Spectra and Structure of Mo₂(CO)₆(μ-Ph₃PNH)₃. A New Bonding Mode for Phosphinimines

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A complete chemical, spectroscopic, and crystallographic study of the complex previously formulated as [Mo(CO)₃-(Ph₃PNH)₂]₂ has shown it to be Mo₂(CO)₆(Ph₃PNH)₃. The crystal and molecular structure of a tetrahydrofuran solvate Mo₂(CO)₆[(C₆H₅)₃PNH]₃·¹/₂C₄H₈O has been determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes in the monoclinic space group C_{2h}^5-$P2_1/c$ with four molecules per unit cell of dimensions a = 19.605 (9) Å, b = 13.507 (10) Å, c = 24.045 (11) Å, β = 91.15 (3)°, and V = 6366 Å³. The calculated density is 1.28 g/cm³. Least-squares refinement of the structure led to a final value of the conventional R factor (on F^2) of 0.096 for the 2154 independent reflections with $F_o^2 > \sigma(F_o^2)$. Each of the molybdenum atoms has distorted octahedral coordination, the face being composed of three bridging nitrogen atoms from the triphenylphosphinimine ligands. The unique bridging phosphinimine ligands function as four-electron donors. The dimensions of the inner coordination sphere are characteristic of a *fac*-Mo(CO)₃L₃ complex where L is a purely σ-donor ligand. Important interatomic distances and angles are as follows: Mo···Mo, 3.354 (6) Å; Mo–N, 2.396 (44) Å; Mo–C, 1.897 (47) Å; P–N, 1.604 (40) Å; Mo₁–N–Mo₂, 88.9 (22)°. There appears to be no metal–metal bond.

Introduction

Triphenylphosphinimine, (C₆H₅)₃PNH, forms typical substituted metal carbonyl complexes, *e.g.*, *cis*-M(CO)₄(Ph₃PNH)₂, M = Mo, W. In these, it functions as a two-electron donor analogous to phosphine oxides, presumably bonding to the metal through the nitrogen lone pair. Coordination lowers the P=N stretching vibration approximately 40 cm⁻¹.[1]

Pyrolysis of *cis*-Mo(CO)₄(Ph₃PNH)₂ results in the formation of a yellow crystalline material formulated as Mo₂(CO)₆-(Ph₃PNH)₄.[2] Two remarkable characteristics of this complex prompted the work reported here. First, the phosphorus–nitrogen vibrational frequency in this dimeric complex is 930 cm⁻¹, an extraordinary 220 cm⁻¹ below the value in *cis*-Mo(CO)₄(Ph₃PNH)₂. Second, assuming no metal–metal bonding and donation of two electrons per Ph₃PNH moiety, the dimer is four electrons short of satisfying the inert-gas rule. Such an observation is exceptional in group VIb. Our attempts to understand these two aspects of "Mo₂(CO)₆(Ph₃PNH)₄" were initially limited to detailed spectroscopic and chemical studies. When these proved inconclusive, a single-crystal X-ray structure determination was initiated.

Experimental Section

Materials. Molybdenum hexacarbonyl was obtained from Climax Molybdenum Co. and triphenylphosphinimine was prepared by a literature method.[3] Microanalyses and molecular weight determinations were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Additional molecular weight determinations were made with a Mechrolab 301 A vapor pressure osmometer. The title compound (henceforth called "the molybdenum dimer") was prepared by the method of Bock and tom Dieck.[2] Further purification was achieved by eluting the complex from a neutral alumina III column with dichloromethane. *Anal.* Calcd for C₇₈H₆₄N₄Mo₂O₆P₄: C, 63.77; H, 4.39; N, 3.81; P, 8.13; Mo, 13.04. Calcd for C₆₀H₄₈N₃-Mo₂O₆P₃: C, 60.5; H, 4.03; N, 3.53; P, 7.80; Mo, 16.1. Found: C, 60.5; H, 4.37; N, 3.58; P, 7.42; Mo, 12.65.

Gas Analyses. Carbon monoxide was determined by first decomposing the complex with bromine at 60° for 15 min. The resulting noncondensable gas was pumped into a measured volume using a Toepler pump. A sample of this gas was also burned over hot CuO and passed through a −78° trap and into a known volume using a Toepler pump. In both instances, identity and purity of the gas were established by mas spectrometry. Determinations on Mo(CO)₆ yielded a Mo:CO ratio of 5.9:1.

(1) G. Singh and H. Zimmer, *Organometal. Chem. Rev.*, **2**, 279 (1967).

(2) H. Bock and H. tom Dieck, *Z. Naturforsch. B*, **21**, 739 (1966).

(3) L. Birkhofer and A. Ritter, *Angew. Chem., Int. Ed. Engl.*, **4**, 417 (1965).

Spectra. The proton nmr was recorded on a Varian Associates HR-220 spectrometer. ³¹P (24.2 MHz) and ¹³C (15.05 MHz) nmr were recorded on a Varian Associates DP-60 spectrometer fitted with a "home-built" Fourier transform facility. Downfield shifts are recorded as negative. ³¹P decoupling power was generated using standard components: an HP-5100B frequency synthesizer, HP-10515A frequency doubler, HP-230B tuned amplifier, and ENI 10-W broadband power amplifier. The additional equipment necessary, a probe-matching network, an attenuator, and a through-line power/SWR meter allowed generation of up to 10 W of 89-MHz decoupling power for the HR-220 probe while observing proton resonance in the frequency sweep mode. Infrared spectra were recorded on a Perkin-Elmer 137 spectrophotometer as Nujol mulls.

Collection and Reduction of Intensity Data. Yellow crystals of the molybdenum dimer were first obtained from hot benzene–hexane. Upon careful visual examination, twinning of these crystals along a plane was observed. After unsuccessful attempts with other solvent systems, single crystals were successfully obtained from a tetrahydrofuran–petroleum ether solvent system. Precession photographs of a crystal mounted along the needle axis and coated with shellac were taken. Photographs of the *h0l*, *h1l*, *0kl*, and *1kl* zones using Ni-filtered Cu Kα radiation (λ 1.5418 Å) confirmed that the crystal belonged to the monoclinic system. The observed extinctions, *l* = 2*n* + 1 for *h0l* and *k* = 2*n* + 1 for *0k0*, uniquely determined the space group as *P2₁/c* (C_{2h}^5: No. 14). The crystals became opaque and produced only a powder pattern before intensity data could be collected. Further attempts produced a second crop of small crystals which provided few large-angle reflections. Strong interest in learning at least the heavy-atom geometry of the compound, coupled with pessimism about producing better crystals, led us to collect data on a crystal from this batch. The lattice constants at 20°, determined from least-squares refinement of the setting angles of 21 strong reflections (with values of 2θ between 15.4 and 23.8°) centered on a Picker four-circle automatic diffractometer using Mo Kα radiation (λ 0.71069 Å), are *a* = 19.605 (9) Å, *b* = 13.507 (10) Å, *c* = 24.045 (11) Å, *β* = 91.15 (3)°, and *V* = 6366 Å³. Because of decomposition by loss of solvent, the density of the crystals used for intensity data could not be measured. Since the density of 1.56 g/cm³ calculated for four formula weights of "Mo₂(CO)₇[(C₆H₅)₃PNH]₄" was reasonable, four dimeric molecules per unit cell were assumed. No symmetry is imposed on the molecule by the space group.

A crystal measuring 0.19 × 0.17 × 0.11 mm was mounted in a random orientation for data collection on an ultrastable goniometer of our own design with translations only. An ω scan indicated that the mosaic spread was small.

The data were collected with unfiltered Mo Kα radiation obtained from the 002 reflection of a highly oriented graphite monochromator. The crystal to source distance (target–monochromator–sample) was 23.5 cm, the crystal to detector distance was 24.9 cm, and the counter aperture size was 3 × 3mm. The takeoff angle was 2.2°. Data were collected using the θ–2θ technique over a symmetrical scan width of 1.7°, plus a dispersion correction. The scan speed was 2°/min and 10-sec background counts were used.

A set of independent intensity data was collected for 4° ≤ 2θ ≤ 40° in the quadrants *hkl* and *hk̄l*. Redundant data were collected for 4° ≤ 2θ ≤ 15° for the entire sphere. The intensities of three stand-

ard reflections, 040, 400, and 006, were monitored every 50 reflections and no systematic trends were observed. The maximum deviation (6.2%) was consistent with earlier observations on the instability of the crystals.

Integrated intensities, I, and standard errors, $\sigma(I)$, were calculated as

$$I = C - 0.5(t_c/t_b)(B_1 + B_2)$$

$$\sigma(I) = [C + 0.25(t_c/t_b)^2(B_1 + B_2) + (\rho I)^2]^{1/2}$$

where C is the total integrated peak count obtained in scan time t_c, B_1 and B_2 are the background counts obtained in total time t_b, and ρ is an empirical coefficient[4] of the net count I. A value of 0.05 was assigned to ρ. Lorentz and polarization corrections were made in the usual manner. Of the 8237 reflections collected, 6229 were independent and only 2154 had intensities greater than $\sigma(I)$. Although the quality of the data was low, refinement was carried out in order to define the heavy-atom geometry. Absorption corrections ($\mu = 5.11$ cm^{-1}) were neglected because of the poor quality of the data. Preliminary scale and temperature factors were determined by Wilson's method[5] based on the formula $Mo_2(CO)_7[(C_6H_5)_3PNH]_4$.

Solution and Refinement of Structure. A sharpened three-dimensional Patterson function yielded positions of the two molybdenum atoms.[6] Structure factors based on the two molybdenum atoms, calculated using 956 reflections with $F_o^2 \geqslant 2.33\sigma(F_o^2)$, yielded $R_1 = 0.44$ where $R_1 = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$.

A subsequent three-dimensional Fourier synthesis revealed 35 peaks which were assigned to carbon, nitrogen, oxygen, and phosphorus atoms. Four peaks having approximately one-third the electron density of molybdenum were presumed to be phosphorus atoms. At this point $R_1 = 0.34$. A second Fourier synthesis revealed 30 additional atoms and produced $R_1 = 0.31$. This high residual, coupled with one exceptionally long Mo–P distance, made one phosphorus assignment questionable. Additionally, the Fourier synthesis showed that the peak height for this phosphorus was smaller than those for the other three. Deletion of this phosphorus and its associated nitrogen produced $R_1 = 0.30$. It was concluded that only three phosphorus atoms were present for every two molybdenum atoms.

The existence of a cluster or polymer involving more than two metal atoms was rejected, since there were no metal–metal distances less than 7.0 Å, except those between molybdenum atoms in the same asymmetric unit.

A third Fourier synthesis, based on those 37 atoms which constituted a chemically reasonable portion of the structure, revealed several additional atoms and reinforced the idea that only three phosphorus atoms were present. R_1 was 0.276 for a model including these atoms. After two more Fourier syntheses, a total of 74 heavy atoms had been found suggesting the formula $Mo_2(CO)_6[(C_6H_5)_3PNH]_3$ and $R_1 = 0.216$. The overall temperature and scale factors were redetermined based on the new formula.

To facilitate refinement, the nine phenyl rings were treated as rigid groups where C–C distances were fixed at 1.390 Å and D_{6h} symmetry was assumed.[7,8] Each atom was initially assigned an isotropic thermal parameter equal to the overall temperature factor. For the refinement, the 2154 reflections with intensity greater than $\sigma(I)$ were used. Three cycles of full-matrix least-squares refinement based on F^2 were performed on positional and isotropic thermal parameters for the nongroup atoms and on positional and group thermal parameters for the rigid groups. The values of R_1 and R_2 were 0.121 and 0.081, respectively, where $R_2 = [\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]$. The function minimized was $\Sigma w(F_o^2 - F_c^2)^2$ where $w = 1/[\sigma(F_o^2)]^2$. The

scattering factors of Cromer and Waber[9] were used in all calculations for nonhydrogen atoms. The hydrogen scattering factors used later were taken from Stewart, Davidson, and Simpson.[10]

Three additional cycles of refinement varying positional parameters, isotropic thermal parameters for the nongroup atoms, and individual isotropic thermal parameters for the rigid groups produced $R_1 = 0.114$ and $R_2 = 0.081$. Refinement with anisotropic temperature factors on two molybdenum atoms did not decrease R_1 or R_2. The large number of parameters and variables did not allow anisotropic refinement for any other atoms. Since the greatest shift for any parameter was 0.19 times the error, refinement was apparently complete. A difference Fourier synthesis showed residual electron density with peak heights 0.3–0.6 times that of a typical carbon atom. These peaks approximated a five-membered ring. Since the decomposition of other crystals resulted from loss of solvent, the presence of some tetrahydrofuran was anticipated. The oxygen atom was assigned to the largest of the five peaks in a corresponding regular Fourier synthesis. The solvent occupancy factor was determined as follows. The values of R_1 and R_2 for various assumed solvent multipliers were 0.109 and 0.066 for a multiplier of 0.25, 0.107 and 0.058 for a multiplier of 0.50, and 0.119 and 0.066 for a multiplier of 1.0. Based on these results, a multiplier of 0.50 was assigned to the solvent atoms.

Computer-storage limitations for the refinement with solvent necessitated that all atoms be treated isotropically. Refinement on positional and isotropic thermal parameters for all 79 atoms yielded $R_1 = 0.099$ and $R_2 = 0.051$, but the solvent molecule exhibited values for shift per error as large as 0.53. Although the solvent thermal parameters were not abnormal, the carbon–carbon bond distances were shorter than those expected for tetrahydrofuran. Although a difference Fourier at this point showed evidence for another THF ring with $^1/_4$ occupancy, refinement was terminated for lack of interest in this ill-defined feature.

Twenty-six of the 45 phenyl hydrogens were observed in the difference Fourier synthesis at values of 0.22 to 0.56 e/Å^3. These hydrogens and the remaining 19 calculated positions of 1.03 Å from the phenyl carbon were included as fixed contributions. The temperature factors of all 45 hydrogens were assigned values 1 Å^2 greater than those of the carbon atom to which they were attached. The imine hydrogens and the solvent hydrogens could not be located with certainty and were not included in the calculation.

Two final cycles of refinement of positional and isotropic thermal parameters using all data and including hydrogen contributions to F_c produced $R_1 = 0.096$ and $R_2 = 0.050$. The largest shift was 0.31 times the error and this occurred for a solvent carbon. A final difference Fourier synthesis revealed no nonmetal peak greater than 0.98 e/Å^3. The error of an observation of unit weight is 0.93 electron. Only three of the "unobserved" reflections had F_c greater than $3\sigma(\text{obsd})$.

The relatively high final residual is attributable mainly to the poor quality crystal used for data collection. This, coupled with the relatively low data-to-parameter ratio (14:1), results in large esd's. The major crystallographic conclusion, a heavy-atom geometry, distinct from that suggested earlier, is unequivocal. The scatter of individual determinations of "chemically equivalent" structural parameters is large enough to prevent comparison to other structures, however.

The final least-squares parameters and their standard errors are given in Table I for nongroup atoms and in Table II for group atoms. The derived parameters of the group atoms are given in Table III. The observed and calculated structure factors for all 2154 reflections used in the refinement (those for which $F_o^2 > \sigma(F_o^2)$) are listed in Table IV.[11]

Results

Physical Measurements. The reported infrared spectrum of the molybdenum dimer, which we confirm, shows two bands in the carbonyl stretching region (1894 and 1770 cm^{-1}). The lower of these lies in what is normally considered the bridging CO region; structure I was therefore suggested by Bock and

(4) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(5) A. J. C. Wilson, *Nature (London)*, **150**, 152 (1942).

(6) Computations were performed on a CDC 6400-6600 computer. In addition to various local programs, those used in the solution and refinement were (a) Gvildys' B 149, a Fourier summation program, (b) Gvildys' ANLFLS (a modification of the Busing, Martin, and Levy ORFLS), a least-squares program used for preliminary structure factor calculations, (c) Ibers' NUCLS, a group least-squares program used for refinement, (d) Ibers' group modification of Busing and Levy's ORFFE, a function and error program, and (e) Johnson's ORTEP, a thermal ellipsoid plotting program.

(7) S. J. La Placa and J. A. Ibers, *Acta Crystallogr.*, **18**, 511 (1965).

(8) R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965).

(9) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

(10) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(11) See paragraph at end of paper regarding supplementary material.

Table I. Positional and Thermal Parameters for $Mo_2(CO)_6[(C_6H_5)_3PNH]_3 \cdot {}^1/_2 C_4H_8O^a$

Atom	x	y	z	B, Å^2
Mo$_1$	0.16567 (20)	0.11868 (31)	0.16774 (16)	3.38 (11)
Mo$_2$	0.33561 (20)	0.14426 (31)	0.17865 (16)	3.31 (11)
P$_1$	0.26443 (65)	0.01497 (98)	0.06084 (53)	3.04 (32)
P$_2$	0.25088 (65)	−0.00073 (99)	0.28134 (52)	3.10 (33)
P$_3$	0.24127 (62)	0.36146 (101)	0.18357 (48)	3.02 (30)
O$_1$	0.0595 (16)	0.2244 (23)	0.0926 (12)	4.48 (83)
O$_2$	0.0680 (16)	−0.0496 (23)	0.1341 (12)	4.53 (85)
O$_3$	0.0523 (15)	0.1466 (24)	0.2511 (12)	5.50 (85)
O$_4$	0.4345 (15)	0.1953 (21)	0.2734 (12)	4.15 (80)
O$_5$	0.4613 (16)	0.0141 (23)	0.1562 (12)	4.65 (82)
O$_6$	0.4347 (18)	0.2855 (26)	0.1206 (14)	6.10 (98)
N$_1$	0.2564 (15)	0.1054 (24)	0.1014 (12)	2.38 (79)
N$_2$	0.2550 (16)	0.0316 (23)	0.2179 (13)	2.47 (86)
N$_3$	0.2419 (14)	0.2427 (21)	0.1995 (11)	1.15 (74)
C$_1$	0.0999 (24)	0.1847 (34)	0.1206 (19)	4.1 (13)
C$_2$	0.1069 (23)	0.0112 (35)	0.1444 (18)	3.5 (12)
C$_3$	0.0986 (21)	0.1355 (35)	0.2201 (17)	3.5 (11)
C$_4$	0.3913 (23)	0.1802 (32)	0.2387 (18)	3.5 (12)
C$_5$	0.4079 (25)	0.0584 (35)	0.1659 (19)	4.6 (13)
C$_6$	0.3957 (26)	0.2398 (38)	0.1423 (20)	4.8 (14)
C$_{S1}$^{b}	0.0041 (50)	0.6690 (66)	0.1172 (38)	3.6 (24)
C$_{S2}$	0.0606 (46)	0.6756 (60)	0.1214 (35)	2.6 (21)
C$_{S3}$	0.0758 (41)	0.6908 (60)	0.0752 (37)	2.2 (21)
C$_{S4}$	0.0301 (42)	0.6733 (58)	0.0406 (32)	1.6 (20)
O$_S$	−0.0113 (33)	0.6125 (54)	0.0733 (29)	7.3 (19)

^{a} Errors in parentheses through this paper refer to the least significant figures. ^{b} The s denotes a solvent atom.
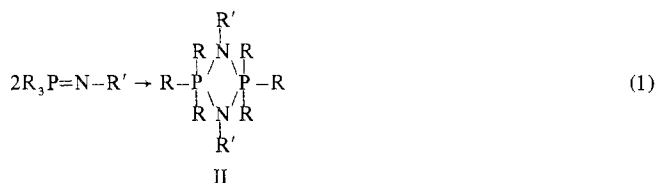

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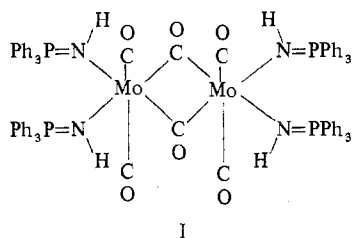
tom Dieck.[12] It may be noted that no other cases are known where CO bridges two molybdenum atoms. However, the presence of nitrogen-base ligands in the complex is known to reduce ν_{CO} due to the low π acidity of such ligands. Thus, a tenable alternative interpretation of the observed vibrational pattern is a structure with local C_{3v} symmetry for Mo(CO)$_3$, with each CO trans to nitrogen. In fact, the frequencies and intensities in the molybdenum dimer match closely those of *fac*-Mo(CO)$_3$(CH$_3$CN)$_3$ and *fac*-Mo(CO)$_3$(amine)$_3$.[13]

The molecular weight of the complex was determined by vapor pressure lowering in CHCl$_3$. The average of four determinations was 1127. This value confirms that the complex is not the monomer Mo(CO)$_3$(Ph$_3$PNH)$_2$, but it is only 77% of the value expected for the formula [Mo(CO)$_3$(Ph$_3$PNH$_2$]$_2$, mol wt 1468. In the course of this work the unfortunate decision was made to trust the elemental analyses and discount the "low" molecular weight.

The proton nmr in CDCl$_3$ (Figure 1) consists of a complex multiplet in the phenyl region (δ 7.24–8.35) and a doublet at δ 0.52; the integrated intensity of these regions is 17.7:1, suggesting that the doublet at higher field is due to the imine protons on nitrogen. The imine proton of the free ligand appears as a doublet at δ 1.61 in CDCl$_3$. This integration confirms that imine hydrogen is not lost on forming the molybdenum dimer. Heteronuclear spin decoupling of ^{31}P

using the known (*vide infra*) phosphorus chemical shift in a 51.7-kG field collapsed the doublet to a sharp singlet. The doublet is therefore confirmed to be due to P–H coupling ($^2J_{PH}$ = 12 Hz), and the molybdenum dimer must possess equivalent imine protons. This result is consistent with structure I but does not exclude other geometries. A survey of the region upfield of TMS gave no support for a structure based on a hydride complex with ortho-bonded phenyl groups. Phosphinimines with electronegative R groups are known to dimerize (eq 1), and II might function as a biden-

$$2R_3P=N-R' \rightarrow R-P \underset{\underset{R'}{\overset{R}{\underset{N}{\big|}}}}{\overset{\overset{R'}{\underset{N}{\big|}}}{\underset{R}{\big\backslash}}} P-R \tag{1}$$

II

tate ligand through nitrogen. The dimeric form, while attractive in terms of explaining the PN vibration in the molybdenum dimer characteristic of a single bond, is inconsistent with the proton nmr. Coupling to two equivalent ^{31}P nuclei would yield a triplet for the imine proton resonance.

The white-noise proton-decoupled Fourier transform ^{31}P nmr in CH$_2$Cl$_2$ consists of a singlet at −43.5 ppm relative to H$_3$PO$_4$. This compares to a value of −17.2 ppm for the free ligand. While the chemical shift value itself is not structurally diagnostic, the phosphorus nuclei must occupy symmetrically equivalent positions. This is again consistent with structure I.

The proton-decoupled Fourier transform ^{13}C nmr was observed at room temperature and at −90°. The room-temperature sample contained ~0.03 M molybdenum complex and 0.1 M Cr(acac)$_3$ in CHCl$_3$. The low-temperature sample contained no Cr(acac)$_3$. At room temperature (pulse delay time 4 sec) the carbonyl carbons appear as a singlet at −26.8 relative to CS$_2$. Upon lowering the temperature to −90° (pulse delay time 1 sec) the carbonyl resonance remains unchanged. Apparent equivalence of the carbonyl groups is demonstrated. Since the carbonyls remain a singlet at −90°, the occurrence of a fluxional process seems unlikely. Thus the carbonyls appear to be in stereochemically rigid and symmetrically equivalent coordination positions. This is the first unequivocal evidence inconsistent with structure I. It is in agreement with a structure based on Mo(CO)$_3$ groups with local C_{3v} symmetry, however. The numerical value of the ^{13}C chemical shift is not structurally diagnostic. While it is known that bridging carbonyls have a ^{13}C chemical shift downfield from terminal groups,[14] the shift observed for the molybdenum dimer is intermediate between the bridge and terminal regions.

One obvious solution to the apparent electron deficiency of "Mo$_2$(CO)$_6$(Ph$_3$PNH)$_4$" would be an erroneous estimate of the carbon monoxide content. To determine the amount of carbon monoxide in the compound, it was decomposed with bromine and the noncondensable CO was pumped into a known volume of a vacuum line. The average of several measurements produced 4.78 mmol of gas/g of complex. To confirm that the gas was entirely CO (*i.e.*, to exclude the possibility that H$_2$ is also produced on decomposition of the dimer) it was passed over hot CuO. CO is oxidized to CO$_2$, while H$_2$ yields H$_2$O. After this treatment, the gas was pumped through a −78° trap and into a known volume.

(12) Two infrared-active CO stretches were incorrectly predicted for structure I under D_2 symmetry.

(13) B. L. Ross, J. G. Grasselli, W. M. Ritchey, and H. D. Kaesz, *Inorg. Chem.*, 2, 1023 (1963).

(14) L. J. Todd, private communication.

Table II. Group Parameters for Mo$_2$(CO)$_6$[(C$_6$H$_5$)$_3$PNH]$_3$·$^1/_2$C$_4$H$_8$O

Group	x_c	y_c	z_c	δ^a	ϵ	η
R$_1$	0.2928 (10)	−0.1784 (14)	0.1320 (7)	0.816 (24)	2.677 (18)	2.662 (19)
R$_2$	0.3924 (10)	0.0543 (15)	−0.0219 (7)	1.111 (35)	−2.274 (17)	0.188 (31)
R$_3$	0.1328 (10)	−0.0119 (17)	−0.0193 (7)	−2.038 (26)	−2.685 (20)	−0.497 (21)
R$_4$	0.1128 (11)	−0.1101 (14)	0.3157 (9)	−1.144 (27)	2.318 (24)	−1.26 (27)
R$_5$	0.2738 (10)	0.1871 (15)	0.3546 (7)	2.339 (27)	2.553 (17)	0.134 (22)
R$_6$	0.3608 (11)	−0.1756 (16)	0.3024 (7)	1.203 (24)	−3.030 (18)	2.750 (18)
R$_7$	0.3815 (10)	0.4721 (13)	0.2125 (8)	2.255 (17)	−2.896 (20)	1.933 (17)
R$_8$	0.1354 (10)	0.4812 (17)	0.2586 (7)	−2.865 (28)	−3.649 (19)	0.415 (22)
R$_9$	0.2004 (11)	0.3825 (14)	0.0597 (9)	−1.887 (26)	−2.387 (25)	−1.485 (26)

^{a} The angles δ, ϵ, and η are in radians.

Table III. Derived Parameters for Ring Carbon Atoms^{a,b}

Atom	x	y	z	B, Å^2
R$_1$C$_1$	0.2797 (17)	−0.0979 (17)	0.0974 (10)	2.5 (11)
R$_1$C$_2$	0.3466 (14)	−0.1265 (23)	0.1090 (11)	2.7 (10)
R$_1$C$_3$	0.3597 (12)	−0.2070 (25)	0.1436 (13)	5.2 (14)
R$_1$C$_4$	0.3059 (19)	−0.2590 (18)	0.1665 (11)	4.9 (14)
R$_1$C$_5$	0.2390 (15)	−0.2304 (22)	0.1549 (10)	3.6 (12)
R$_1$C$_6$	0.2259 (11)	−0.1498 (24)	0.1203 (12)	3.1 (11)
R$_2$C$_1$	0.3368 (12)	0.0378 (26)	0.0119 (12)	1.2 (11)
R$_2$C$_2$	0.03524 (17)	−0.0298 (19)	−0.0295 (15)	4.6 (16)
R$_2$C$_3$	0.4080 (19)	−0.0133 (23)	−0.0633 (11)	5.0 (16)
R$_2$C$_4$	0.4479 (13)	0.0707 (28)	−0.0557 (11)	2.0 (12)
R$_2$C$_5$	0.4323 (14)	0.1384 (19)	−0.0143 (13)	1.6 (11)
R$_2$C$_6$	0.3768 (16)	0.1219 (21)	0.0195 (10)	1.0 (10)
R$_3$C$_1$	0.1894 (12)	−0.0027 (28)	0.0161 (10)	0.9 (10)
R$_3$C$_2$	0.1476 (18)	0.0785 (19)	0.0057 (12)	2.1 (12)
R$_3$C$_3$	0.0910 (16)	0.0693 (24)	−0.0297 (14)	5.3 (16)
R$_3$C$_4$	0.0762 (13)	−0.0211 (32)	−0.0547 (11)	4.3 (15)
R$_3$C$_5$	0.1181 (19)	−0.1024 (22)	−0.0443 (13)	5.2 (15)
R$_3$C$_6$	0.1747 (16)	−0.0932 (21)	−0.0089 (14)	4.3 (15)
R$_4$C$_1$	0.1689 (13)	−0.0560 (21)	0.2986 (16)	2.7 (13)
R$_4$C$_2$	0.1490 (18)	−0.0519 (22)	0.3537 (14)	5.6 (16)
R$_4$C$_3$	0.0930 (19)	−0.1060 (27)	0.3708 (10)	4.6 (14)
R$_4$C$_4$	0.0568 (13)	−0.1643 (22)	0.3328 (16)	3.1 (13)
R$_4$C$_5$	0.0766 (16)	−0.1684 (21)	0.2777 (14)	3.3 (14)
R$_4$C$_6$	0.1327 (17)	−0.1142 (24)	0.2606 (10)	1.8 (11)
R$_5$C$_1$	0.2634 (17)	0.1016 (18)	0.3235 (11)	2.0 (10)
R$_5$C$_2$	0.3264 (13)	0.1191 (22)	0.3491 (12)	3.4 (11)
R$_5$C$_3$	0.3368 (13)	0.2046 (27)	0.3802 (11)	4.8 (14)
R$_5$C$_4$	0.2842 (20)	0.2727 (19)	0.3858 (11)	5.8 (14)
R$_5$C$_5$	0.2212 (15)	0.2552 (21)	0.3602 (13)	4.8 (13)
R$_5$C$_6$	0.2108 (11)	0.1697 (25)	0.3290 (12)	3.6 (12)
R$_6$C$_1$	0.3142 (16)	−0.0986 (22)	0.2963 (12)	1.2 (10)
R$_6$C$_2$	0.3815 (19)	−0.0853 (19)	0.2808 (12)	3.3 (13)
R$_6$C$_3$	0.4281 (12)	−0.1623 (29)	0.2870 (12)	3.8 (14)
R$_6$C$_4$	0.4073 (18)	−0.2526 (22)	0.3086 (12)	3.0 (13)
R$_6$C$_5$	0.3400 (21)	−0.2659 (19)	0.3240 (12)	5.4 (15)
R$_6$C$_6$	0.2934 (12)	−0.1889 (29)	0.3179 (12)	4.0 (14)
R$_7$C$_1$	0.3211 (11)	0.4242 (20)	0.1975 (14)	1.9 (11)
R$_7$C$_2$	0.3531 (16)	0.4856 (23)	0.1596 (9)	2.8 (12)
R$_7$C$_3$	0.4135 (15)	0.5334 (19)	0.1746 (12)	3.2 (12)
R$_7$C$_4$	0.4419 (12)	0.5200 (22)	0.2275 (14)	3.7 (12)
R$_7$C$_5$	0.4099 (16)	0.4586 (24)	0.2654 (9)	3.7 (13)
R$_7$C$_6$	0.3495 (16)	0.4108 (19)	0.2504 (12)	3.9 (13)
R$_8$C$_1$	0.1794 (15)	0.4288 (26)	0.2248 (10)	1.1 (11)
R$_8$C$_2$	0.1940 (13)	0.5264 (27)	0.2392 (13)	3.0 (13)
R$_8$C$_3$	0.1500 (20)	0.5787 (18)	0.2730 (14)	6.1 (17)
R$_8$C$_4$	0.0914 (17)	0.5336 (29)	0.2924 (12)	3.8 (14)
R$_8$C$_5$	0.0768 (13)	0.4361 (30)	0.2780 (13)	3.6 (15)
R$_8$C$_6$	0.1208 (19)	0.3837 (18)	0.2442 (13)	3.3 (13)
R$_9$C$_1$	0.2209 (18)	0.3774 (23)	0.1153 (9)	1.2 (10)
R$_9$C$_2$	0.1564 (16)	0.4128 (23)	0.1010 (15)	4.1 (15)
R$_9$C$_3$	0.1359 (13)	0.4178 (24)	0.0454 (18)	6.5 (18)
R$_9$C$_4$	0.1800 (21)	0.3876 (27)	0.0041 (10)	5.4 (16)
R$_9$C$_5$	0.2445 (18)	0.3522 (25)	0.0185 (12)	5.9 (16)
R$_9$C$_6$	0.2650 (12)	0.3471 (22)	0.0741 (15)	1.6 (11)

^{a} C$_1$ is attached to P; other C atoms are numbered in succession so that C$_4$ is para to C$_1$. ^{b} R$_1$, R$_2$, R$_3$ are attached to P$_1$; R$_4$, R$_5$, R$_6$ are attached to P$_2$; R$_7$, R$_8$, R$_9$ are attached to P$_3$.

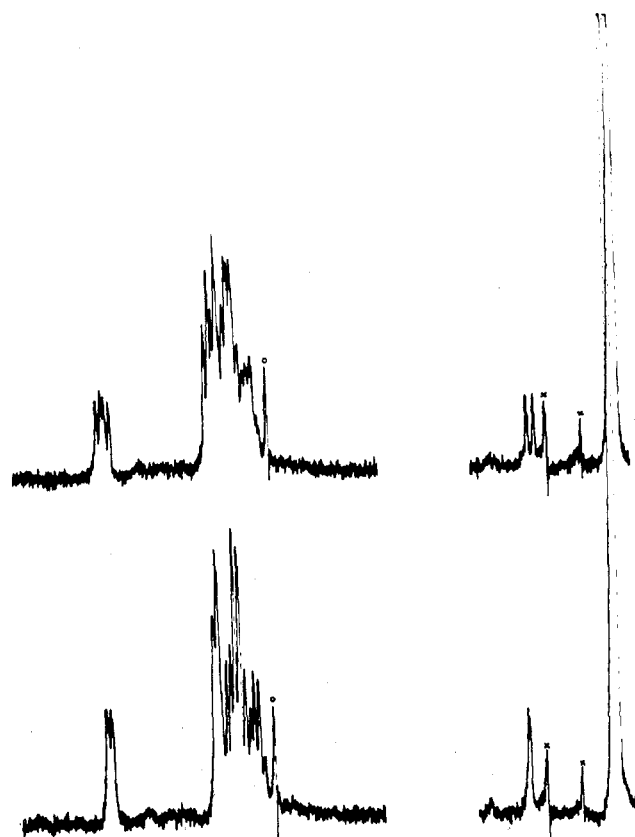Since essentially all the gas was recovered, the evolved gas from the complex is carbon monoxide.

Figure 1. Normal (upper) and ³¹P-decoupled (lower) 220-MHz spectrum of Mo₂(CO)₆(μ-Ph₃PNH)₃ in CDCl₃ at 15°. Phenyl region appears at left; TMS is at far right: ×, spinning side band; ○, CHCl₃ impurity.

If one assumes the molybdenum analysis to be correct (the same value was obtained in this work and by Bock), the ratio of millimoles of CO to millimoles of Mo is calculated to be 3.5. This value conflicts with the earlier determination[2] that 0.92 mmol of CO is evolved in the pyrolysis of cis-Mo(CO)₄-(Ph₃PNH)₂ (eq 2). The reproducibility of our measurements,

$$cis\text{-Mo(CO)}_4(\text{Ph}_3\text{PNH})_2 \rightarrow {}^1/_2\text{``Mo}_2(\text{CO})_6(\text{Ph}_3\text{PNH})_4\text{''} + CO \qquad (2)$$
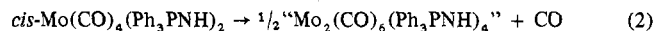
coupled with the accuracy of the method when applied to Mo(CO)₆ (see Experimental Section), made our results credible, at least to us.[15] Unfortunately, the resulting formula, Mo₂(CO)₇(Ph₃PNH)₄, is at least as inconsistent with the ¹³C nmr data as is structure I.

A determined application of numerous chemical and spectroscopic techniques therefore failed to explain either of the anomalies which prompted this study. We therefore reluctantly forsook sporting methods.

(15) Systematically low CO determinations are possible, but high values are not.

Table V. Interatomic Distances[a]

Atoms	Distance, Å	Atoms	Distance, Å
Mo_1–Mo_2	3.354 (6)	P_1–R_1C_1	1.782 (27)
		P_1–R_2C_1	1.887 (29)
Mo_1–C_1	1.919 (47)	P_1–R_3C_1	1.821 (27)
Mo_1–C_2	1.930 (46)	P_2–R_4C_1	1.827 (30)
Mo_1–C_3	1.851 (42)	P_2–R_5C_1	1.728 (28)
Mo_2–C_4	1.857 (44)	P_2–R_6C_1	1.843 (33)
Mo_2–C_5	1.862 (49)	P_3–R_7C_1	1.806 (27)
Mo_2–C_6	1.965 (51)	P_3–R_8C_1	1.826 (33)
Av 1.897 (47)		P_3–R_9C_1	1.694 (26)
		Av 1.802 (59)	
Mo_1–N_1	2.420 (30)		
Mo_1–N_2	2.412 (31)	C_1–O_1	1.160 (55)
Mo_1–N_3	2.362 (29)	C_2–O_2	1.144 (56)
Mo_2–N_1	2.454 (30)	C_3–O_3	1.196 (52)
Mo_2–N_2	2.400 (32)	C_4–O_4	1.195 (53)
Mo_2–N_3	2.330 (29)	C_5–O_5	1.232 (58)
Av 2.396 (44)		C_6–O_6	1.119 (62)
		Av 1.174 (41)	
Mo_1–P_1	3.538 (14)		
Mo_1–P_2	3.559 (13)	$N_1 \cdots N_2$	2.974 (43)
Mo_1–P_3	3.616 (14)	$N_1 \cdots N_3$	3.019 (42)
Mo_2–P_1	3.586 (13)	$N_2 \cdots N_3$	2.896 (43)
Mo_2–P_2	3.586 (14)	Av 2.963 (66)	
Mo_2–P_3	3.471 (14)		
		$O_1 \cdots O_2$	3.836 (44)
P_1–N_1	1.573 (34)	$O_1 \cdots O_3$	3.958 (42)
P_2–N_2	1.591 (33)	$O_2 \cdots O_3$	3.881 (44)
P_3–N_3	1.649 (32)	$O_4 \cdots O_5$	3.776 (41)
Av 1.604 (40)		$O_5 \cdots O_6$	3.798 (47)
		$O_4 \cdots O_6$	3.870 (44)
C_{S1}–C_{S2}	1.11 (13)		
C_{S2}–C_{S3}	1.17 (12)		
C_{S3}–C_{S4}	1.23 (11)		
O_S–C_{S1}	1.33 (11)		
O_S–C_{S4}	1.40 (10)		

[a] Esd's for mean bond lengths were calculated from the equation $\sigma^2 = [\Sigma_{i=1}^{i=N}(X_i - \bar{X})^2]/(N - 1)$, where X_i is the ith bond length and $\bar{X}$ is the mean of the N equivalent bond lengths.
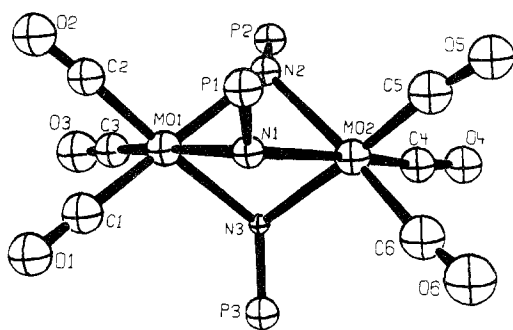

Figure 2. Inner coordination sphere. Thermal ellipsoids shown at 50% probability.

Table VI. Interatomic Angles[a]

Atoms 1, 2, 3	Angle, deg	Atoms 1, 2, 3	Angle, deg
C_1–Mo_1–C_2	77.7 (19)	N_1–Mo_1–N_2	76.0 (10)
C_1–Mo_1–C_3	82.3 (19)	N_1–Mo_1–N_3	78.3 (10)
C_2–Mo_1–C_3	82.1 (19)	N_2–Mo_1–N_3	74.7 (10)
C_4–Mo_2–C_5	81.6 (20)	N_1–Mo_2–N_2	75.5 (10)
C_4–Mo_2–C_6	80.0 (20)	N_1–Mo_2–N_3	78.2 (10)
C_5–Mo_2–C_6	82.6 (21)	N_2–Mo_2–N_3	75.5 (10)
Av 81.0 (19)		Av 76.4 (15)	
Mo_1–N_1–Mo_2	87.0 (10)	Mo_1–N_1–P_1	123.4 (17)
Mo_1–N_2–Mo_2	88.4 (10)	Mo_2–N_1–P_1	124.4 (17)
Mo_1–N_3–Mo_2	91.3 (10)	Mo_1–N_2–P_2	124.3 (17)
Av 88.9 (22)		Mo_2–N_2–P_2	126.7 (17)
		Mo_1–N_3–P_3	127.8 (15)
C_1–Mo_1–N_1	98.0 (16)	Mo_2–N_3–P_3	120.5 (15)
C_2–Mo_1–N_1	101.2 (15)	Av 124.5 (26)	
C_3–Mo_1–N_1	176.7 (16)		
C_1–Mo_1–N_2	173.7 (16)	Mo_1–C_1–O_1	179.1 (40)
C_2–Mo_1–N_2	101.6 (16)	Mo_1–C_2–O_2	173.8 (39)
C_3–Mo_1–N_2	103.8 (15)	Mo_1–C_3–O_3	175.8 (35)
C_1–Mo_1–N_3	105.9 (16)	Mo_2–C_4–O_4	170.2 (38)
C_2–Mo_1–N_3	176.3 (15)	Mo_2–C_5–O_5	170.4 (40)
C_3–Mo_1–N_3	98.4 (15)	Mo_2–C_6–O_6	172.2 (45)
C_4–Mo_2–N_1	176.1 (16)	Av 173.6 (34)	
C_5–Mo_2–N_1	102.4 (16)		
C_6–Mo_2–N_1	100.3 (16)	N_1–P_1–R_1C_1	112.2 (15)
C_4–Mo_2–N_2	104.0 (16)	N_1–P_1–R_2C_1	110.2 (17)
C_5–Mo_2–N_2	100.3 (17)	N_1–P_1–R_3C_1	112.2 (17)
C_6–Mo_2–N_2	175.4 (16)	N_2–P_2–R_4C_1	113.1 (18)
C_4–Mo_2–N_3	97.9 (15)	N_2–P_2–R_5C_1	109.5 (16)
C_5–Mo_2–N_3	175.5 (16)	N_2–P_2–R_6C_1	109.7 (16)
C_6–Mo_2–N_3	101.7 (17)	N_3–P_3–R_7C_1	114.2 (15)
		N_3–P_3–R_8C_1	111.2 (16)
R_1C_1–P_1–R_2C_1	109.1 (16)	N_3–P_3–R_9C_1	110.4 (16)
R_1C_1–P_1–R_3C_1	107.7 (17)		
R_2C_1–P_1–R_3C_1	105.1 (13)	N_1–N_2–N_3	61.9 (10)
R_4C_1–P_2–R_5C_1	107.9 (16)	N_1–N_3–N_2	60.3 (10)
R_4C_1–P_2–R_6C_1	104.7 (15)	N_2–N_1–N_3	57.8 (10)
R_5C_1–P_2–R_6C_1	111.9 (15)	Av 60.0 (21)	
R_7C_1–P_3–R_8C_1	104.4 (15)		
R_7C_1–P_3–R_9C_1	107.8 (17)	O_4–O_5–O_6	61.4 (08)
R_8C_1–P_3–R_9C_1	108.4 (16)	O_5–O_4–O_6	59.5 (08)
		O_4–O_6–O_5	59.0 (08)
P_1–R_1C_1–R_1C_2	119.0 (23)	O_1–O_2–O_3	61.7 (08)
P_1–R_1C_1–R_1C_6	120.4 (24)	O_1–O_3–O_2	58.6 (08)
P_1–R_2C_1–R_2C_2	121.2 (24)	O_2–O_1–O_3	59.7 (08)
P_1–R_2C_1–R_2C_6	118.7 (22)		
P_1–R_3C_1–R_3C_2	118.0 (26)	C_{S1}–C_{S2}–C_{S3}	101.6 (90)
P_1–R_3C_1–R_3C_6	122.0 (25)	C_{S2}–C_{S3}–C_{S4}	114.2 (86)
P_2–R_4C_1–R_4C_2	117.7 (25)	C_{S3}–C_{S4}–O_S	98.9 (70)
P_2–R_4C_1–R_4C_6	121.4 (27)	C_{S4}–O_S–C_{S1}	89.1 (66)
P_2–R_5C_1–R_5C_2	120.6 (23)	O_S–C_{S1}–C_{S2}	109.0 (89)
P_2–R_5C_1–R_5C_6	119.2 (23)		
P_2–R_6C_1–R_6C_2	119.6 (22)		
P_2–R_6C_1–R_6C_6	120.1 (23)		
P_3–R_7C_1–R_7C_2	124.0 (23)		
P_3–R_7C_1–R_7C_6	116.0 (22)		
P_3–R_8C_1–R_8C_2	118.1 (23)		
P_3–R_8C_1–R_8C_6	121.8 (25)		
P_3–R_9C_1–R_9C_2	118.7 (24)		
P_3–R_9C_1–R_9C_6	121.0 (26)		

[a] Esd's for the mean bond angles were calculated from the equation given in footnote a of Table V.

Description of the Structure. The structure consists of discrete dimeric units of formula $Mo_2(CO)_6[(C_6H_5)_3PNH]_3 \cdot \frac{1}{2}C_4H_8O$. Important intramolecular distances and angles are given in Tables V and VI, respectively. Figure 2 presents the inner coordination sphere about the molybdenums and the numbering system used. Figure 3 is a stereoscopic view of the molecule looking down the molybdenum–molybdenum axis. Figure 4 is a stereoscopic view looking perpendicular to the metal–metal axis.

The molecule can be described as two octahedrally coordinated molybdenum atoms sharing a face composed of three bridging nitrogen atoms. Examination of Table VI indicates that the coordination is actually slightly distorted from true octahedral geometry. Various distances and angles in Tables V and VI reveal the statistical equivalence of the three cis carbonyls on each molybdenum. Additionally, the three nitrogen atoms are each equidistant from the two molybdenum atoms and all distances and angles involving Mo and N atoms are equivalent. Each bridging nitrogen is trans to two carbonyl groups, one on each molybdenum atom. These equivalences give the inner coordination sphere pseudo-threefold symmetry. Figure 3 demonstrates that this threefold symmetry extends to the three phosphorus atoms and even to the phenyl rings. If perfect threefold symmetry were present, a mirror plane perpendicular to the Mo–Mo axis would be expected for this molecule. The deviations from this mirror symmetry can be seen in Figure 4.

Since the closest contact between the solvent molecule and the dimer is 3.94 Å, the solvent is apparently noncoordinated. Intramolecular distances between carbons in different phenyl
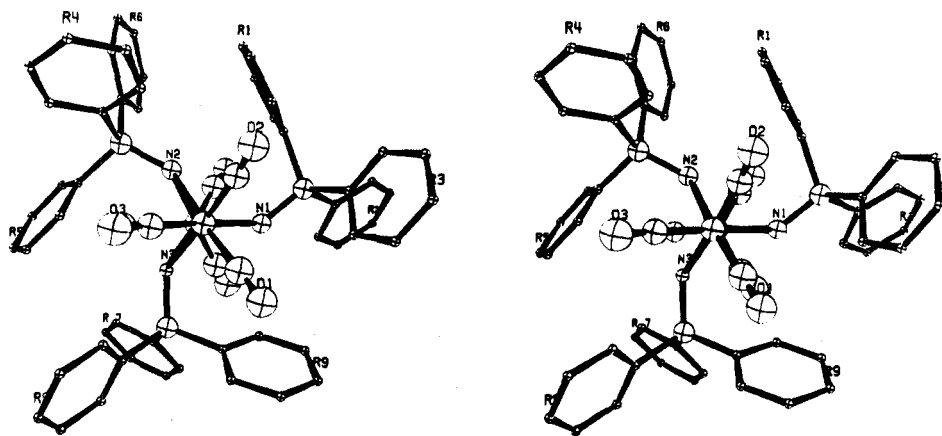
Figure 3. Stereoscopic view down the line $Mo_1\cdots Mo_2$. Phenyl carbons are given artifically small and equal thermal parameters. Other ellipsoids shown at 50% probability.
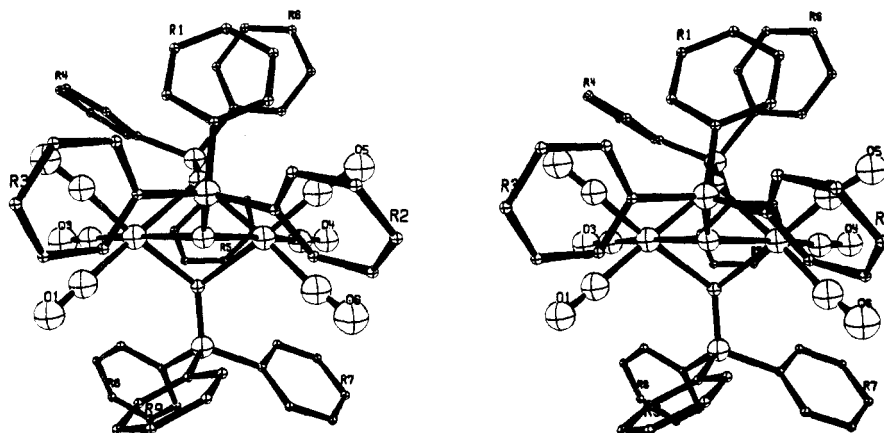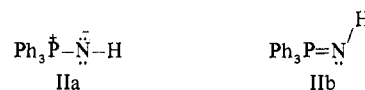

Figure 4. Stereoscopic view perpendicular to the line $Mo_1\cdots Mo_2$. Phenyl carbons are given artificially small and equal thermal parameters. Other ellipsoids shown at 50% probability.

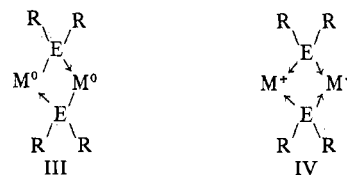rings all exceed 3.7 Å. Numerous intramolecular $O\cdots H$ distances in the range 2.3–2.7 Å occur in the dimer.

Discussion

As one might hope, the observed structure yields an explanation of the two anomalies which prompted this work and also allows a consistent interpretation of all spectroscopic data. The complex possesses $Mo(CO)_3$ groups with local C_{3v} symmetry. The two infrared-active CO stretches are thus the A_1 and E modes in this idealized symmetry. Even the molecular symmetry of the entire molecule, C_{3h}, yields only two infrared-active vibrations, A'' and E'. There are no bridging carbonyls, and the tentative conclusion offered above for the low terminal C–O frequencies is correct: each carbonyl is trans to a purely σ-donor ligand. C_{3h} symmetry results in equivalence of the six carbonyl carbons as well as the three phosphorus nuclei and the three imine protons; no fluxional process is needed to explain the spectroscopic results. The high electron density on carbon which results from extensive back-bonding also is the origin of the unusually low ^{13}C chemical shift.[16]

From its inception, this work sought an explanation for the vibrational band characteristic of a P–N single bond. The presence of a bridging nitrogen in the crystal structure clarifies this point. Each nitrogen is bound to two molybdenum atoms, phosphorus, and (nmr evidence) a proton.[17] This implies sp^3 hybridization at nitrogen (IIa) with no contribu-

tion from the double-bonded (IIb) form of the phosphinimine.[18] That is, in the complex $Mo_2(CO)_6(\mu\text{-}Ph_3PNH)_3$, Ph_3PNH exists entirely as the dipolar or zwitterionic valence-bond form IIa. The phosphonium–amide structure possesses the P–N single bond required by the infrared data. As a result of the zwitterionic nature of the phosphinimine in this complex, the bridging nitrogen is unique in functioning as a four-electron donor atom. This contrasts with bridging amide and phosphide groups, where the distinction between three- (III) and four-electron (IV) donation is only a matter

$$Ph_3\overset{+}{P}-\overset{..}{\underset{..}{N}}-H \qquad\qquad Ph_3P=N\overset{\displaystyle H}{\diagup}$$

$$\text{IIa} \qquad\qquad\qquad\qquad \text{IIb}$$

$$
\begin{array}{ccc}
R\diagdown & & \diagup R \\
 & E & \\
M^0\diagup & \diagdown & \diagdown M^0 \\
 & E & \\
R\diagup & & \diagdown R \\
 & \text{III} &
\end{array}
\qquad\qquad
\begin{array}{ccc}
R\diagdown & & \diagup R \\
 & E & \\
M^+\diagup & \diagdown & \diagdown M^+ \\
 & E & \\
R\diagup & & \diagdown R \\
 & \text{IV} &
\end{array}
$$

of convention.[19,20] As a result, the complex is electronically

(16) O. A. Gansow, B. Y. Kimura, G. R. Dobson, and R. Brown, *J. Amer. Chem. Soc.*, **93**, 5922 (1971).

(17) A referee has suggested the P–N distances may indicate two deprotonated $Ph_3P=N$ ligands and a single Ph_3PNH. The proton nmr data are inconsistent with this proposal. Given the large esd's, the P–N distances do not differ significantly.

(18) Form IIb presumably predominates in *cis*-$Mo(CO)_4(Ph_3PNH)_2$, where the phosphinimine is monodentate.

(19) M. Kilner, *Advan. Organometal. Chem.*, **10**, 115 (1972).

(20) R. G. Little and R. J. Doedens, *Inorg. Chem.*, **11**, 1392 (1972), and references therein.

similar to $W_2(CO)_6(\mu\text{-}OH)_3{}^{3-}$ [21] and $Mn_2(CO)_6(\mu\text{-}N_3)_3{}^-$,[22] with the exception that the phosphonium moieties in $Mo_2\text{-}(CO)_6(\mu\text{-}Ph_3PNH)_3$ function as the counterions. Coordinative saturation is achieved without a metal–metal bond; each molybdenum is bonded to six two-electron donors.

The structural formulation found here nicely accounts for Bock and tom Dieck's failure to isolate an analogous complex of $Ph_3P=CHCH_3$. This ylide possesses only one lone pair in the dipolar form, making bridging impossible.

The proton nmr (220 MHz) of the phenyl protons of $Mo_2(CO)_6(\mu\text{-}Ph_3PNH)_3$ in $CDCl_3$ consists of a poorly resolved multiplet upfield of a well-resolved 1:1:1:1 quartet (Figure 1). This is an unusual pattern for a triphenylphosphine group. Integration of the quartet against the imine proton doublet demonstrates that the quartet is due to two protons per Ph_3PNH. This again is unusual and implies two rings are fundamentally different from the third on a given Ph_3P group. In the solid state the complex closely approaches C_{3h} symmetry, even when the phenyl rings are considered. The phenyl rings may be idealized to two types: six (R_2, R_3, R_4, R_6, R_7, R_8) lie off the idealized mirror plane and three (R_1, R_5, R_9) are bisected by this same plane. Each of the latter three is positioned in a V-shaped "pocket" formed by a pair of rings of the former kind (Figure 4). This relationship holds for a given ring (*e.g.*, R_1) with the rings on the same phosphorus (R_2 and R_3) as well as with the more distant pair (R_4 and R_6). The local magnetic field generated by ring currents in this "pocket" is apparently responsible for resolving the resonance of two protons of a given Ph_3PNH ligand. It can be seen that R_1 in particular lies in the de-shielding region of R_2 and R_3, consistent with the chemical shift observed in solution for the unique pairs of Ph_3P protons on the molybdenum dimer. We suggest that dissolution of the molybdenum dimer yields a time-averaged structure for R_1, R_5, and R_9 similar to that found for R_1 with respect to R_2 and R_3 in the solid state. Since ortho protons appear as a doublet on monosubstituted phenyl groups, the observed quartet is assigned to the ortho protons of these three phenyl groups further split by ^{31}P. Consistent with this, we find that irradiation at the ^{31}P frequency which collapses the imine proton doublet also collapses this phenyl quartet to a doublet (Figure 1). This entire argument assumes highly hindered rotation of the Ph_3P group about the PN bond in solution; Figures 3 and 4 make this conclusion plausible.

The separation of the molybdenum atoms is 3.354 (6) Å. This distance is slightly longer than the 3.22 Å for a single covalent bond based on a value of 1.61 Å for the covalent radius of zerovalent molybdenum.[23] However, the 3.354 Å is only slightly longer than the Mo–Mo distances in the following compounds: 3.265 Å in $(i\text{-}C_3H_7)(CH_3)_2C_{10}H_5Mo_2\text{-}(CO)_6$,[24] 3.22 Å in $[\pi\text{-}C_5H_5Mo(CO)_3]_2$,[23] and 3.262 Å in $[(C_5H_5)_2Mo_2H\{P(CH_3)_2\}(CO)_4]$.[25]

The large esd's in this study preclude any detailed comparison of distances determined here with those in related complexes. The most appropriate reference compound is *cis*-(diethylenetriamine)molybdenum tricarbonyl.[26] Although not statistically significant, the Mo–N and Mo–C

distances in the molybdenum dimer are nominally longer and shorter, respectively, than in *cis*-(dien)Mo(CO)$_3$. This is as expected. The large esd's for the P–N distance frustrate any attempt at determining a P–N bond order, since P–N bonds of multiplicity 1 and 2 differ by only 0.03 Å.[27]

The Mo–N–P angles in the dimer (Table VI) range from 120.5 (15) to 127.8 (15)°. If the ligand itself contains sp^2 nitrogen before reaction, the angle $H-N=P$ is expected to be approximately 120° with some distortion due to lone pair–bond pair repulsions. The angle is 124.2° in $Ph_3P=NC_6\text{-}H_4Br$[28] and 119.1° in $Ph_2FP=NMe$.[29] Rehydridization to sp^3 as nitrogen becomes four-coordinated should decrease this angle. This change is not observed. However, the Mo_1-N-Mo_2 angles, which average 88.9 (22)°, also deviate from 109.5°. This acute angle may yield an Mo–N–P angle of ~120° as a result of some intermediate hybridization.

This last structural feature, the acute Mo_1-N-Mo_2 angle (88.9°) deserves comment. This parameter must also be considered in light of the Mo···Mo distance which is almost as short as authentic metal–metal bonds (see above). The angles in Table VI show that the octahedra in the molybdenum dimer are elongated along the $Mo_1···Mo_2$ line. Such a distortion is characteristic of repulsion between metal atoms.[30] Indeed, no metal–metal bond is required in the dimer as we have formulated it. However, in a triply bridged molecule there are some obvious constraints placed upon the metal–metal separation. Since angle bending is energetically less costly than bond stretching, the most accommodating structural parameters are expected to be the angles Mo_1-N-Mo_2 and N–Mo–N. Assuming Mo–N bond lengthening is not a feasible mechanism for relieving $Mo_1···Mo_2$ repulsions, the only alternative is to compress angles at Mo and enlarge them at N; this elongates the octahedra and decreases the length of the sides of the triangle formed by N_1, N_2, and N_3. This latter effect introduces nonbonded repulsions between nitrogen atoms, as well as repulsions between Ph_3P groups on different nitrogen atoms; these, in turn, will cause the $Mo_1···Mo_2$ distance to equilibrate at some value shorter than a true nonbonding distance. The net result is that nonbonded repulsions between bridging groups are minimized while the Mo_1-N-Mo_2 angle is still acute. There is substantial precedent for claiming that the 88.9° Mo_1-N-Mo_2 angle observed here is indeed normal for a bridge between nonbonded metals in pseudooctahedral structures. Numerous structures of the type $[Fe(CO)_3NR_2]_2$, where Fe–Fe distances average 2.5 Å, exhibit Fe–N–Fe' angles of 72–74°.[19,20] The conclusion of a general survey[31] of metal–metal separations in dimers is that the angle M–B–M (B is the bridging atom) is the best criterion for the presence or absence of metal–metal bonds. On the scale established there, 88.9° does not imply metal–metal bonding. Finally, the nonbonding N···N distances in the molybdenum dimer deserve comment. Nonbonded distances between nitrogen atoms of the azide bridges in $Pd_2(N_3)_6{}^{2-}$[32] and $Mn_2(CO)_6(N_3)_3{}^-$[22] are 2.49 and 2.6 Å, respectively. The relative constancy of this value through changes in stereochemistry[33] suggests this may

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(33) The metal–metal separations also change markedly: Pd···Pd = 3.14 Å; Mn···Mn = 2.89 Å.

represent a true minimum N···N separation. The average N···N separation of 2.96 Å in the molybdenum dimer greatly exceeds this minimum distance, indicating repulsions between PPh₃ moieties probably dictate the equilibrium Mo–N–Mo angle and Mo₁···Mo₂ distance; the threefold symmetric arrangement of the PN bonds is also determined by PPh₃···PPh₃ repulsions. This is clearly shown in Figure 3. We summarize our position as follows: a metal–metal bond produces short metal–metal separations, but a short metal–metal separation does not necessarily imply the existence of a metal–metal bond. We therefore conclude the $Mo_2(CO)_6$-$(\mu$-$Ph_3PNH)_3$, $Mn_2(CO)_6(N_3)_3^-$, and $W_2(CO)_6(OH)_3^{3-}$ all lack bonding metal–metal interactions.

The erroneous formulation of this complex as $Mo_2(CO)_6$-$(Ph_3PNH)_4$ is solely the result of low molybdenum analyses. This also accounts for the CO:Mo ratio of 7:2 determined in the course of this work. When our CO evolution data (4.78 mmol of CO/g of complex) are recalculated using the actual molecular weight (1191), one finds 5.7 mmol of CO/mmol of dimer. Colorimetric assay by the original workers[2] and on our samples yielded 12.46, 12.47, 12.65% Mo. An atomic absorption determination on a sample prepared here yielded 14.87% Mo. When the structure determination was complete and the true molybdenum content known, a gravimetric (lead molybdate) procedure yielded 15.16% Mo. It is curious that the content of massive ligand was in error, while the normally difficult CO assay was correct as originally formulated. Structure I suggested earlier was, of course, based on the erroneous molybdenum analyses. The problem was compounded because this is not a simple hexacarbonyl substitution product; the phosphonium–amide functionality is without precedent, making it impossible to determine the molecular formula by analogy to known compounds. Hindsight shows that vapor pressure osmometric molecular weight

determinations carried out in this study were accurate for $Mo_2(CO)_6(\mu$-$Ph_3PNH)_3$, but these were discounted as being "low" due to ligand dissociation and/or decomposition. Attempts to obtain a mass spectrum yielded only fragments of Ph₃PNH.

The complex as now formulated, $Mo_2(CO)_6(\mu$-$Ph_3PNH)_3$, is in agreement with the inert gas formalism without invoking a metal–metal bond. Each bridging phosphinimine donates four electrons and each CO two for a total of 24 electrons per dimer. This example serves to reinforce Tolman's comment[34] that the burden of proof lies with anyone who claims a violation of the 18-electron rule by more than two electrons.

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Crystal and Molecular Structures of Di-μ-chloro-dichlorobis(cyclopentene)diplatinum(II) and Di-μ-chloro-dichlorobis(cycloheptene)diplatinum(II)

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The crystal and molecular structures of di-μ-chloro-dichlorobis(cyclopentene)diplatinum(II) and the corresponding cycloheptene complex have been determined. Three-dimensional data were collected with Mo Kα radiation on a Syntex *P*Ī diffractometer to a maximum 2θ of 60° employing a θ–2θ scan technique. The compound $[PtCl_2(C_5H_8)]_2$ crystallizes in the orthorhombic space group *Ibam* with a = 9.537 (4) Å, b = 18.703 (7) Å, c = 8.290 (5) Å, and Z = 4. The molecular point group is C_{2h}. The compound $[PtCl_2(C_7H_{12})]_2$ crystallizes in the monoclinic space group $P2_1/c$ with a = 6.035 (2) Å, b = 8.030 (3) Å, c = 19.355 (8) Å, β = 91.03°, and Z = 2. The molecular point group is C_i. All the coordinates and the anisotropic temperature factors of the nonhydrogen atoms were refined in a full-matrix least-squares manner. The final R indices were 0.081 for $[PtCl_2(C_5H_8)]_2$ and 0.093 for $[PtCl_2(C_7H_{12})]_2$. The structures of the cyclic olefin ligands were found to be almost identical with the calculated structures of the free olefins except for slight elongations of the double bonds.

Introduction

The nature of the platinum–olefin bond has been the object of extensive investigation. The presently accepted bonding scheme[1] consists of two parts: a σ bond involving donation of electrons from the filled σ and π molecular orbitals of the

olefin to an empty dsp² hybrid orbital on the platinum and a π bond formed by the back-donation of electrons from a platinum dp hybrid orbital into the empty π* antibonding orbital of the olefin. The relative contribution of the σ and π bonds in the metal–olefin bonding scheme is, however, still the subject of considerable controversy.

X-Ray studies of Zeise's salt, KPtCl₃(C₂H₄)·H₂O, have

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