion)

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(25) Wolfsberger, W.; Schmidbaur, H. *Synth. React. Inorg. Met.-Org. Chem.* **1974**, *4*, 149–156.

Table IV. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

compd	*cis*-[Mo(N_2)$_2$(PMe_3)$_4$] (1)	*trans*-[Mo(C_2H_4)$_2$(PMe_3)$_4$] (3)	*trans,mer*-[Mo(C_2H_4)(CO)(PMe_3)$_3$] (4)
M_r	456.3	456.4	408.3
space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
cell constants			
a, Å	9.371 (4)	10.165 (3)	10.637 (3)
b, Å	15.890 (6)	13.683 (3)	13.069 (3)
c, Å	16.692 (7)	17.139 (4)	15.201 (4)
β, deg	106.58 (4)	98.84 (3)	98.45 (2)
cell vol, Å^3	2382.2	2355.5	2090.2
molecules/unit cell	4	4	4
ρ(calcd), g cm^{-3}	1.27	1.29	1.30
μ(calcd), cm^{-1}	8.07	8.14	8.40
radiatn	Mo Kα	Mo Kα	Mo Kα
max cryst dimensns, mm	0.41 × 0.55 × 0.73	0.50 × 0.50 × 1.00	0.25 × 0.88 × 1.13
scan width	0.80 + 0.20 tan θ	0.80 + 0.20 tan θ	0.80 + 0.20 tan θ
standard reflcntns	(500), (0,10,0), (0,0,10)	(400), (080)	(800), (080), (0,0,10)
decay of standards, %	±2	±2	±2
reflctns measured	3677	5659	4107
2θ range, deg	$\leq$46	$\leq$50	$\leq$50
reflctns collected	1720	2715	2764
no. of parameters varied	217	190	172
GOF	2.36	0.60	0.98
R	0.038	0.043	0.037
R_w	0.050	0.048	0.043

Table V. Final Fractional Coordinates for *cis*-[Mo(N_2)$_2$(PMe_3)$_4$] (1)

atom	*x/a*	*y/b*	*z/c*
Mo	0.8038 (1)	0.66410 (5)	0.73429 (5)
P(1)	0.6631 (4)	0.5519 (2)	0.7769 (2)
P(2)	0.8999 (4)	0.5719 (2)	0.6432 (2)
P(3)	0.5872 (4)	0.7130 (2)	0.6235 (2)
P(4)	1.0205 (4)	0.6444 (3)	0.8567 (2)
N(1)	0.912 (1)	0.7568 (7)	0.6992 (7)
N(2)	0.975 (2)	0.8121 (9)	0.680 (1)
N(3)	0.739 (1)	0.7473 (7)	0.8043 (6)
N(4)	0.704 (2)	0.7987 (9)	0.8426 (8)
C(1)	0.756 (2)	0.4591 (9)	0.835 (1)
C(2)	0.508 (2)	0.498 (1)	0.700 (1)
C(3)	0.558 (2)	0.587 (1)	0.851 (1)
C(4)[a]	1.073 (3)	0.509 (2)	0.688 (2)
C(5)	0.792 (3)	0.483 (2)	0.589 (2)
C(6)	0.945 (4)	0.624 (2)	0.557 (2)
C(4)P	0.785 (4)	0.556 (3)	0.533 (2)
C(5)P	0.910 (6)	0.459 (2)	0.657 (2)
C(6)P	1.065 (4)	0.611 (3)	0.621 (3)
C(7)	0.496 (2)	0.656 (1)	0.526 (1)
C(8)	0.615 (2)	0.821 (1)	0.584 (1)
C(9)	0.420 (2)	0.739 (1)	0.655 (1)
C(10)	1.134 (2)	0.549 (1)	0.877 (1)
C(11)	1.174 (2)	0.719 (1)	0.860 (1)
C(12)	0.988 (2)	0.662 (2)	0.9575 (8)

[a] Atoms C(4)–C(6) and atoms C(4)P–C(6)P have occupancy factors of 0.5.

molecular weight determinations for **3**, both under N_2 and under He, consistently gave lower values than expected (265 (N_2), 370 (He), to be compared to an expected value of 456).

Interaction of *trans*-[Mo(C_2H_4)$_2$(PMe_3)$_4$] (3) with N_2. Complex **3** (1.82 g, ca. 4 mmol) was dissolved in 80 mL of petroleum and stirred at room temperature while a slow stream of N_2 was bubbled through. The weak absorption at 2070 cm^{-1}, characteristic of the petroleum ether solutions of **3** prepared under N_2, increased in intensity and was very intense after stirring for 7–8 h, when the reaction was considered complete. As already discussed, evaporation of the solution in vacuo produced a bright yellow crystalline solid which redissolved on admission of N_2. The same material was obtained by removing the solvent with the aid of a stream of N_2 until saturation and cooling at 0 °C. The total yield of solid collected from this and subsequent crystallizations of the mother liquor was ca. 0.85 g. This compound reacts instantly with neat PMe_3 to give **3**. IR (Nujol) 3030 w, ν(=C—H); 2070 m, 1975 vw, ν(N≡N); 1430 s, 1375 m, 1290 m, 1275 s, 1160 s, 1120 w, 930 vs, 840 m, 710 sh, 700 m, 685 m, 650 m cm^{-1}; ^{1}H NMR (C_6H_6, 35 °C) δ 1.7 (br) and 1.6 (s), C_2H_4; 0.9 (br, s, PMe_3). At 20 °C (C_6D_6, 200 MHz), the ethylene protons give rise to several broad, weak bands between δ 2 and 1, while the PMe_3 ligands appear as a slightly broad singlet at δ 0.9 (18 H) and a doublet at δ 0.72 (9 H, ^2J(HP) = 5.2 Hz). ^{31}P {^{1}H} NMR (THF-C_6D_6) δ 6.00 (t, 1), -0.61 (d, 2), ^2J(PP) = 21 Hz; -62.35 (free PMe_3). Although consistent analytical data have been obtained for this solid (C, 43.92 and 43.69; H, 9.35 and 9.49; N, 2.97 and 3.03%, for two independent determinations), we are unable to propose a reasonable structure accounting for these and the spectroscopic data. The analytical samples were crystalline materials of excellent appearance and apparently suitable for X-ray studies. Unfortunately, they were not single crystals and all attempts to determine the structure of this complex were unsuccessful.

***trans*,*mer*-[Mo(C_2H_4)$_2$(CO)(PMe_3)$_3$] (4).** A solution of **3** was prepared by dissolving 0.91 g (ca. 2 mmol) in 40 mL of petroleum ether under N_2. This solution was cooled at -30 °C and maintained at this temperature for about 5 min. The admission of nitrogen was then closed and the N_2 atmosphere inside the flask replaced by CO, using a syringe needle connected to a CO cylinder as the gas inlet and another needle as the outlet. The admission of CO was cut off after ca. 1 min, during which time the solution of **3** was kept at -30 °C without stirring. Then the solution was stirred for 30–45 s at -30 °C and allowed to warm at room temperature without stirring, the solvent was stripped off in vacuo and the residue extracted with petroleum. Crystallization at -20 °C afforded white crystals of **4** (0.73 g, 90% yield): IR (Nujol) 3060, 3020, ν(=C—H); 1860, ν(C≡O) and 1486 cm^{-1} ν(C=C). ^{1}**H NMR** (C_7D_8, 35 °C) δ 1.6 (br), C_2H_4, 0.9 (t) and 0.7 (d), PMe_3; ^{31}P {^{1}H} NMR (THF-C_6D_6), δ -2.02 (d, 2), -12.71 (t, 1), ^2J(PP) = 24.5 Hz. Anal. Calcd for $MoC_{14}H_{35}OP_3$: C, 41.18; H, 8.58; P, 22.79. Found: C, 41.24; H, 8.44; P, 23.11.

Reactions of 1 with Alkyl Halides, Iodine, and Carbon Monoxide. (a) Complex **1**, (0.45 g, ca. 1 mmol) was dissolved in 25 mL of petroleum ether and the mixture stirred at room temperature with 3–4 equiv of Me_3SiCH_2Cl. A yellow solid precipitated after ca. 10–15 min. The stirring was continued for 2 h, after which time a yellow microcrystalline solid (85% yield) and an essentially colorless solution were obtained. The yellow solid was recrystallized from toluene and shown to be *trans*-[$MoCl_2$(PMe_3)$_4$] by comparison of its IR and ^{1}H NMR spectra with those of an authentic sample.[5]

A similar reaction took place between **1** and EtBr, yielding *trans*-[$MoBr_2$(PMe_3)$_4$][14] in 75% yield. The reactions of **1** with MeI and I_2 were carried out in petroleum ether and benzene, respectively, and yielded *trans*-[MoI_2(PMe_3)$_4$][14] in 70% yield, after stirring at room temperature for 15–30 min.

(b) Carbon monoxide was bubbled through a solution of **1** (0.45 g, 1 mmol) in 40 mL of petroleum ether, cooled at -30 °C for 10 min; the temperature was raised and maintained at 0 °C for a further period of 2 h, after which time the two IR absorptions of **1** at 2010 and 1960 cm^{-1} had been replaced by two strong bands at 1870 and 1810 cm^{-1}. From the resulting solution, the known[16] complex *cis*-[Mo(CO)$_2$(PMe_3)$_4$] was isolated. A similar reaction carried out at room temperature for ca. 4 h, yielded *fac*- and *mer*-[Mo(CO)$_3$(PMe_3)$_3$] in addition to the cis dicarbonyl complex. Small amounts of *cis*-[Mo(CO)$_4$(PMe_3)$_2$] were also detected.

X-ray Data Collection, Structure Determination, and Refinement for *cis*-[Mo(N_2)$_2$(PMe_3)$_4$] (1). Single crystals of the air-sensitive compound were sealed under N_2 in thin-walled glass capillaries. Final lattice pa-

Table VI. Final Fractional Coordinates for *trans*-$[Mo(C_2H_4)_2(PMe_3)_4]$ (3)

atom	*x*/*a*	*y*/*b*	*z*/*c*
Mo	−0.03442 (5)	0.14811 (4)	0.21568 (3)
P(1)	0.1937 (2)	0.1295 (1)	0.2907 (1)
P(2)	−0.1341 (2)	0.1127 (2)	0.3365 (1)
P(3)	−0.2527 (2)	0.1207 (1)	0.1285 (1)
P(4)	0.0572 (2)	0.2304 (1)	0.1064 (1)
C(1)	−0.0164 (8)	−0.0177 (5)	0.2182 (5)
C(2)	0.0146 (8)	0.0153 (5)	0.1462 (4)
C(3)	−0.1351 (7)	0.2929 (5)	0.2316 (4)
C(4)	0.0004 (8)	0.3014 (5)	0.2654 (4)
C(5)	0.3015 (8)	0.2351 (6)	0.3239 (5)
C(6)	0.2196 (8)	0.0633 (6)	0.3239 (5)
C(7)	0.3147 (8)	0.0549 (7)	0.3860 (5)
C(8)	−0.3167 (9)	0.1205 (9)	0.3350 (5)
C(9)	−0.113 (1)	−0.0060 (7)	0.3862 (5)
C(10)	−0.090 (1)	0.1936 (7)	0.4226 (5)
C(11)	−0.2637 (9)	0.1273 (7)	0.0203 (5)
C(12)	−0.3322 (9)	0.0011 (7)	0.1307 (5)
C(13)	−0.3987 (9)	0.1993 (8)	0.1347 (6)
C(14)	−0.029 (1)	0.3405 (6)	0.0625 (5)
C(15)	0.078 (1)	0.1645 (7)	0.0155 (4)
C(16)	0.2242 (8)	0.2844 (7)	0.1231 (5)
H(1)[C(1)]	0.0602	−0.0480	0.2603
H(2)[C(1)]	−0.1052	−0.0619	0.2188
H(3)[C(2)]	−0.0560	0.0053	0.0959
H(4)[C(2)]	0.1127	0.0120	0.1356
H(5)[C(3)]	−0.1523	0.3353	0.1825
H(6)[C(3)]	−0.2136	0.2951	0.2647
H(7)[C(4)]	0.0604	0.3501	0.2332
H(8)[C(4)]	0.0218	0.3091	0.3209
H(9)[C(5)]	0.3821	0.2035	0.3584
H(10)[C(5)]	0.2889	0.2782	0.2763
H(11)[C(5)]	0.2706	0.2843	0.3654
H(12)[C(6)]	0.3237	0.0595	0.4069
H(13)[C(6)]	0.1796	−0.0054	0.3872
H(14)[C(6)]	0.1856	0.1089	0.4208
H(15)[C(7)]	0.4035	0.0411	0.2818
H(16)[C(7)]	0.2654	−0.0256	0.2345
H(17)[C(7)]	0.3281	0.0778	0.2043
H(18)[C(8)]	−0.3399	0.0965	0.3844
H(19)[C(8)]	−0.3410	0.2007	0.3175
H(20)[C(8)]	−0.3286	0.0813	0.2931
H(21)[C(9)]	−0.1512	−0.0554	0.3473
H(22)[C(9)]	−0.0126	−0.0147	0.3908
H(23)[C(9)]	−0.1452	−0.0272	0.4412
H(24)[C(10)]	0.0197	0.1996	0.4362
H(25)[C(10)]	−0.0798	0.1650	0.4767
H(26)[C(10)]	−0.1165	0.2603	0.4186
H(27)[C(11)]	−0.3610	0.1038	−0.0060
H(28)[C(11)]	−0.2054	0.0744	0.0051
H(29)[C(11)]	−0.2385	0.2046	0.0054
H(30)[C(12)]	−0.3390	−0.0151	0.1824
H(31)[C(12)]	−0.2908	−0.0646	0.1204
H(32)[C(12)]	−0.4183	−0.0033	0.0947
H(33)[C(13)]	−0.4769	0.1894	0.0989
H(34)[C(13)]	−0.3938	0.2760	0.1117
H(35)[C(13)]	−0.4127	0.1825	0.1992
H(36)[C(14)]	−0.0173	0.3973	0.1122
H(37)[C(14)]	−0.1343	0.3278	0.0469
H(38)[C(14)]	0.0089	0.3778	0.0137
H(39)[C(15)]	0.0218	0.1177	−0.0153
H(40)[C(15)]	0.1091	0.2169	−0.0233
H(41)[C(15)]	0.1250	0.0959	0.0248
H(42)[C(16)]	0.2842	0.2351	0.1373
H(43)[C(16)]	0.2400	0.3197	0.0820
H(44)[C(16)]	0.2282	0.3363	0.1701

Table VII. Final Fractional Coordinates for *trans,mer*-$[Mo(C_2H_4)_2(CO)(PMe_3)_3]$ (4)

atom	*x*/*a*	*y*/*b*	*z*/*c*
Mo	0.43145 (4)	0.33608 (3)	0.28232 (3)
P(1)	0.2343 (2)	0.3322 (1)	0.3525 (1)
P(2)	0.5535 (2)	0.2294 (1)	0.40818 (9)
P(3)	0.6226 (2)	0.3779 (1)	0.2131 (1)
O	0.2700 (5)	0.4429 (3)	0.1207 (3)
C(1)	0.5021 (6)	0.4588 (4)	0.3861 (4)
C(2)	0.4352 (6)	0.5107 (4)	0.3118 (4)
C(3)	0.4490 (7)	0.1992 (4)	0.1918 (4)
C(4)	0.3361 (6)	0.1892 (4)	0.2286 (4)
C(5)	0.0896 (7)	0.3610 (8)	0.2789 (5)
C(6)	0.1809 (8)	0.2157 (6)	0.4031 (5)
C(7)	0.2124 (8)	0.4234 (6)	0.4410 (5)
C(8)	0.7249 (7)	0.2380 (7)	0.4274 (5)
C(9)	0.5225 (9)	0.2513 (6)	0.5205 (4)
C(10)	0.5373 (8)	0.0904 (5)	0.4045 (5)
C(11)	0.5863 (8)	0.4415 (6)	0.1035 (5)
C(12)	0.7335 (7)	0.2807 (6)	0.1846 (5)
C(13)	0.7417 (7)	0.4701 (6)	0.2677 (5)
C(14)	0.3307 (6)	0.4030 (4)	0.1808 (4)
H(1)[C(1)]	0.6051	0.4659	0.3911
H(2)[C(1)]	0.4419	0.4521	0.4452
H(3)[C(2)]	0.5072	0.5612	0.2763
H(4)[C(2)]	0.3331	0.5421	0.3200
H(5)[C(3)]	0.5453	0.1483	0.2103
H(6)[C(3)]	0.4456	0.2126	0.1191
H(7)[C(4)]	0.3241	0.1358	0.2674
H(8)[C(4)]	0.2560	0.1988	0.1947
H(9)[C(5)]	−0.0161	0.3521	0.3061
H(10)[C(5)]	0.0739	0.3180	0.2337
H(11)[C(5)]	0.1004	0.4230	0.2549
H(12)[C(6)]	0.0743	0.2164	0.4247
H(13)[C(6)]	0.1617	0.1721	0.3602
H(14)[C(6)]	0.2655	0.1884	0.4591
H(15)[C(7)]	0.2416	0.4950	0.4353
H(16)[C(7)]	0.1291	0.4229	0.4568
H(17)[C(7)]	0.2629	0.3958	0.4913
H(18)[C(8)]	0.7426	0.3037	0.4489
H(19)[C(8)]	0.7601	0.1983	0.4763
H(20)[C(8)]	0.7845	0.2186	0.3788
H(21)[C(9)]	0.4221	0.2470	0.5315
H(22)[C(9)]	0.5536	0.2121	0.5603
H(23)[C(9)]	0.5332	0.3138	0.5334
H(24)[C(10)]	0.4317	0.0826	0.4149
H(25)[C(10)]	0.5391	0.0641	0.3581
H(26)[C(10)]	0.5889	0.4615	0.4422
H(27)[C(11)]	0.6752	0.5085	0.0729
H(28)[C(11)]	0.5282	0.3977	0.1132
H(29)[C(11)]	0.5311	0.2957	0.0668
H(30)[C(12)]	0.8215	0.2376	0.1605
H(31)[C(12)]	0.7811	0.2300	0.2398
H(32)[C(12)]	0.6847	0.4940	0.1467
H(33)[C(13)]	0.8118	0.5471	0.2284
H(34)[C(13)]	0.6815	0.4431	0.2807
H(35)[C(13)]	0.7746		0.3236

rameters as determined from a least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 15 reflection ($2\theta > 36°$) accurately centered on the diffractometer are given in Table IV. The space group was uniquely determined as $P2_1/c$ from systematic absences.

Data were collected on an Enraf-Nonius CAD-4 diffractometer by the θ–2θ scan technique. The method has been previously described.[26] A summary of the data collection parameters is given in Table IV. The intensities were corrected for Lorentz and polarization effects but not for absorption.

Calculations were carried out with the SHELX system of computer programs.[27] Neutral atom scattering factors for Mo, P, N, and C were taken from Cromer and Waber,[28] and the scattering for molybdenum was corrected for real and imaginary components of anomalous dispersion by using the table of Cromer and Liberman.[29] Scattering factors for H were from ref 30.

The position of the molybdenum atom was revealed by the inspection of a Patterson map. A difference Fourier map phased on the molybdenum atom readily revealed the positions of the non-hydrogen atoms. Least-squares refinement with isotropic thermal parameters led to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.082$. Although high thermal motion was asso-

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(26) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 45–53.

(27) SHELX, a system of computer programs for X-ray structure determination by G. M. Sheldrick, 1976.

(28) Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104–109.

(29) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891–1898.

(30) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4, p 72.

ciated with all the methyl carbon atoms (consistent with the low decomposition temperature of **1**), a resolvable rotational disorder could only be found for the methyls on P(2). On the basis of relative peak heights, occupancy factors of 0.5 (50%) were assigned carbon atoms C(4)–C(6) and C(4)′–C(6)′. The occupancy factors were not refined. Due to the disorder and high thermal motion of the carbon atoms, the hydrogen atoms could not be located and were not included in the final refinement. Refinement of the non-hydrogen atoms with anisotropic temperature factors led to final values of $R = 0.038$ and $R_w = 0.050$. A final difference Fourier showed no feature greater than $0.3\ e^-\ Å^3$. The weighting scheme was based on unit weights; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameters are given in Table V.[31]

X-ray Data Collection, Structure Determination, and Refinement for *trans*-$[Mo(C_2H_4)_2(PMe_3)_4]$ (3). Single crystals of the compound were sealed in thin-walled glass capillaries prior to X-ray examination. Final lattice parameters as determined from a least-squares refinement of the angular settings of 15 reflections ($2\theta > 36°$) accurately centered on the diffractometer are given in Table IV. Systematic absences defined the space group as $P2_1/n$.

Data were collected as described for the previous compound. The intensities were corrected for Lorentz and polarization effects but not for absorption. Neutral atom scattering factors were obtained as noted above, and that of molybdenum was corrected for the real and imaginary components of anomalous dispersion.

The position of the molybdenum atom was revealed by the inspection of a Patterson map, and the subsequent calculation of a difference Fourier map allowed the location of the remaining non-hydrogen atoms. Refinement with isotropic thermal parameters led to a reliability index of $R = 0.078$. The hydrogen atoms were located with the aid of a difference Fourier map and included in the final refinement with fixed contributions. Refinement of the non-hydrogen atoms with anisotropic temperature factors led to final values of $R = 0.043$ and $R_w = 0.048$. A final difference Fourier showed no feature greater than $0.3\ e^-/Å^3$. The weighting scheme was based on unit weights; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameters are given in Table VI.[31]

X-ray Data Collection, Structure Determination, and Refinement for *trans,mer*-$[Mo(C_2H_4)_2(CO)(PMe_3)_3]$ (4). The data were collected and treated as described above. Final lattice parameters from a least-squares refinement of the angular settings of 15 reflections ($2\theta > 42°$) accurately centered on the diffractometer are given in Table IV. The space group, uniquely determined from systematic absences, is $P2_1/n$.

The molybdenum atom position was revealed by the inspection of a Patterson map, and the remaining non-hydrogen atoms located on a difference Fourier map. Refinement with isotropic thermal parameters led to $R = 0.097$. Location of the hydrogen atoms on a difference Fourier map, inclusion with fixed contributions, and anisotropic refinement of the non-hydrogen atoms led to final values of $R = 0.037$ and $R_w = 0.043$. A final difference Fourier showed no feature greater than $0.3\ e^-/Å^3$. The weighting scheme was based on unit weights; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameters are given in Table VII.[31]

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Supplementary Material Available: Tables of thermal parameters and observed and calculated structure factors for **1**, **3**, and **5** (47 pages). Ordering information is given on any current masthead page.

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[31] See paragraph at the end of paper regarding supplementary material.

Steric and Electronic Influences of Methyl Substitution on Transition-Metal Complexes of Tetrabenzo[*b,f,j,n*][1,5,9,13]tetraazacyclohexadecine

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Abstract: Transition-metal complexes of a tetraaza macrocyclic ligand obtained from Schiff base condensations of 2-amino-5-methylbenzaldehyde were synthesized and characterized ($(M(MeTAAB)^{2+}$, M = Co^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pd^{2+}, and Pt^{2+}). The crystal structure of $[Cu(MeTAAB)(NO_3)][NO_3]$ was determined by using X-ray crystallographic techniques. The complex crystallizes in the space group $P2_1/c$ with unit cell dimensions $a = 13.136$ (6) Å, $b = 17.294$ (7) Å, $c = 17.391$ (4) Å, and $\beta = 127.66$ (2)°. The coordination sphere of the copper ion is six-coordinate, N_4O_2, with a symmetrically bidentate nitrate making the overall geometry a bicapped square pyramid. The macrocyclic ligand is, as expected, distinctly saddle shaped, with S_4 symmetry.

The propensity of *o*-aminobenzaldehyde for self-condensation has been found to be extremely sensitive to the chemical environment. The nature of the products formed was first clarified as early as 1926 by Seidel[1,2] and later, in the 1960s, by McGeachin[3] and Melson and Busch.[4-7] Since then numerous studies of condensation reactions of *o*-aminobenzaldehyde in the presence of a variety of transition-metal ions have been made.[8-14] It is now well substantiated that in the absence of metal ions various polycyclic derivatives of condensates of *o*-aminobenzaldehyde are formed.[1-3,15] On the other hand, transition-metal ions have the ability to act as templates, whereby closed-ring macrocyclic ligands can be isolated as their metal complexes. A

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