

Neutron Diffraction Studies of the Metal-Hydrogen-Metal Bond. I. The Symmetric, Bent, Three-Center, Two-Electron Molybdenum-Hydrogen-Molybdenum Bond in  $\mu$ -Hydrido- $\mu$ -dimethylphosphido-bis( $\eta^5$ -cyclopentadienyldicarbonylmolybdenum),  $\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_4(\mu_2\text{-H})(\mu_2\text{-P}(\text{CH}_3)_2)^1$

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**Abstract:** A neutron diffraction investigation of  $\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_4(\mu_2\text{-H})(\mu_2\text{-P}(\text{CH}_3)_2)$  has corroborated the proposed location in this complex of a hydrogen atom symmetrically bridging two metal atoms (deduced indirectly from an earlier X-ray diffraction determination of the nonhydrogen positions). The first direct, definitive evidence is provided that the hydrogen nucleus in a three-center, electron-pair M-H-M bond of a transition metal complex can be symmetrically located between the two metal atoms in an "effectively" single-minimum potential well. The molecular configuration possesses a pseudo-twofold axis which passes through the bridging phosphorus and hydrogen atoms that link the two analogous  $\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2$  moieties to each other. The bridging hydrogen atom within the bent Mo-H-Mo system of angle  $122.9(2)^\circ$  is essentially equidistant (*viz.*, 1.851(4) and 1.869(4) Å) from the two molybdenum atoms. The bridging phosphorus atom shows a greater indication of a slight asymmetry as given by the two Mo-P bond lengths of 2.432(3) and 2.411(3) Å being different by  $5.3\sigma$ . The fact that the Mo-Mo distance of 3.267(2) Å is only slightly longer than the electron-pair Mo-Mo bond of 3.235(1) Å in the structurally related  $\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_6$  molecule is in harmony with extensive metal-metal bonding character being present in the bent three-center, two-electron Mo-H-Mo bond. Our conclusion that the hydrogen nucleus is in a single-minimum potential well rather than in a double-minimum potential well is based on a detailed analysis of the sizes, shapes, and orientations of the determined atomic thermal ellipsoids of the planar  $\text{Mo}_2\text{HP}$  ring. Although the cyclopentadienyl C-C distances range from 1.377(4) to 1.428(5) Å for one ring and from 1.398(4) to 1.421(4) Å for the other ring, the five cyclopentadienyl carbon atoms in each ring are coplanar within 0.003 Å; however, several hydrogen atoms in each ring were found to be significantly displaced above the ring carbon plane away from the coordinated molybdenum atom. The compound crystallizes with four molecules in a triclinic unit cell of symmetry  $C\bar{1}$  with  $a = 9.192(11)$  Å,  $b = 16.631(20)$  Å,  $c = 11.592(14)$  Å,  $\alpha = 93.06(6)^\circ$ ,  $\beta = 97.56(7)^\circ$ ,  $\gamma = 90.68(9)^\circ$ , and  $V = 1753.9$  Å<sup>3</sup>. Anisotropic least-squares refinement (on  $F_o^2$ ), including an isotropic secondary-extinction correction, gave  $R(F_o^2) = 0.094$  [ $\sigma_1 = 1.15$ ] for all 3484 independent reflections (of which 3034 had non-zero intensity) and  $R(F_o^2) = 0.076$  for data with  $F_o^2 > 1.5\sigma(F_o^2)$  [ $\sigma_1 = 1.34$ ], where  $\sigma_1$  is the standard deviation of an observation of unit weight. Intensities were measured out to  $(\sin \theta)/\lambda = 0.619$  by counter methods at the CP-5 reactor of Argonne National Laboratory.

Although the field of (transition metal)-hydride cluster chemistry has grown immensely in the past decade, detailed structural information about the nature of hydrogen bonding in these complexes has been extremely limited. In even the most precise X-ray studies where the hydrogen atoms were unambiguously located and refined by least squares, the estimated standard deviations of the M-H distances have ranged from 0.1 to 0.2 Å, and in none of these studies has it been possible to obtain physically meaningful thermal ellipsoids.<sup>3</sup> The reasons for the intrinsically severe limitations of X-ray diffraction compared to neutron diffraction in determining accurate hydrogen positions (and meaningful thermal motions) have been given elsewhere.<sup>4,5</sup> The immensely superior power of

neutron diffraction in hydrogen bonding studies is clearly displayed in the recent structural determination by Williams and Schneemeyer<sup>6</sup> of *p*-toluidinium bifluoride in which the asymmetric crystal environment about the  $(\text{HF}_2)^-$  anion was shown to produce a highly asymmetric location of the bridging hydrogen atom in contradistinction to the previously accepted notion that this shortest and strongest hydrogen-bonded system was invariably of a symmetrical (centered) nature in all salts.

We undertook a single-crystal neutron diffraction investigation of  $\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_4(\mu_2\text{-H})(\mu_2\text{-P}(\text{CH}_3)_2)^7$  in order to determine precisely the location and thermal motion of the bridging hydrogen atom. Our selection of this molecular compound was a consequence of its earlier X-ray diffraction study by Doedens and Dahl<sup>8</sup> (*via* three-dimensional photographic data from which

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(2) (a) University of Wisconsin. (b) Argonne National Laboratory.

(3) (a) B. A. Frenz and J. A. Ibers in "Transition Metal Hydrides," E. L. Muetterties, Ed., Marcel Dekker, New York, N. Y., 1971, pp 33-74; (b) H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, **72**, 231 (1972); (c) H. D. Kaesz, *Chem. Brit.*, **9**, 344 (1973); (d) S. W. Kirtley, J. P. Olsen, and R. Bau, *J. Amer. Chem. Soc.*, **95**, 4532 (1973), and references cited therein.

(4) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, New York, N. Y., 1968.

(5) (a) M. R. Churchill, *Inorg. Chem.*, **12**, 1213 (1973); (b) A. L. MacDonald, J. C. Speakman, and D. Hadži, *J. Chem. Soc., Perkin Trans. 2*, 825 (1972).

(6) J. M. Williams and L. F. Schneemeyer, *J. Amer. Chem. Soc.*, **95**, 5780 (1973).

(7) R. G. Hayter, *Inorg. Chem.*, **2**, 1031 (1963).

(8) R. J. Doedens and L. F. Dahl, *J. Amer. Chem. Soc.*, **87**, 2576 (1965).

the coordinates of the nonhydrogen atoms were determined) which furnished the first evidence for the existence of symmetric three-center, electron-pair M–H–M bonds (without the additional invoking of separate M–M bonds) in transition metal complexes. On the basis that the metal-coordinated hydrogen atom occupies a distinct coordination site, they<sup>8</sup> concluded from the two similar localized molybdenum environments that the hydrogen atom was equally associated with both molybdenum atoms; furthermore, from the close resemblance of the molybdenum coordination in  $\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_4(\mu_2\text{-H})(\mu_2\text{-P}(\text{CH}_3)_2)$  with those in related complexes, they estimated the probable position of the bridging hydrogen atom at a regular coordination site located at 1.8 Å from each molybdenum atom.

The three-center, electron-pair bonding representation of a M–H–M system was subsequently extended to the  $[\text{Cr}_2(\text{CO})_{10}(\mu_2\text{-H})]^-$  anion which was shown from an X-ray determination<sup>9</sup> to represent the first example of a linearly protonated metal–metal bond.<sup>10–15</sup> At that time it was pointed out,<sup>9a</sup> from analogy to the previous arguments utilized by Ibers<sup>4,16</sup> for O–H–O and F–H–F systems, that this bridging hydrogen atom lying on a crystallographic center of symmetry may be either truly equidistant from the two symmetry-equivalent metal atoms (corresponding to its being in a symmetric single-minimum potential well) or statistically symmetrical (or time averaged) owing to its being randomly distributed in one or two equivalent sites displaced from the center but still bonding at any instant to both metal atoms (corresponding to its being in a symmetric double-minimum potential well). This difficulty of being able to distinguish between a single-minimum and double-minimum potential well for a crystallographically symmetric bridging hydrogen atom was later elaborated in detail by Doedens, Robinson, and Ibers<sup>17</sup> in connection with their X-ray structural

determination of  $\text{Mn}_2(\text{CO})_8(\mu_2\text{-H})(\mu_2\text{-P}(\text{C}_6\text{H}_5)_2)$  for which the hydrogen atom was directly located from a difference Fourier map on a crystallographic twofold axis such that the molecule possesses the predicted geometry with a “bent” Mn–H–Mn linkage. The same symmetry problem arises in the case of  $\text{Mn}_3(\text{CO})_{10}(\text{B}_2\text{H}_6)(\mu_2\text{-H})$  for which an X-ray diffraction analysis<sup>18</sup> revealed from difference Fourier maps the positions of all independent hydrogen atoms with a crystallographic mirror plane passing through the hydrogen atom of the “bent” Mn–H–Mn system.

It was decided that the  $\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_4(\mu_2\text{-H})(\mu_2\text{-P}(\text{CH}_3)_2)$  complex was best suited for a further crystallographic examination by neutron diffraction in order to assess whether a symmetric single-minimum hydrogen bond can be differentiated from a statistically symmetric double-minimum one under favorable circumstances. The X-ray work<sup>8</sup> on this compound showed no indication of any crystal order–disorder phenomenon for the determined nonhydrogen atoms (*i.e.*, the cyclopentadienyl carbon atoms were found to be thermally well behaved); also, the observation that the two molybdenum atoms are chemically but *not* crystallographically related to each other avoids the intrinsic uncertainty problem encountered<sup>4,19</sup> in an accurate location of the hydrogen atom by diffraction methods when special crystallographic site symmetry is imposed at the hydrogen atom.

This investigation by neutron diffraction of a M–H–M system<sup>20</sup> not only has substantiated the proposed location of the hydrogen atom deduced<sup>8</sup> from the X-ray diffraction examination but also, from an analysis of the determined thermal ellipsoid of the bridging hydrogen atom relative to those of the other atoms, has afforded convincing evidence of prime theoretical and experimental significance that the hydrogen atom resides in a single-minimum potential well which is “effectively” symmetric. In addition, this precise structural determination of the positions and thermal motions of the hydrogen nuclei has provided a bonus in furnishing significant information about the geometrical consequences of an interaction of a transition metal with a  $\pi$ -cyclopentadienyl ring.

## Experimental Section

**Crystal Preparation.** Several crystals of  $\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_4(\mu_2\text{-H})(\mu_2\text{-P}(\text{CH}_3)_2)$  were grown from benzene–hexane mixtures by slow evaporation of solvent from saturated solutions of the material placed in a  $\text{N}_2$ -filled desiccator over magnesium perchlorate. Upon saturation of the solution, several seed crystals were added

(9) (a) L. B. Handy, P. M. Treichel, L. F. Dahl, and R. G. Hayter, *J. Amer. Chem. Soc.*, **88**, 366 (1966); (b) L. B. Handy, J. K. Ruff, and L. F. Dahl, *ibid.*, **92**, 7312 (1970).

(10) Although the position of the bridging hydrogen atom in the  $[\text{Cr}_2(\text{CO})_{10}(\mu_2\text{-H})]^-$  monoanion, which has an idealized tetragonal  $D_{4h}$  geometry and crystallographic  $C_{2v}$  site symmetry in the tetraethylammonium salt, was not directly revealed in the X-ray diffraction examination, there is *no doubt* of its being located between and bonded to the metal atoms along the fourfold axis. A typical transition metal bonded hydrogen proton nmr is observed for this ion,  $\tau$  29,<sup>11a</sup> and nearly exact octahedral-like coordination of the carbonyl groups about each metal atom leaves the metal–metal axis as the only remaining coordination site. In addition, the equivalent association of the hydrogen atom with both tungsten atoms in the corresponding  $[\text{W}_2(\text{CO})_{10}(\mu_2\text{-H})]^-$  monoanion was shown from the relative intensity bands of the triplet components of the high-field proton resonance peak.<sup>11,12</sup>

(11) (a) R. G. Hayter, *J. Amer. Chem. Soc.*, **88**, 4376 (1966); (b) U. Anders and W. A. G. Graham, *Chem. Commun.*, 499 (1965).

(12) Whereas both the molecular  $\text{CrRe}(\text{CO})_{10}(\mu_2\text{-H})$  compound<sup>13</sup> and the  $[\text{Cr}_2(\text{CO})_{10}(\mu_2\text{-H})]^-$  monoanion (structurally characterized as the tetraethylammonium salt)<sup>9</sup> were found from X-ray diffraction investigations to possess linear M–H–M fragments, the structure of the  $[\text{W}_2(\text{CO})_{10}(\mu_2\text{-H})]^-$  monoanion in the crystalline state with the bis(tri-phenylphosphine)iminium counterion was shown unexpectedly from two independent X-ray crystallographic examinations<sup>14,15</sup> to have a nonlinear W–H–W geometry (based on an octahedral-like coordination of the five carbonyl ligands and the bridging hydrogen atom about each metal atom).

(13) A. S. Foust, W. A. G. Graham, and R. P. Stewart, Jr., *J. Organometal. Chem.*, **54**, C22 (1973).

(14) S. Graham and R. Bau, private communication to L. F. Dahl, April 1974.

(15) J. L. Petersen, J. P. O'Connor, J. K. Ruff, and L. F. Dahl, unpublished research, 1974.

(16) (a) B. L. McGaw and J. A. Ibers, *J. Chem. Phys.*, **39**, 2677 (1963); (b) J. A. Ibers, *ibid.*, **41**, 25 (1964).

(17) R. J. Doedens, W. T. Robinson, and J. A. Ibers, *J. Amer. Chem. Soc.*, **89**, 4323 (1967).

(18) H. D. Kaesz, W. Fellmann, G. R. Wilkes, and L. F. Dahl, *J. Amer. Chem. Soc.*, **87**, 2753 (1965).

(19) J. C. Speakman, *Struct. Bonding (Berlin)*, **12**, 166 (1972).

(20) Since the completion of this work, we have learned that neutron studies of two crystalline modifications of  $\text{W}_2(\text{CO})_8(\text{NO})(\mu_2\text{-H})$  have been carried out (J. P. Olsen, R. Bau, S. W. Kirtley, and T. F. Koetzle, Abstracts of the American Crystallographic Association, Berkeley, Calif., March 24–28, 1974). Its molecular geometry, which is analogous to both crystalline phases, possesses a nonlinear W–H–W framework with each tungsten atom being in a localized octahedral-like environment. The two crystal structures are each disordered with the nitrosyl ligand occupying the axial position trans to the bridging hydrogen atom. The two orientations of a given molecule are related to each other by a twofold axis passing through the bridging hydrogen atom. This twofold axis is crystallographically required in the monoclinic structure but not in the triclinic structure in which the bent W–H–W system is still experimentally symmetric. The reported W–W and W–H distances are 3.329 (3) and 1.873 (3) Å, respectively, while the W–H–W bond angle is 125.5 (4)°.

to the solution to initiate crystallization. This procedure yielded well-formed, deep-red crystals with dimensions of 2–3 mm on a side.

**Unit Cell and Space Group.** Since Doedens and Dahl<sup>9</sup> reported their X-ray diffraction results in terms of a nonstandard C-centered triclinic cell of centrosymmetric symmetry  $C\bar{1}$  rather than the reduced triclinic primitive cell (on account of the three interaxial angles being much closer to 90°), we have elected to use the same cell for data collection and subsequent calculations. The lattice parameters for the  $C\bar{1}$  cell were determined from 29 intense reflections ranging in  $2\theta$  from 40 to 60°. A least-squares fit of the angles  $2\theta$ ,  $\chi$ , and  $\phi$  of these reflections, measured at 22° with a neutron wavelength of 1.142 (1) Å, produced  $a = 9.192$  (11) Å,  $b = 16.631$  (20) Å,  $c = 11.592$  (14) Å,  $\alpha = 93.06$  (6)°,  $\beta = 97.56$  (7)°,  $\gamma = 90.68$  (9)°, and  $V = 1753.9$  Å<sup>3</sup>; these values for the nonprimitive cell are comparable to those given previously.<sup>8</sup> The corresponding parameters for the triclinic reduced  $P\bar{1}$  cell are  $a' = 9.453$  Å,  $b' = 11.592$  Å,  $c' = 9.192$  Å,  $\alpha' = 97.56$ °,  $\beta' = 118.41$ °, and  $\gamma' = 83.63$ °. The base vectors for the  $C\bar{1}$  cell are related to those of the  $P\bar{1}$  cell by the transformation

$$\begin{pmatrix} \mathbf{a}' \\ \mathbf{b}' \\ \mathbf{c}' \end{pmatrix} = \begin{pmatrix} 0.5 & 0.5 & 0 \\ 0 & 0 & -1 \\ -1 & 0 & 0 \end{pmatrix} \begin{pmatrix} \mathbf{a} \\ \mathbf{b} \\ \mathbf{c} \end{pmatrix}$$

The experimental density of 1.89 g cm<sup>-3</sup> (flotation method) agrees well with the calculated value of 1.88 g cm<sup>-3</sup> based on four molecules in the C-centered cell (or two molecules per reduced primitive cell).

**Data Collection.** A well-formed crystal of approximate dimensions 2.6 × 2.0 × 3.5 mm and weighing 17.05 mg was sealed in a lead-glass capillary for data collection. The crystal was mounted in a general orientation on an Electronics-and-Alloys four-circle diffractometer at the CP-5 reactor. This fully automated diffractometer is controlled with a Sigma V computer via a locally developed operation package.<sup>21</sup> A monochromatic neutron beam is produced by reflection from the (110) plane of a Be crystal at a monochromator angle of  $\theta_m = 30$ °. Calibration of the neutron wavelength of 1.142 (1) Å was made with two standard cubic crystals: NaCl ( $a = 5.6397$  Å) and Si ( $a = 5.4308$  Å) at 22 ± 2°. Measurements of the neutron flux at the sample position with calibrated Au foils yielded an intensity of 2.9 × 10<sup>6</sup> n cm<sup>-2</sup> sec<sup>-1</sup>, which is comparable to that available at even the highest flux U. S. research reactors.

From the orientation matrix calculated from three reflections, 29 intense reflections (40° < 2θ < 60°) were automatically centered<sup>22</sup> in the neutron detector, and the determined angles were used in a least-squares refinement to yield an improved orientation matrix for data collection. Data were automatically taken by the  $\theta$ - $2\theta$  step-scan method out to (sin θ)/λ = 0.619 with 0.1° step intervals and preset scan ranges of 55–75 steps. Background intensity measurements were obtained on both sides of each peak with the crystal and the counter simultaneously being stationary.

The intensities of 3578 reflections were measured at 22 ± 2° from four independent octants of the reciprocal lattice. Some equivalent reflections were purposely duplicated during data collection, and their integrated intensities were averaged to give 3484 independent reflections of which 3034 had nonzero intensity.<sup>23</sup> The reference reflections were repeated after every 40 reflections to monitor instrument stability and crystal alignment; their integrated intensities did not vary more than 2% during the entire data collection. The observed integrated intensity of each reflection was corrected for absorption ( $\mu = 1.708$  cm<sup>-1</sup>), for which the minimum and maximum transmission coefficients were 0.695 and 0.785, respectively. The  $F_o^2$  were obtained from the absorption-corrected integrated intensities  $I$  by application of the following equation<sup>24</sup>  $F_o^2 = (\omega I \sin 2\theta) / (I_0 \lambda^3 N^2 V)$  where  $I_0$  is the incident intensity,  $\lambda$  the wavelength,  $\omega$  the angular velocity of rotation of the crystal,  $N$  the number of unit cells per unit volume,  $V$  the specimen volume, and  $\theta$  the Bragg angle. A well-characterized

(21) P. Day and J. Hines, *Operating Systems Rev.*, **7**, 28 (1973).

(22) This routine was developed by Dr. A. Zielen of the ANL Chemistry Division.

(23) No reflections were rejected on the grounds that they were not significantly above background. A negative intensity obtained for any reflection was reset to zero; the retention of its negative value in least-squares refinements has been advocated recently by others (cf. F. L. Hirshfeld and D. Rabinovich, *Acta Crystallogr., Sect. A*, **29**, 510 (1973)).

(24) S. W. Peterson and H. A. Levy, *J. Chem. Phys.*, **20**, 704 (1952).

NaCl crystal, for which precise absorption and secondary-extinction corrections had been made for all sampled reflections, was used to obtain  $I_0$  and thereby place the  $F_o^2$  on an initial absolute scale. The variances of  $F_o^2$  were calculated from  $\sigma^2(F_o^2) = \sigma_c^2(F_o^2) + (0.02F_o^2)^2$ , where  $\sigma_c^2(F_o^2)$  is determined from the counting statistics and 0.02 is an added factor (often considered an arbitrary coefficient<sup>25</sup>) deduced from the 2% maximum variation in the integrated intensities of the reference reflections.

**Hydrogen Atom Location and Structure Refinement.** A full-matrix least-squares refinement<sup>26,27</sup> was performed on the non-hydrogen atomic coordinates obtained from the X-ray diffraction analysis with isotropic temperature factors and a scale factor set at unity.<sup>28</sup> At this stage the discrepancy indices<sup>29</sup> were  $R(F_o) = 0.37$ ,  $R(F_o^2) = 0.48$ , and  $R_w(F_o^2) = 0.52$  for all data. The 17 hydrogen atoms located from a Fourier map of nuclear scattering density were included along with the scale factor as variables in a further isotropic least-squares refinement which reduced  $R(F_o)$  to 0.25,  $R(F_o^2)$  to 0.28, and  $R_w(F_o^2)$  to 0.27. At this point an isotropic secondary extinction parameter<sup>30,31</sup> was introduced in the refinement together with anisotropic thermal parameters for all atoms. After two cycles of full-matrix least-squares refinement (matrix setup time per cycle was 35 sec on the ANL IBM 360/195 for 3484 observations and 362 varied parameters), convergence was complete. The final change-to-esd ratio was 0.01 for most parameters with the maximum ratio being 0.05. The extinction correction factors ranged from 1.0 to 1.4 with an isotropic extinction coefficient ( $g$ ) of 0.23 (1).<sup>30</sup> The final scale factor ( $S$ ) was 0.778 (2), while the standard deviation of an observation of unit weight (Table I) was 1.15 for all 3484 independent reflections (Table I).

**Table I.** Final Discrepancy Indices

Data selection	No. of reflections	$R(F_o)$	$R(F_o^2)$	$R_w(F_o^2)$	$\sigma_1^a$
All reflections	3484	0.128	0.094	0.083	1.15
Reflections with $F_o^2 > 1.0\sigma$	2558	0.080	0.082	0.079	1.31
Reflections with $F_o^2 > 1.5\sigma$	2318	0.068	0.076	0.077	1.34

<sup>a</sup> $\sigma_1$ , the standard deviation of an observation of unit weight, is defined by  $[\sum w_i |F_o^2 - F_c^2| / (n - p)]^{1/2}$  where  $w_i^{-1} = \sigma^2(F_o^2) = \sigma_c^2(F_o^2) + (0.02F_o^2)^2$ , where  $\sigma_c$  is determined by counting statistics,  $n$  the number of observations, and  $p$  the number of parameters varied (*viz.*, 362) during the least-squares refinement. For appropriately weighted data and normally distributed errors the expected value of  $\sigma_1$  is unity.

A final difference Fourier synthesis was virtually featureless thereby indicating the completeness and correctness of the structural analysis and least-squares refinement. The final discrepancy indices are given in Table I. Positional and anisotropic thermal parameters from the output of the last least-squares cycle are presented in Table II.<sup>32</sup> Interatomic distances and bond angles with

(25) S. W. Peterson and H. A. Levy, *Acta Crystallogr.*, **10**, 70 (1957).J

(26) All least-squares refinements were based on the minimization of  $\sum w_i |F_o^2 - F_c^2|^2$  with the individual weights  $w_i = 1/\sigma^2(F_o^2)$ . The neutron scattering amplitudes used<sup>27</sup> in this study were  $b_{Mg} = 0.697$ ,  $b_P = 0.510$ ,  $b_C = 0.663$ ,  $b_O = 0.580$ , and  $b_H = -0.374$  (all in units of 10<sup>-12</sup> cm).

(27) G. E. Bacon, *Acta Crystallogr., Sect. A*, **28**, 357 (1972).

(28) Since the data were scaled against those from a standard crystal, the scale factor on  $F_o^2$  is approximately 1.0. A refined scale factor was obtained from least squares.

(29)  $R(F_o) = \sum |F_o| - |F_c| / \sum |F_o|$ ,  $R(F_o^2) = \sum |F_o^2 - F_c^2| / \sum F_o^2$ , and  $R_w(F_o^2) = [\sum w_i |F_o^2 - F_c^2|^2 / \sum w_i F_o^4]^{1/2}$ .

(30) The Zachariasen approximation<sup>31a</sup> was used for the overall isotropic  $g$  parameter as defined and scaled by Coppens and Hamilton.<sup>31b</sup> The  $|F_o|$  values were corrected for extinction from the expression  $|F_o|_{corr} = |F_o| (1 + T 2g \lambda^3 |F_o|^2 V^2 \sin 2\theta)^{-1/4}$ , where  $|F_o|$  is on an absolute scale,  $\lambda$  is the wavelength (Å),  $g$  the refined extinction parameter,  $T$  the mean absorption-weighted path length in the crystal in centimeters (calculated simultaneously during the computation of absorption corrections), and  $V$  the unit cell volume (Å<sup>3</sup>).

(31) (a) W. H. Zachariasen, *Acta Crystallogr.*, **23**, 558 (1967); (b) P. Coppens and W. C. Hamilton, *Acta Crystallogr., Sect. A*, **26**, 71 (1970).

(32) For a listing of the observed and calculated structure factors, see paragraph at end of paper regarding supplementary material.

**Table II.** Positional and Thermal Parameters for  $\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_4(\mu_2\text{-H})(\mu_2\text{-P}(\text{CH}_3)_2)$  and Root-Mean-Square Thermal Displacements (in Å) of Atoms along Their Principal Ellipsoidal Axes<sup>a,b</sup>

	10 <sup>4</sup> x	10 <sup>4</sup> y	10 <sup>4</sup> z	10 <sup>4</sup> β <sub>11</sub>	10 <sup>4</sup> β <sub>22</sub>	10 <sup>4</sup> β <sub>33</sub>	10 <sup>4</sup> β <sub>12</sub>	10 <sup>4</sup> β <sub>13</sub>	10 <sup>4</sup> β <sub>23</sub>	10 <sup>3</sup> μ(1)	10 <sup>3</sup> μ(2)	10 <sup>3</sup> μ(3)
Mo(1)	4852 (2)	3362 (1)	2455 (2)	52 (2)	21 (1)	42 (1)	-3 (1)	4 (1)	5 (1)	146 (3)	160 (3)	181 (3)
Mo(2)	8258 (2)	3686 (1)	2045 (1)	60 (2)	19 (1)	40 (1)	0 (1)	14 (1)	3 (1)	144 (3)	163 (3)	173 (3)
P	6693 (3)	4356 (1)	3303 (2)	64 (3)	18 (1)	47 (2)	-4 (1)	11 (2)	-2 (1)	149 (4)	163 (4)	185 (4)
C(1)	3749 (2)	4367 (1)	2428 (2)	71 (2)	28 (1)	57 (2)	11 (1)	2 (2)	-1 (1)	160 (3)	190 (3)	218 (3)
O(1)	3067 (3)	4943 (2)	2396 (3)	122 (4)	37 (1)	104 (3)	31 (2)	-9 (3)	-8 (2)	169 (4)	237 (4)	303 (4)
C(2)	4295 (2)	3468 (1)	788 (2)	73 (2)	32 (1)	44 (2)	2 (1)	-6 (2)	3 (1)	154 (3)	195 (3)	213 (3)
O(2)	3915 (3)	3510 (2)	-196 (2)	145 (4)	63 (2)	44 (2)	13 (2)	-16 (2)	6 (1)	157 (4)	257 (4)	302 (4)
C(3)	9577 (2)	3884 (1)	3501 (2)	72 (2)	28 (1)	54 (2)	-7 (1)	-8 (2)	5 (1)	158 (3)	189 (3)	217 (3)
O(3)	10394 (3)	3992 (2)	4335 (3)	113 (4)	53 (2)	76 (3)	-17 (2)	-34 (3)	4 (2)	163 (4)	257 (4)	293 (4)
C(4)	8676 (2)	2589 (1)	2509 (2)	85 (3)	20 (1)	72 (2)	6 (1)	9 (2)	11 (1)	153 (3)	191 (3)	224 (3)
O(4)	8964 (3)	1950 (2)	2780 (3)	151 (5)	25 (1)	148 (4)	18 (2)	6 (3)	22 (2)	156 (4)	262 (4)	322 (4)
C(5)	7108 (3)	4373 (2)	4891 (2)	124 (4)	47 (1)	41 (2)	-19 (2)	17 (2)	-13 (1)	152 (4)	208 (4)	283 (3)
C(6)	6475 (3)	5436 (1)	3129 (3)	123 (4)	19 (1)	109 (3)	2 (2)	41 (3)	-3 (1)	160 (4)	209 (4)	281 (3)
C(7)	2963 (3)	2562 (2)	2899 (3)	84 (4)	49 (1)	173 (4)	-15 (2)	36 (3)	41 (2)	148 (4)	244 (4)	364 (4)
C(8)	3869 (3)	2043 (2)	2354 (3)	155 (4)	31 (1)	98 (3)	-28 (2)	9 (3)	12 (1)	165 (4)	252 (4)	290 (4)
C(9)	5199 (3)	2018 (2)	3041 (3)	127 (4)	28 (1)	125 (3)	-8 (2)	23 (3)	25 (1)	160 (4)	237 (4)	301 (4)
C(10)	5181 (4)	2519 (2)	4033 (2)	211 (5)	43 (1)	76 (2)	-39 (2)	-37 (3)	32 (2)	158 (4)	217 (4)	364 (4)
C(11)	3769 (5)	2869 (2)	3966 (3)	327 (8)	37 (1)	112 (3)	-14 (3)	140 (4)	8 (2)	154 (4)	235 (4)	412 (5)
C(12)	10045 (3)	3887 (2)	875 (2)	85 (3)	51 (1)	78 (2)	3 (2)	43 (2)	18 (1)	145 (4)	232 (3)	281 (3)
C(13)	8896 (3)	3467 (2)	161 (2)	170 (4)	36 (1)	60 (2)	-5 (2)	49 (2)	-3 (1)	169 (4)	221 (3)	283 (3)
C(14)	7677 (3)	3965 (2)	36 (2)	113 (4)	70 (2)	49 (2)	-13 (2)	11 (2)	21 (1)	162 (3)	215 (4)	322 (4)
C(15)	8075 (3)	4700 (2)	685 (2)	184 (5)	40 (1)	76 (2)	34 (2)	62 (3)	32 (1)	153 (3)	207 (4)	330 (4)
C(16)	9537 (3)	4646 (2)	1200 (2)	151 (4)	36 (1)	72 (2)	-25 (2)	30 (2)	13 (1)	155 (3)	237 (3)	280 (3)
H(1)	7364 (8)	3786 (5)	5173 (5)	320 (14)	70 (3)	68 (5)	-2 (6)	-9 (6)	23 (3)	196 (7)	317 (8)	376 (8)
H(2)	6169 (7)	4573 (5)	5280 (5)	204 (11)	134 (6)	86 (5)	-2 (6)	65 (6)	-34 (4)	182 (8)	308 (7)	449 (9)
H(3)	8023 (7)	4767 (4)	5203 (5)	222 (10)	82 (4)	88 (5)	-58 (5)	0 (6)	-17 (3)	205 (7)	278 (7)	391 (8)
H(4)	6138 (8)	5566 (3)	2249 (7)	284 (13)	41 (2)	146 (7)	33 (4)	58 (8)	32 (4)	200 (7)	296 (7)	371 (8)
H(5)	7503 (7)	5748 (3)	3421 (7)	193 (9)	30 (2)	213 (9)	-34 (4)	11 (7)	-11 (3)	167 (8)	309 (7)	383 (8)
H(6)	5656 (7)	5678 (3)	3627 (6)	235 (11)	36 (2)	203 (9)	14 (4)	114 (8)	-9 (3)	198 (8)	270 (7)	403 (8)
H(7)	1850 (7)	2681 (5)	2584 (10)	99 (8)	105 (5)	427 (18)	-16 (5)	22 (9)	113 (8)	194 (8)	306 (8)	578 (12)
H(8)	3565 (10)	1728 (4)	1550 (7)	446 (20)	53 (3)	133 (7)	-93 (6)	-35 (9)	8 (4)	195 (8)	293 (8)	487 (10)
H(9)	6108 (9)	1677 (4)	2848 (8)	260 (13)	44 (3)	301 (13)	27 (5)	105 (11)	48 (5)	220 (8)	303 (8)	467 (10)
H(10)	6066 (10)	2604 (5)	4740 (7)	440 (19)	105 (5)	177 (9)	-113 (8)	-173 (11)	88 (6)	204 (8)	275 (8)	595 (12)
H(11)	3389 (14)	3284 (5)	4622 (8)	833 (35)	68 (4)	235 (12)	-15 (10)	386 (19)	-13 (5)	175 (10)	307 (8)	661 (14)
H(12)	11130 (6)	3669 (5)	1098 (6)	121 (8)	104 (4)	162 (8)	29 (5)	66 (6)	43 (5)	194 (7)	296 (7)	410 (8)
H(13)	8948 (9)	2874 (4)	-232 (6)	449 (19)	52 (3)	119 (6)	2 (6)	129 (9)	-22 (4)	194 (9)	297 (7)	453 (9)
H(14)	6638 (7)	3815 (5)	-471 (5)	152 (9)	150 (6)	92 (5)	-41 (6)	-25 (6)	44 (5)	209 (8)	258 (7)	477 (10)
H(15)	7376 (9)	5213 (4)	736 (6)	398 (16)	72 (3)	174 (8)	116 (7)	134 (10)	67 (5)	187 (8)	274 (7)	503 (10)
H(16)	10172 (9)	5116 (4)	1713 (6)	367 (16)	65 (3)	139 (7)	-94 (6)	38 (9)	11 (4)	196 (8)	307 (8)	453 (9)
H(17)	6490 (4)	3102 (3)	1741 (4)	94 (5)	35 (2)	86 (4)	-10 (2)	24 (4)	-13 (2)	186 (5)	198 (6)	270 (5)

<sup>a</sup> The estimated standard deviations in parentheses for this and all subsequent tables refer to the least significant figure. <sup>b</sup> The form of the temperature factor is  $\exp\{-\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl\}$ .

esd's calculated from the variance-covariance matrix are given in Table III. Least-squares planes of interest are provided in Table IV.<sup>33,34</sup>

## Results and Discussion

**General Description of the Crystal and Molecular Structure.** The molecular configuration of  $\mu$ -hydrido- $\mu$ -dimethylphosphido-bis( $\eta$ -cyclopentadienyldicarbonylmolybdenum) is illustrated stereographically in Figure 1, which includes the atom labeling scheme. The arrangement of the four molecules in the centrosymmetric C-centered cell is shown in Figure 2. The molecular packing is assumed to be primarily dictated by van der Waals forces because the closest intermolecular contacts (*viz.*, (methyl)H...H(methyl), 2.27 Å; (Cp)H...H(Cp), 2.48 Å; (Cp)H...H(methyl), 2.65 Å; (Cp)H...OC, 2.77 Å; and CO...OC, 3.42 Å)

(33) The computer programs which were used in performing the necessary calculations, with their accession names in the World List of Crystallographic Computer Programs (3rd ed), are as follows: data reduction and absorption correction, DATLIB; data averaging and sort, DATASORT; Fourier summation, FORDAP; least-squares refinement, ORXLS3; error analysis of distances and angles, ORFFE3, and structural drawings, ORTEP. For determination of least-squares planes the program PLNJO was used.<sup>34</sup>

(34) J.-O. Lundgren, University of Uppsala, Uppsala, Sweden; based on the method of D. Blow, *Acta Crystallogr.*, 13, 168 (1960).

do not indicate any abnormal intermolecular interactions. The positional parameters of the nonhydrogen atoms obtained from the neutron diffraction study are in good agreement with those from the earlier X-ray diffraction determination but expectedly are much more precise.

The determined position of the bridging hydrogen atom, H(17), coincides almost exactly with that previously obtained<sup>8</sup> indirectly from the X-ray analysis and thereby corroborates the viewpoint that the hydrogen atom occupies a distinct coordination site and the molecular configuration possesses a pseudo-twofold axis which passes through the bridging phosphorus and hydrogen atoms that link the two analogous Mo( $\eta^5\text{-C}_5\text{H}_5$ )(CO)<sub>2</sub> moieties to each other. Table III, which gives the intramolecular distances and bond angles averaged according to C<sub>2</sub>-2 symmetry, shows that all corresponding pairs of distances and angles, except possibly those involving the bridging phosphorus and hydrogen atoms, are experimentally equivalent to each other.

The localized environment of the cyclopentadienyl ring, the two carbonyl ligands, and the bridging hydrogen and phosphorus atoms about each molybdenum atom closely resembles that found from X-ray determi-

**Table III.** Interatomic Distances (Å) and Bond Angles (deg) for  $\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_4(\mu_2\text{-H})(\mu_2\text{-P}(\text{CH}_3)_2)$  Averaged on the Basis of Idealized  $\text{C}_2\text{-2}$  Geometry<sup>a,b</sup>

(A) Distances around Molybdenum Atoms			
Mo(1)–Mo(2)	3.267 (2)	Mo(1)–C(8)	2.354 (3)
Mo(1)–H(17)	1.851 (4)	Mo(2)–C(13)	2.341 (3)
Mo(2)–H(17)	1.869 (4)		2.348 (av)
	1.860 (av)	Mo(1)–C(9)	2.384 (3)
Mo(1)–P	2.432 (3)	Mo(2)–C(14)	2.396 (3)
Mo(2)–P	2.411 (3)		2.390 (av)
	2.422 (av)	Mo(1)–C(10)	2.357 (3)
Mo(1)–C(1)	1.964 (3)	Mo(2)–C(15)	2.363 (3)
Mo(2)–C(3)	1.964 (3)		2.360 (av)
	1.964 (av)	Mo(1)–C(11)	2.301 (3)
Mo(1)–C(2)	1.955 (3)	Mo(2)–C(16)	2.301 (3)
Mo(2)–C(4)	1.959 (3)		2.301 (av)
	1.957 (av)	Mo(1)–C <sub>5</sub> H <sub>5</sub> (c) <sup>b</sup>	2.013
Mo(1)–C(7)	2.299 (3)	Mo(2)–C <sub>5</sub> H <sub>5</sub> (c) <sup>b</sup>	2.009
Mo(2)–C(12)	2.288 (3)		2.011 (av)
	2.294 (av)		
(B) Distances within the Dimethylphosphido Group			
P–C(5)	1.832 (3)	C(5)–H(2)	1.070 (7)
P–C(6)	1.829 (3)	C(6)–H(5)	1.074 (7)
	1.831 (av)		1.072 (av)
C(5)–H(1)	1.066 (9)	C(5)–H(3)	1.076 (7)
C(6)–H(4)	1.064 (9)	C(6)–H(6)	1.081 (7)
	1.065 (av)		1.079 (av)
(C) Carbon–Oxygen Distances			
C(1)–O(1)	1.151 (3)	C(2)–O(2)	1.158 (3)
C(3)–O(3)	1.153 (3)	C(4)–O(4)	1.149 (3)
	1.152 (av)		1.154 (av)
(D) Distances within Cyclopentadienyl Rings (Averaged for Each Ring)			
C(7)–C(8)	1.387 (4)	C(12)–C(13)	1.413 (4)
C(8)–C(9)	1.377 (4)	C(13)–C(14)	1.398 (4)
C(9)–C(10)	1.385 (4)	C(14)–C(15)	1.421 (4)
C(10)–C(11)	1.425 (5)	C(15)–C(16)	1.408 (4)
C(7)–C(11)	1.428 (5)	C(12)–C(16)	1.399 (4)
	1.400 (av)		1.408 (av)
C(7)–H(7)	1.068 (8)	C(12)–H(12)	1.072 (7)
C(8)–H(8)	1.050 (9)	C(13)–H(13)	1.069 (7)
C(9)–H(9)	1.056 (9)	C(14)–H(14)	1.077 (7)
C(10)–H(10)	1.083 (8)	C(15)–H(15)	1.078 (7)
C(11)–H(11)	1.091 (9)	C(16)–H(16)	1.077 (8)
	1.070 (av)		1.075 (av)
(E) Angles about H(17), P, and Mo Atoms			
Mo(1)–H(17)–Mo(2)	122.9 (2)	P–Mo(1)–C(2)	112.8 (1)
Mo(1)–P–Mo(2)	84.8 (1)	P–Mo(2)–C(4)	111.1 (1)
			112.0 (av)
P–Mo(1)–H(17)	76.0 (1)	C(1)–Mo(1)–C(2)	77.7 (1)
P–Mo(2)–H(17)	76.3 (1)	C(3)–Mo(2)–C(4)	78.1 (1)
	76.2 (av)		77.9 (av)
H(17)–Mo(1)–C(1)	128.9 (2)	Mo(1)–P–C(5)	115.3 (1)
H(17)–Mo(2)–C(3)	130.5 (2)	Mo(2)–P–C(6)	115.5 (1)
	129.7 (av)		115.4 (av)
H(17)–Mo(1)–C(2)	73.7 (2)	Mo(1)–P–C(6)	122.5 (2)
H(17)–Mo(2)–C(4)	73.4 (2)	Mo(2)–P–C(5)	121.5 (2)
	73.6 (av)		122.0 (av)

Table III (Continued)

P-Mo(1)-C(1)	77.3 (1)	C(5)-P-C(6)	99.1 (2)
P-Mo(2)-C(3)	77.5 (1)	C <sub>5</sub> H <sub>5</sub> (c)-Mo(1)-C(1)	121.5
	77.4 (av)	C <sub>5</sub> H <sub>5</sub> (c)-Mo(2)-C(3)	118.0
C <sub>5</sub> H <sub>5</sub> (c)-Mo(1)-H(17)	109.5		119.8 (av)
C <sub>5</sub> H <sub>5</sub> (c)-Mo(2)-H(17)	111.5	C <sub>5</sub> H <sub>5</sub> (c)-Mo(1)-C(2)	121.2
	110.5 (av)	C <sub>5</sub> H <sub>5</sub> (c)-Mo(2)-C(4)	123.7
C <sub>5</sub> H <sub>5</sub> (c)-Mo(1)-P	125.1		122.5 (av)
C <sub>5</sub> H <sub>5</sub> (c)-Mo(2)-P	124.7		
	124.9 (av)		
(F) Angles around Carbonyl Carbon Atoms			
Mo(1)-C(1)-O(1)	177.9 (2)	Mo(1)-C(2)-O(2)	177.2 (2)
Mo(2)-C(3)-O(3)	177.5 (2)	Mo(2)-C(4)-O(4)	178.0 (2)
	177.7 (av)		177.6 (av)
(G) Angles around Methyl Carbon Atoms			
P-C(5)-H(1)	110.9 (4)	H(1)-C(5)-H(2)	108.0 (6)
P-C(6)-H(4)	112.1 (4)	H(4)-C(6)-H(5)	108.8 (6)
	111.5 (av)		108.4 (av)
P-C(5)-H(2)	109.4 (4)	H(1)-C(5)-H(3)	107.9 (6)
P-C(6)-H(5)	109.5 (4)	H(4)-C(6)-H(6)	106.4 (6)
	109.5 (av)		107.2 (av)
P-C(5)-H(3)	111.7 (4)	H(2)-C(5)-H(3)	108.8 (6)
P-C(6)-H(6)	111.5 (4)	H(5)-C(6)-H(6)	108.3 (5)
	111.6 (av)		108.6 (av)
(H) Angles within Cyclopentadienyl Rings (Averaged for Each Ring)			
C(7)-C(8)-C(9)	108.7 (3)	C(12)-C(13)-C(14)	108.5 (2)
C(8)-C(9)-C(10)	109.8 (3)	C(13)-C(14)-C(15)	107.3 (2)
C(9)-C(10)-C(11)	107.1 (3)	C(14)-C(15)-C(16)	108.2 (2)
C(10)-C(11)-C(7)	106.8 (3)	C(15)-C(16)-C(12)	107.9 (2)
C(11)-C(7)-C(8)	107.6 (3)	C(16)-C(12)-C(13)	108.1 (2)
	108.0 (av)		108.0 (av)
H(7)-C(7)-C(8)	125.3 (7)	H(12)-C(12)-C(13)	125.7 (5)
H(7)-C(7)-C(11)	127.0 (7)	H(12)-C(12)-C(16)	126.2 (5)
H(8)-C(8)-C(9)	126.8 (6)	H(13)-C(13)-C(14)	125.4 (5)
H(8)-C(8)-C(7)	124.5 (6)	H(13)-C(13)-C(12)	126.1 (5)
H(9)-C(9)-C(10)	124.4 (6)	H(14)-C(14)-C(15)	126.8 (5)
H(9)-C(9)-C(8)	125.8 (6)	H(14)-C(14)-C(13)	125.8 (6)
H(10)-C(10)-C(11)	126.9 (7)	H(15)-C(15)-C(16)	126.8 (6)
H(10)-C(10)-C(9)	125.9 (7)	H(15)-C(15)-C(14)	125.0 (6)
H(11)-C(11)-C(7)	127.5 (8)	H(16)-C(16)-C(12)	126.0 (5)
H(11)-C(11)-C(10)	125.7 (8)	H(16)-C(16)-C(15)	126.1 (6)
	126.0 (av)		126.0 (av)
(I) Angles around Cyclopentadienyl Ring Centroid, C <sub>5</sub> H <sub>5</sub> (c)			
C(7)-C <sub>5</sub> H <sub>5</sub> (c)-Mo(1)	87.6	C(10)-C <sub>5</sub> H <sub>5</sub> (c)-Mo(1)	90.7
C(12)-C <sub>5</sub> H <sub>5</sub> (c)-Mo(2)	87.3	C(15)-C <sub>5</sub> H <sub>5</sub> (c)-Mo(2)	91.4
	87.5 (av)		91.1 (av)
C(8)-C <sub>5</sub> H <sub>5</sub> (c)-Mo(1)	91.1	C(11)-C <sub>5</sub> H <sub>5</sub> (c)-Mo(1)	87.5
C(13)-C <sub>5</sub> H <sub>5</sub> (c)-Mo(2)	90.2	C(16)-C <sub>5</sub> H <sub>5</sub> (c)-Mo(2)	87.8
	90.7 (av)		87.7 (av)
C(9)-C <sub>5</sub> H <sub>5</sub> (c)-Mo(1)	93.1		
C(14)-C <sub>5</sub> H <sub>5</sub> (c)-Mo(2)	93.1		
	93.1 (av)		

<sup>a</sup> Distances and angles are uncorrected for thermal motion. <sup>b</sup> C<sub>5</sub>H<sub>5</sub>(c) designates the centroid of the ring.

nations<sup>35, 36</sup> in a considerable number of other Mo( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>XY complexes where X arbitrarily repre-

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(36) M. R. Churchill, *Perspect. Struct. Chem.*, **3**, 157 (1970).

**Table IV.** Equations of "Best" Least-Squares Planes, Perpendicular Distances (Å) from these Planes, and Dihedral Angles between Normals of Planes<sup>a,b</sup>

(A) Plane I through Mo(1), Mo(2), H(17), and P					
$-2.0462x + 10.8992y - 8.3852z - 0.6107 = 0$					
Mo(1)	0.003 (2)	H(17)	-0.019 (5)		
Mo(2)	0.003 (2)	P	-0.003 (3)		
(B) Plane II through H(17), P, C(5), and C(6)					
$9.1230x + 1.4732y - 2.3843z - 5.9615 = 0$					
H(17)	-0.002 (3)	C(6)	0.001 (3)		
P	-0.002 (4)	Mo(1)	-1.626 (2)		
C(5)	0.001 (3)	Mo(2)	1.628 (2)		
(C) Plane III through Mo(1), C(1), and C(2)					
$7.8268x + 8.5295y - 2.0746z - 6.1553 = 0$					
O(1)	-0.037 (3)	O(2)	-0.057 (4)		
(D) Plane IV through Mo(2), C(3), and C(4)					
$-7.9072x + 0.0130y + 7.1681z + 5.0584 = 0$					
O(3)	-0.048 (3)	O(4)	-0.035 (4)		
(E) Plane V through C(7), C(8), C(9), C(10), and C(11)					
$-3.5839x - 13.0854y + 6.4999z + 2.5290 = 0$					
C(7)	-0.001 (4)	H(7)	0.038 (10)		
C(8)	-0.001 (3)	H(8)	-0.003 (8)		
C(9)	0.002 (3)	H(9)	-0.004 (8)		
C(10)	-0.003 (3)	H(10)	0.028 (9)		
C(11)	0.002 (4)	H(11)	0.022 (10)		
Mo(1)	-2.014 (2)				
(F) Plane VI through C(12), C(13), C(14), C(15), and C(16)					
$3.8294x + 6.8829y - 10.1602z - 5.6309 = 0$					
C(12)	0.002 (3)	H(12)	0.042 (7)		
C(13)	-0.002 (3)	H(13)	0.010 (7)		
C(14)	0.002 (3)	H(14)	0.015 (7)		
C(15)	-0.001 (3)	H(15)	0.035 (8)		
C(16)	-0.002 (3)	H(16)	0.046 (8)		
Mo(2)	-2.010 (2)				
(G) Plane VII through H(7), H(8), H(9), H(10), and H(11)					
$-3.5386x - 13.1765y + 6.4372z - 2.5365 = 0$					
H(7)	0.013 (10)	C(7)	-0.022 (4)		
H(8)	-0.005 (8)	C(8)	-0.010 (3)		
H(9)	-0.002 (8)	C(9)	-0.005 (3)		
H(10)	0.010 (9)	C(10)	-0.020 (3)		
H(11)	-0.015 (10)	C(11)	-0.025 (4)		
Mo(1)	-2.030 (2)				
(H) Plane VIII through H(12), H(13), H(14), H(15), and H(16)					
$3.7895x + 6.7902y - 10.2086z - 5.5838 = 0$					
H(12)	0.005 (7)	C(12)	-0.032 (3)		
H(13)	-0.004 (8)	C(13)	-0.024 (3)		
H(14)	0.001 (8)	C(14)	-0.019 (3)		
H(15)	0.003 (7)	C(15)	-0.033 (3)		
H(16)	-0.005 (7)	C(16)	-0.041 (3)		
Mo(2)	-2.040 (2)				
Dihedral Angles (deg) between Normals of Planes					
I and II	84.0	II and VI	59.2	IV and VI	39.3
I and III	80.1	II and VII	60.3	IV and VII	54.8
I and IV	78.9	II and VIII	59.5	IV and VIII	39.4
I and V	40.1	III and IV	40.8	V and VI	29.1
I and VI	39.6	III and V	40.2	V and VII	0.5
I and VII	40.0	III and VI	52.8	V and VIII	29.5
I and VIII	39.5	III and VII	53.2	VI and VII	29.6
II and III	25.8	III and VIII	53.2	VI and VIII	0.5
II and IV	27.1	IV and V	54.3	VII and VIII	30.0
II and V	60.0				

<sup>a</sup> The equations of the planes are expressed in the triclinic fractional coordinates  $x, y, z$ . <sup>b</sup> The atomic positions used in the calculation of a given plane were weighted according to the errors in the fractional coordinates.

sents a monodentate two-electron  $\sigma$  donor (e.g., CO or  $\text{P}(\text{C}_6\text{H}_5)_3$ ) and Y a monodentate one-electron donor (e.g.,  $\text{C}_2\text{H}_5$ ,<sup>35b</sup>  $\text{CH}_2\text{CO}_2\text{H}$ ,<sup>35d</sup> or  $\text{Sn}[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]_2\text{-Cl}$ <sup>35e</sup>). In the case of  $\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_4(\mu_2\text{-H})(\mu_2\text{-P}(\text{CH}_3)_2)$ , X and Y together signify two coordination

sites of a bidentate three-electron donor,  $(\mu_2\text{-H})[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2](\mu_2\text{-P}(\text{CH}_3)_2)$ . An analogous disposition of ligands<sup>37</sup> about the central metal atom(s) is also found in  $\text{Nb}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_4$ <sup>35g</sup> and in  $\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_6$ ;<sup>35a</sup> in the latter dimer which is stabilized by a direct Mo-Mo electron-pair bond, one-half of the molecule (*viz.*,  $\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3$ ) formally represents the monodentate one-electron  $\sigma$  donor to the other molybdenum atom. The common metal stereochemistry in these complexes has been previously interpreted<sup>35g</sup> in terms of a seven-coordinated metal atom having the  $[\text{NbF}_7]^{2-}$  configuration with the cyclopentadienyl ring occupying three coordination sites.

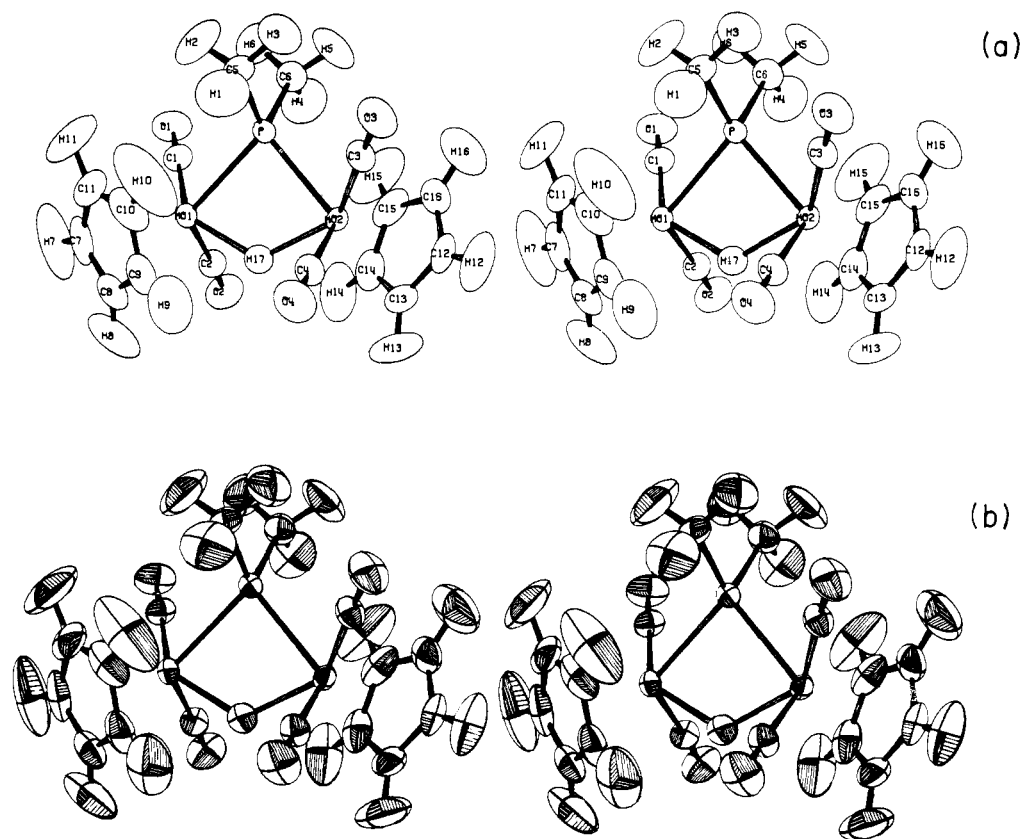
The spatial disposition of the bridging H and P atoms and two carbonyl ligands about each  $\text{Mo}(\text{C}_5\text{H}_5)$  fragment can be described in terms of a "four-legged stool" with adjacent P and H legs. The twofold-averaged bond angles between adjacent legs of OC-Mo-CO, 77.9°, OC-Mo-H, 73.6°, H-Mo-P, 76.2°, and P-Mo-CO, 77.4°, are not unlike the corresponding acute angles in other  $\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{XY}$  complexes;<sup>35, 36</sup> the appreciable difference between the H-Mo-CO and P-Mo-CO bond angles of 129.7 and 112.0°, respectively, which correspond to the two angles between opposite legs, presumably reflects the much different steric and electronic requirements imposed by the nonequivalent legs.

The high precision of this neutron diffraction study is strongly evidenced by the maximum difference of only 0.009 Å, both among the four crystallographically independent Mo-CO bond lengths of 1.955 (3)–1.964 (3) Å range and among the four C-O bond lengths of 1.149 (3)–1.158 (3) Å range. The four Mo-C-O bond angles are all within the narrow range of 177.2 (2)–178.0 (2)°.

**The  $\text{Mo}_2(\mu_2\text{-H})(\mu_2\text{-P})$  Framework.** A least-squares plane calculation (Table IV, plane I) shows the four atoms in the  $\text{Mo}_2\text{HP}$  core of  $\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_4(\mu_2\text{-H})(\mu_2\text{-P}(\text{CH}_3)_2)$  to be coplanar within 0.02 Å. The bridging hydrogen atom within the bent Mo-H-Mo system of angle 122.9 (2)° is essentially equidistant from the two molybdenum atoms with Mo(1)-H(17) and Mo(2)-H(17) distances of 1.851 (4) and 1.869 (4) Å, respectively; the bond-length difference of  $2.7\sigma$  is on the edge of statistical significance.<sup>38</sup> The position of the bridging phosphorus atom shows a greater indication of a slight asymmetry with respect to the positions of the two molybdenum atoms, as given by the Mo(1)-P and Mo(2)-P bond lengths of 2.432 (3) and 2.411 (3) Å, respectively, being different by  $5.3\sigma$ . The implication

(37) The close similarities of the localized environments about the metal atoms in  $\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_4(\mu_2\text{-H})(\mu_2\text{-P}(\text{CH}_3)_2)$ ,  $\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_6$ ,<sup>35a</sup> and  $\text{Nb}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_4$ <sup>35g</sup> are clearly shown from corresponding views shown in Figures 2 and 3 of ref 8.

(38) In an attempt to verify this slight possible asymmetry in the Mo-H distances through an assessment of the sensitivity of the coordinates of the bridging hydrogen atom to its thermal model, two cycles of least-squares refinement were repeated with anisotropic thermal motion allowed for all atoms except for that of the bridging hydrogen atom which was refined isotropically. The resulting coordinates of the bridging hydrogen atom are virtually identical with those from the full anisotropic refinement such that the difference between the two Mo-H distances of 0.016 (8) Å (*i.e.*,  $2.0\sigma$ ) and that between the two Mo-P distances of 0.021 (4) Å (*i.e.*,  $5.3\sigma$ ) correspond within experimental error to those based on the completely anisotropic refinement. The anisotropic-isotropic refinement yielded a reasonable isotropic temperature factor of 3.85 (8) Å<sup>2</sup> for the bridging hydrogen atom. The discrepancy indices (for all  $F_o^2 > 1.0\sigma(F_o^2)$ ) increased slightly as follows:  $R(F_o)$  from 0.080 to 0.082;  $R(F_o^2)$  from 0.082 to 0.084; and  $R_w(F_o^2)$  from 0.079 to 0.081.



**Figure 1.** Stereoscopic drawings of the molecular configuration of  $\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_4(\mu_2\text{-H})(\mu_2\text{-P}(\text{CH}_3)_2)$  showing (a) the atom labeling and (b) thermal ellipsoids of nuclear motion for all atoms scaled to enclose 50% probability. The entire molecule possesses a pseudo-twofold axis passing through the bridging hydrogen and phosphorus atoms.

of these possible bond-length differences in terms of a potential-well representation of the Mo–H–Mo bond is discussed later. The Mo(1)–Mo(2) distance of 3.267 (2) Å is slightly longer than that of 3.235 (1) Å in the unprotonated  $\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_6$ <sup>35a</sup> in accord with expectation. In fact, this difference in the metal–metal separation (with and without the hydrogen) of 0.032 Å associated with an M–H–M angle of 122.9° is consistent with the findings by X-ray diffraction studies<sup>3,7,17,18,39</sup> on other complexes that bridging hydrogen atoms involving analogously bent M–H–M systems produce comparably longer metal–metal bond lengths.<sup>40</sup> The considerably smaller electron-pair Mo–Mo distances found in the  $[\text{Mo}_2(\text{CO})_{10}]^{2-}$  dianion (3.123 (7) Å)<sup>9b</sup> and in two edge-bridged, bioctahedral complexes,  $\text{Mo}_2(\text{CO})_8(\mu_2\text{-P}(\text{C}_2\text{H}_5)_2)_2$  (3.057 (6) Å)<sup>41a</sup> and  $\text{Mo}_2(\text{CO})_6(\text{P}(\text{C}_2\text{H}_5)_3)_2(\mu_2\text{-P}(\text{CH}_3)_2)_2$  (3.090 (2) Å),<sup>41b</sup> do not neces-

sarily imply stronger Mo–Mo interactions in that it is extremely difficult to extrapolate trends in metal–metal distances in metal cluster systems with different basic geometries.

The acute Mo–P–Mo bridging angle of 84.8 (1)° in the planar  $\text{Mo}_2(\mu_2\text{-H})(\mu_2\text{-P})$  framework of  $\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_4(\mu_2\text{-H})(\mu_2\text{-P}(\text{CH}_3)_2)$  is attributed to the formation of the Mo–H–Mo bond which reduces the Mo–P–Mo angle from a normally obtuse value found in complexes with nonbonding metal–metal distances (e.g., the edge-bridged bioctahedral  $\text{Fe}_2(\text{CO})_6\text{I}_2(\mu_2\text{-P}(\text{CH}_3)_2)_2$  molecule (Fe–P–Fe, 102.6 (2)°; Fe···Fe, 3.590 (4) Å)<sup>42a</sup> and the edge-bridged pseudo-bioctahedral *cis*- $\text{Fe}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_2(\mu_2\text{-P}(\text{C}_6\text{H}_5)_2)_2$  molecule (Fe–P–Fe, 101.4°; Fe···Fe, 3.498 (4) Å)).<sup>42b</sup> A much sharper Mo–P–Mo bridging angle of 78.2° is observed in the planar  $\text{Mo}_2(\mu_2\text{-P})_2$  framework of the previously mentioned bioctahedral  $\text{Mo}_2(\text{CO})_6(\text{P}(\text{C}_2\text{H}_5)_3)_2(\mu_2\text{-P}(\text{CH}_3)_2)_2$  dimer<sup>41b</sup> which possesses an electron-pair Mo–Mo bond. The smaller Mo–P–Mo angles in the  $\text{Mo}_2(\mu_2\text{-P})_2$  complex arise from its Mo–Mo distance being 0.18 Å less than that in the  $\text{Mo}_2(\mu_2\text{-H})(\mu_2\text{-P})$ . The average Mo–P bond length in the  $\text{Mo}_2(\mu_2\text{-H})(\mu_2\text{-P})$  complex is 0.029 Å shorter than that of 2.451 Å in the  $\text{Mo}_2(\mu_2\text{-P})_2$  complex. It has been previously noted<sup>8,41b</sup> that the Mo–P bond lengths in these two complexes are appreciably shorter than the predicted single-bond length (of 2.54 or 2.71 Å depending upon the use of either 1.44 or 1.61 Å for the covalent molybdenum

(39) (a) H. D. Kaesz, R. Bau, and M. R. Churchill, *J. Amer. Chem. Soc.*, **89**, 2775 (1967); M. R. Churchill and R. Bau, *Inorg. Chem.*, **6**, 2086 (1967); (b) R. P. White, Jr., T. E. Block, and L. F. Dahl, unpublished results. (c) M. R. Churchill, S. A. Bezman, J. A. Osborn, and J. Wormald, *Inorg. Chem.*, **11**, 1818 (1972); (d) R. Bau, S. W. Kirtley, T. N. Sorrell, and S. Winarko, *J. Amer. Chem. Soc.*, **96**, 988 (1974), and references cited therein.

(40) The largest internuclear separation of the metal atoms in a M–H–M bond occurs when the hydrogen atom is collinear with the two metal atoms. A maximum decrease in distance between the metal atoms is then expected upon deprotonation as illustrated by the marked shortening of 0.44 Å between the chromium atoms in the  $[\text{Cr}_2(\text{CO})_{10}(\mu_2\text{-H})]^-$  monoanion due to deprotonation to give the  $[\text{Cr}_2(\text{CO})_{10}]^{2-}$  dianion.<sup>9b</sup> The similar metal–metal distances in these bent M–H–M bonds with those corresponding to unprotonated M–M electron-pair bonds point to extensive direct metal–metal bonding in a bent three-center, electron-pair M–H–M system.

(41) (a) L. R. Nassimbeni, *Inorg. Nucl. Chem. Lett.*, **7**, 909 (1971); (b) R. H. B. Mais, P. G. Owston, and D. T. Thompson, *J. Chem. Soc. A*, 1735 (1967).

(42) (a) G. R. Davies, R. H. B. Mais, P. G. Owston, and D. T. Thompson, *J. Chem. Soc. A*, 1251 (1968); (b) J. D. Sinclair, N. G. Connelly, and L. F. Dahl, submitted for publication.



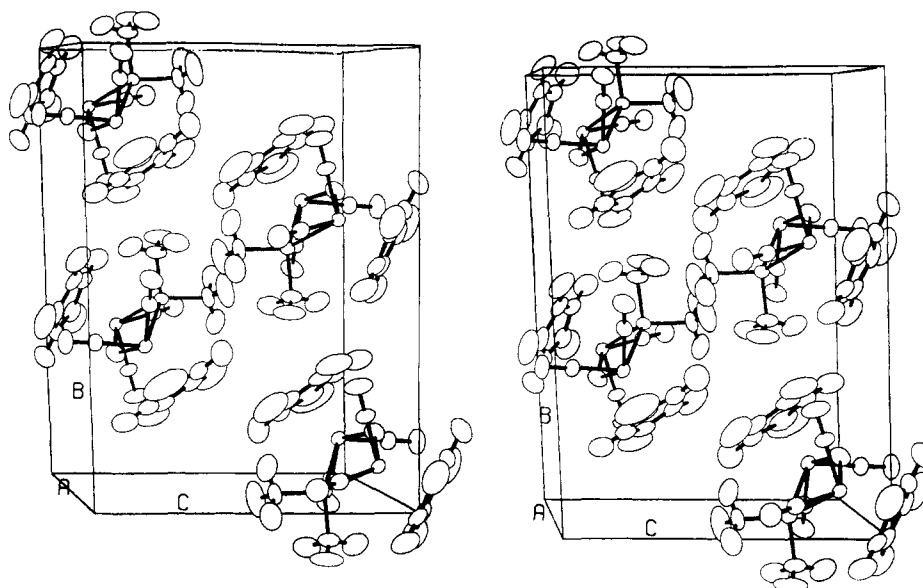


Figure 2. Stereoscopic view of the four  $\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_4(\mu_2\text{-H})(\mu_2\text{-P}(\text{CH}_3)_2)$  molecules in the triclinic unit cell of symmetry  $\bar{C}1$ .

radius with the value of 1.10 Å for the covalent phosphorus radius) in harmony with the occurrence of significant Mo–P  $\pi$ -bonding.

**Stereochemical Effects Imposed on the  $\pi$ -Cyclopentadienyl Carbon and Hydrogen Atoms.** The individual carbon–carbon internuclear distances vary from 1.377 (4) to 1.428 (5) Å in the  $\text{C}_5\text{H}_5(1)$  ring and from 1.398 (4) to 1.421 (4) Å in the  $\text{C}_5\text{H}_5(2)$  ring; the mean values of 1.400 and 1.408 Å, respectively, are virtually identical. These distances are analogous to those obtained from X-ray diffraction studies of numerous other metal cyclopentadienyl complexes. The significant shortening influence on the C–C distances due to the librational motion of the rings has been noted by Churchill and Kalra<sup>43</sup> from a comparison of structures with varying degrees of ring movement. The C–H internuclear bond lengths (Table III), which are comparable to the internuclear C–H distances found in the two methyl groups, also exhibit a variable shortening effect that can be ascribed to anisotropic thermal motion.

A prominent structural feature determined from this neutron diffraction investigation of  $\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_4(\mu_2\text{-H})(\mu_2\text{-P}(\text{CH}_3)_2)$  is that the cyclopentadienyl hydrogen atoms are significantly displaced from the planar ring upon metal complexation. Although the cyclopentadienyl carbon atoms in each ring are coplanar within 0.003 Å (Table IV, planes V and VI), the ring hydrogen atoms are displaced by different amounts out of the mean carbon plane *away* from the coordinated molybdenum atom, the maximum perpendicular displacement being 0.038 (10) Å from the  $\text{C}_5\text{H}_5(1)$  ring and 0.046 (8) Å from the  $\text{C}_5\text{H}_5(2)$  ring. This hydrogen deformation away from the molybdenum atom is further demonstrated from the difference calculated (Table IV, planes V–VIII) between the perpendicular distance from the molybdenum atom to its mean cyclopentadienyl carbon and hydrogen planes; these differences are 0.016 Å for the  $\text{C}_5\text{H}_5(1)$  ring and 0.030 Å for the  $\text{C}_5\text{H}_5(2)$  ring. For a given cyclopentadienyl ring these carbon and hydrogen planes are essentially parallel in that the

angle between the normals of these two planes is  $0.5^\circ$  for both rings. In contrast, an opposite displacement of the hydrogen atoms from the mean cyclopentadienyl carbon plane toward the metal atom was previously indicated from a neutron diffraction study by Epstein and Bernal<sup>44</sup> of  $\text{Ti}[(\eta^5\text{-C}_5\text{H}_4)(\text{CH}_2)_3(\eta^5\text{-C}_5\text{H}_4)]\text{Cl}_2$ . From an identical analysis, they found for both cyclopentadienyl rings a perpendicular displacement of the mean hydrogen plane by 0.02 Å below the corresponding mean carbon plane toward the titanium atom.

In each cyclopentadienyl ring the Mo–C distances show a similar variation of 0.10 Å (Table III) with the longest Mo–C distance of 2.390 Å (av) involving the cyclopentadienyl carbon atom (*viz.*, C(9) in the  $\text{C}_5\text{H}_5(1)$  ring and C(14) in the  $\text{C}_5\text{H}_5(2)$  ring) trans to the two carbonyl ligands. These different Mo–C distances reflect the fact that each cyclopentadienyl carbon ring is tilted such that a line from the molybdenum atom to the centroid of the ring is *not* parallel with the normal to the ring but instead forms an angle of  $1.6^\circ$  for  $\text{C}_5\text{H}_5(1)$  and  $2.1^\circ$  for  $\text{C}_5\text{H}_5(2)$ . A similar “tilting” of the  $\pi$ -cyclopentadienyl ring as a general structural feature in the  $\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{XY}$  class of compounds was previously noted from a survey by Churchill and Fennessey.<sup>35c,f</sup> Since the longest Mo–C distances were usually observed for the cyclopentadienyl carbon atoms trans to the carbonyl groups, Churchill and Fennessey<sup>35c,f</sup> ascribed the systematic Mo–C variations to steric repulsion and/or a trans effect due to the greater  $\pi$  character in the molybdenum–carbonyl bonds.

In these  $\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{XY}$  complexes (*e.g.*, for which X = CO, Y =  $\text{C}_2\text{H}_5$ <sup>35b</sup>; X = CO, Y =  $\text{CH}_2\text{-CO}_2\text{H}$ <sup>35d</sup>), the arrangement of these terminal ligands about the central molybdenum atom results in similar  $\text{C}_5\text{H}_5(\text{c})\text{-Mo-X}$  (or Y) angles. However, a distortion in the coordination about each molybdenum atom is observed in  $\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_4(\mu_2\text{-H})(\mu_2\text{-P}(\text{CH}_3)_2)$ ; the  $\text{C}_5\text{H}_5(\text{c})\text{-Mo-H}$  angle of  $110.5^\circ$  (av) is markedly smaller than the  $\text{C}_5\text{H}_5(\text{c})\text{-Mo-CO}$  angles of  $119.8^\circ$  (av) and  $122.5^\circ$  (av) and the  $\text{C}_5\text{H}_5(\text{c})\text{-Mo-P}$  angle of  $124.9^\circ$  (av).

(43) M. R. Churchill and K. L. Kalra, *Inorg. Chem.*, **12**, 1650 (1973).

(44) E. F. Epstein and I. Bernal, *Inorg. Chim. Acta*, **7**, 211 (1973).

This variation may be associated with the displacements of both cyclopentadienyl rings toward the bridging hydrogen atom. This phenomenon of the ligands adjacent to a hydride ligand being displaced toward the hydrogen ligand has been pointed out by Frenz and Ibers<sup>3a</sup> from their examination of the structural features of a number of transition metal hydrides.

The average Mo–C distances of 2.340 Å for the C<sub>5</sub>H<sub>5</sub>(1) ring and 2.338 Å for the C<sub>5</sub>H<sub>5</sub>(2) ring as well as the perpendicular distances of 2.014 (2) Å from Mo(1) to the C<sub>5</sub>H<sub>5</sub>(1) carbon ring and 2.010 (2) Å from Mo(2) to the C<sub>5</sub>H<sub>5</sub>(2) carbon ring are close to the corresponding values reported in the other Mo( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>XY molecules.<sup>35</sup>

**Analysis of the Anisotropic Thermal Motion of the Atoms.** A quantitative indication of the thermal anisotropy of the atoms in the molecular crystal of Mo<sub>2</sub>( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(CO)<sub>4</sub>( $\mu_2$ -H)( $\mu_2$ -P(CH<sub>3</sub>)<sub>2</sub>) can be obtained from an analysis of the atomic thermal ellipsoids, for each of which the rms components of thermal displacement (*i.e.*,  $\mu(r)$ ) along the three principal (orthogonal) axes ( $r = 1, 2, 3$ ) have been calculated<sup>45</sup> from the atomic  $\beta_{ij}$  coefficients. The atomic thermal ellipsoids shown in Figure 1 for the molecule and in Figure 3 for the cyclopentadienyl rings reveal pronounced anisotropy characteristic of considerable hindered rotational motion for the two cyclopentadienyl rings and two methyl groups.

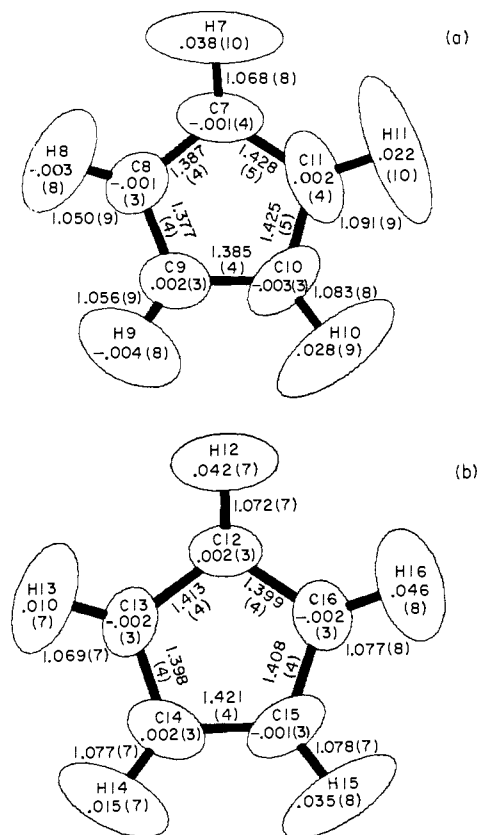
Both the carbon and oxygen atoms of three of the four carbonyl ligands display a similar degree of thermal anisotropy with the smallest atomic rms component (0.15–0.17 Å) nearly along the Mo–CO bond direction and with the other two larger atomic rms components (0.19–0.22 Å for the carbon atoms and 0.24–0.32 Å for the oxygen atoms) approximately perpendicular to the Mo–CO direction.

**Neutron Diffraction Evidence for a Single-Well Potential in the Bent Mo–H–Mo Bond.** The neutron diffraction data for Mo<sub>2</sub>( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(CO)<sub>4</sub>( $\mu_2$ -H)( $\mu_2$ -P(CH<sub>3</sub>)<sub>2</sub>) have provided for this particular bent M–H–M system considerable *direct* evidence which in our opinion strongly favors the “effectively” symmetric hydrogen atom oscillating about a single equilibrium point rather than being randomly distributed in the crystal lattice between two equilibrium positions displaced from the center.

Figure 1 clearly shows that the thermal motion of the bridging hydrogen atom is comparable to those of the molybdenum and phosphorus atoms in the central Mo<sub>2</sub>HP core but is significantly smaller than those of the other hydrogen atoms of the molecule. This implies that the Mo<sub>2</sub>( $\mu_2$ -H)( $\mu_2$ -P) core is relatively rigid. The low thermal motion of this bridging hydrogen atom, as also reflected in its small isotropic thermal parameter value of 3.85 (8) Å<sup>2</sup> (see ref 38), furnishes support for only a single equilibrium site in that a composite thermal motion about two reasonably separated equilibrium sites would be expected to produce a much larger thermal ellipsoid and a correspondingly increased isotropic temperature factor for the hydrogen nucleus.

A comparison of the rms components (Table II) and directions of thermal displacement for the bridging hydrogen and phosphorus atoms (*vide infra*) provides further definite evidence that the hydrogen atom

(45) H. A. Levy and W. R. Busing, *Acta Crystallogr.*, **11**, 450 (1958).



**Figure 3.** View normal to the mean plane of each of the two crystallographically independent cyclopentadienyl rings showing all atoms as 50% probability thermal ellipsoids: (a) the C<sub>5</sub>H<sub>5</sub>(1) ring (with C and H atoms numbered from 7 through 11) coordinated to Mo(1) and (b) the C<sub>5</sub>H<sub>5</sub>(2) ring (with C and H atoms numbered from 12 through 16) coordinated to Mo(2). Bond lengths and perpendicular displacements of atoms from the least-squares plane defined by the five carbon atoms are presented for each ring. Prominent structural features that are discernible include: (1) The C<sub>5</sub>H<sub>5</sub>(2) ring exhibits somewhat less librational ring motion than that of the C<sub>5</sub>H<sub>5</sub>(1) ring. In accord with the lesser rotational nuclear motion, the five internuclear C–C distances in the C<sub>5</sub>H<sub>5</sub>(2) ring are nearer to equivalence in magnitude as also are the corresponding five internuclear C–H distances. (2) While the five carbon atoms in the C<sub>5</sub>H<sub>5</sub>(1) ring are coplanar within 0.003 Å and those in the C<sub>5</sub>H<sub>5</sub>(2) ring within 0.002 Å, several of the hydrogen atoms in each ring are significantly displaced out of the mean carbon plane in an upward direction away from the Mo atom located below the plane.

occupies only one equilibrium position. The thermal ellipsoids of both the hydrogen and phosphorus atoms are symmetrically positioned with respect to the planar Mo<sub>2</sub>( $\mu_2$ -H)( $\mu_2$ -P) core with the largest principal axis component essentially perpendicular to the Mo<sub>2</sub>HP plane (*viz.*, within 2 (3)° for the H atom and 16 (4)° for the P atom). Of prime importance is that within experimental error the shapes of the thermal ellipsoids for the hydrogen and phosphorus atoms are isotropic within the Mo<sub>2</sub>HP plane. Furthermore, despite its much greater mass and additional coordination to the two methyl substituents, the isotropic value of 0.156 Å for the phosphorus atom within the Mo<sub>2</sub>HP plane (*i.e.*, taken as the mean of  $\mu(1) = 0.149$  Å and  $\mu(2) = 0.163$  (4) Å) is only 0.036 Å less than that of 0.192 Å for the hydrogen atom within the Mo<sub>2</sub>HP plane (*i.e.*, the mean of  $\mu(1) = 0.186$  (6) Å and  $\mu(2) = 0.198$  (6) Å). For the situation with the hydrogen atom statistically disordered between two equilibrium points within the

Mo<sub>2</sub>HP plane in a symmetric double-minimum potential, the  $\mu(1)$  and  $\mu(2)$  components of the hydrogen atom would be expected to be not only larger in magnitude but also different from each other (corresponding to unequivocal thermal anisotropy within the Mo<sub>2</sub>HP plane). Moreover, its maximum thermal displacement component (*viz.*,  $\mu(3) = 0.270$  (5) Å) perpendicular to the Mo–H–Mo bond is 0.078 Å *greater* than the isotropic value in the Mo<sub>2</sub>HP plane. This value is 0.085 Å larger than the correspondingly directed maximum thermal displacement component (*viz.*,  $\mu(3) = 0.185$  (4) Å) for the phosphorus atom. This much greater thermal anisotropy of the bridging H atom perpendicular to the Mo<sub>2</sub>HP plane than within it, relative to that for the bridging phosphorus atom, strongly supports our premise that the experimentally obtained isotropic thermal cross section of 0.192 Å<sup>2</sup> (av) does not conform in either size or shape to any reasonable composite of normal nuclear thermal motion arising from the superposition of the thermal ellipsoids for a hydrogen nucleus occupying two equilibrium positions within the Mo<sub>2</sub>HP plane.

The small and statistically borderline difference of 0.019 (7) Å (*i.e.*,  $2.7\sigma$ ) between the two Mo–H distances can be readily attributed to a slight asymmetry in the potential energy surface associated with the bridging hydrogen nucleus. This asymmetry may be the result of the inseparable electronic and steric effects imposed by the small asymmetry in the position of the bridging phosphorus atom, as manifested by the Mo–P bond-length difference of 0.021 (4) Å (*i.e.*,  $5.3\sigma$ ). It is apparent, as in the case of doubly bridging carbonyl groups in different metal carbonyl complexes taking on a number of unsymmetrical configurations which are intermediate between terminal and symmetric doubly bridging ones, that the extent of asymmetry of a M–H–M bond will be markedly influenced by the asymmetric effects dictated by the metal atoms and other ligands.<sup>46–50</sup>

In summary, *the size, shape, and orientation of the thermal ellipsoid for the bridging hydrogen atom in Mo<sub>2</sub>( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(CO)<sub>4</sub>( $\mu_2$ -H)( $\mu_2$ -P(CH<sub>3</sub>)<sub>2</sub>) provide no evidence for other than a single-minimum potential well.*<sup>51</sup>

**Supplementary Material Available.** A listing of observed and calculated structure factors will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 nm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-6610.

(46) From neutron diffraction studies<sup>4,6,19,47</sup> that have been performed on various three-center, four-electron O–H–O and F–H–F bonds, the nature of the potential surface associated with the hydrogen nucleus has been shown to be strongly dependent upon the environment about these hydrogen-bonded systems. It has been suggested<sup>6</sup> that the well-known "symmetric" hydrogen bond only arises in these systems when the combined electronic and crystal environment lacks sufficient asymmetry to distort the potential surface "seen" by the bridging hydrogen nucleus.

(47) (a) R. D. Ellison and H. A. Levy, *Acta Crystallogr.*, **19**, 260 (1965); (b) E. O. Schlemper, W. C. Hamilton, and S. J. LaPlaca, *J. Chem. Phys.*, **54**, 3990 (1971); (c) A. Sequeira, C. A. Berkebile, and W. C. Hamilton, *J. Mol. Struct.*, **1**, 283 (1967).

(48) Rundle<sup>49</sup> has suggested (for the case of short symmetrical O–H–O bonds with both a double-minimum potential and central energy barrier only slightly above the vibrational zero-point level) that the O–D–O bond should be noticeably longer than the O–H–O bond; if such is not the case, then a single-minimum potential is indicated. These conclusions are in agreement with theoretical calculations subsequently performed by Singh and Wood<sup>50</sup> which show that the change in the O···O distance on deuteration is a useful indication of the "presence" or "absence" of a double-minimum potential. Although these results pertain to the linear O–H–O hydrogen bond, they suggest the desirability of X-ray and neutron diffraction studies of the deuterium-bridged analogs to determine whether a similar detectable variation in the M–M internuclear separations can be observed in M–H–M bonds.

(49) R. E. Rundle, *J. Phys. Radium*, **25**, 487 (1964).

(50) T. R. Singh and J. L. Wood, *J. Chem. Phys.*, **50**, 3572 (1969); J. L. Wood, *J. Mol. Struct.*, **17**, 307 (1973).

(51) In the hope of shedding even more light on the nature of the bridging H atom coordination in this compound, we are preparing (R. P. Stewart, Jr., private communication to J. M. Williams and J. L. Petersen) the deuterium-bridged compound for neutron diffraction study.