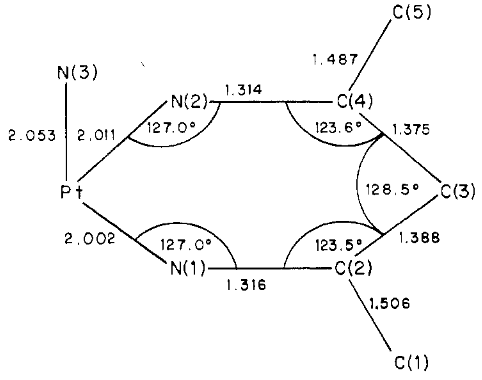

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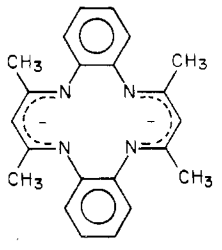

J

these complexes, C–C and C–N bond lengths in the β-diiminate rings are very close to those observed for C(2)–C(3), C(3)–C(4) and for N(1)–C(2), N(2)–C(4), respectively, in complex II. The C–CH_3 bond distances found for J range from 1.49 to 1.53 Å[17-19] and are comparable to the average value of 1.50 Å found for II.

The perchlorate ions are ordered but show some distortion from rigorous tetrahedrality. The Cl–O(1) bond is somewhat shorter than the others, and O–Cl–O bond angles range from 106.3 to 113.9°.

Acknowledgment. We are indebted to Drs. K. Bowman Mertes and B. Lee of this department for valuable advice during solution of the crystal structure. We also thank Dr. G. Pearson of the University of Iowa and Dr. J. Paukstelis of Kansas State University for obtaining the carbon-13 NMR spectra. A generous allocation of computer time was provided by the University of Kansas Computation Center. We thank Matthey Bishop, Inc., and Engelhard Minerals and Chemicals Corp. for generous loans of platinum starting materials.

Registry No. I, 61158-28-9; II, 65732-06-1; III, 65681-99-4; IV, 65681-97-2; [Pt(en)(*N,N′*-bis(2-aminoethyl)-2,4-pentanediiminate)]Cl_3, 65681-93-8; V, 65681-96-1; VI, 65681-95-0; [$Pt(NH_3)_6$]Cl_4, 16893-12-2; [$Pt(en)_3$]Cl_4, 12079-33-3; [$Au(en)_2$]Cl_3, 15278-22-5; 2,4-pentanedione, 123-54-6; ^{13}C, 14762-74-4.

Supplementary Material Available: Table III, listing observed and calculated structure factor amplitudes for II, and Table IV, listing positional and thermal parameters for hydrogen atoms (11 pages). Ordering information is given on any current masthead page.

References and Notes

(1) NSF Undergraduate Research Participant, 1975.
(2) I. P. Evans, G. W. Everett, Jr., and A. M. Sargeson, *J. Chem. Soc., Chem. Commun.*, 139 (1975).
(3) I. P. Evans, G. W. Everett, Jr., and A. M. Sargeson, *J. Am. Chem. Soc.*, **98**, 8041 (1976).
(4) D. C. Giedt and C. J. Nyman, *Inorg. Synth.*, **8**, 239 (1966).
(5) B. P. Block and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **73**, 4722 (1951).
(6) N. F. M. Henry and K. Lonsdale, Ed., "International Tables for X-Ray Crystallography", Vol. I, Kynoch Press, Birmingham, England, 1965.
(7) Absorption correction factors were obtained from Table 5.3.6B in J. S. Kasper and K. Lonsdale, Ed., "International Tables for X-Ray Crystallography", Vol. II, Kynoch Press, Birmingham, England, 1967.
(8) Computer programs used are local modificiations of FORDAP by A. Zalkin for Fourier summation, W. Busing, K. Martin, and H. Levy's ORFLS and ORFFE-II for least-squares refinement and computation of molecular dimensions, and C. K. Johnson's ORTEP-II for the structural drawing. All computations were carried out on a Honeywell 66/60 computer located at the University of Kansas.
(9) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).
(10) L. Tschugajeff, *Z. Anorg. Allg. Chem.*, **137**, 1, 401 (1924).
(11) B. Klein and L. Heck, *Z. Anorg. Allg. Chem.*, **416**, 269 (1975).
(12) A. Grinberg and K. I. Gildengerschel, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 479 (1948).
(13) R. C. Johnson, F. Basolo, and R. G. Pearson, *J. Inorg. Nucl. Chem.*, **24**, 59 (1962).
(14) Y. N. Kukuschkin and V. V. Sibirskaya, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), **14**, 409 (1969).
(15) J.-H. Kim and G. W. Everett, Jr., unpublished observations.
(16) T. J. Truex and R. H. Holm, *J. Am. Chem. Soc.*, **93**, 285 (1971); **94**, 4529 (1972).
(17) M. C. Weiss, B. Bursten, S.-M. Peng, and V. L. Goedken, *J. Am. Chem. Soc.*, **98**, 8021 (1976).
(18) V. L. Goedken, S.-M. Peng, J. Molin-Norris, and Y.-A. Park, *J. Am. Chem. Soc.*, **98**, 8391 (1976).
(19) M. C. Weiss and V. L. Goedken, *J. Chem. Soc., Chem. Commun.*, 531 (1976).
(20) M. C. Weiss, G. Gordon, and V. L. Goedken, *Inorg. Chem.*, **16**, 305 (1977).

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A Critical Evaluation of the Location and Refinement of a Bridging Hydrogen Atom in a Transition-Metal Hydride, $Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}H)(\mu\text{-}P(CH_3)_2)$, by X-Ray Diffraction[1]

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A comparison of the structural parameters obtained by x-ray and neutron diffraction for the transition-metal hydride complex $Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}H)(\mu\text{-}P(CH_3)_2)$ was performed to examine the discrepancies between the "x-ray-determined" and "neutron-determined" values for the structural parameters associated with the bridging hydride ligand. Within the experimental limitations of the x-ray analysis, the x-ray-determined hydrogen position reflects the covalent character of the bent Mo–H–Mo bond with the estimated region of maximum overlap displaced ca. 0.2 Å from the hydrogen nucleus along the Mo–H–Mo bisector toward the centroid of the Mo–H–Mo triangle. The consequences of this displacement are (1) an apparent shortening of 0.1 Å in the average x-ray-determined Mo–H distance of 1.79 (15) Å compared to the average neutron-determined Mo–H distance of 1.86 (1) Å and (2) a large increase in the Mo–H–Mo bond angle from the neutron-determined value of 122.9 (2)° to the x-ray-determined value of 133 (3)°. For closed-type, bent metal–hydrogen–metal bonds, one should then expect to find shorter average M–H bond distances and larger M–H–M bond angles by x-ray diffraction than by neutron diffraction.

In the past several years, a number of x-ray structural papers[3] in which the authors have located and refined a position for the hydride ligand in a transition-metal hydride complex have appeared in the literature. Due to the low x-ray scattering power of the hydrogen atom, the structural parameters calculated from the "refined" hydrogen position normally have anomalous values with correspondingly large standard errors. A related problem has been discussed previously by Churchill,[4] who has demonstrated from a survey of crystallographic papers that for terminal hydrogen atoms bonded to C, N, and O the "x-ray-determined" C–H, N–H, and O–H bond distances are short by 0.1–0.2 Å. This shortening arises primarily because the x-ray-determined bond length is a measure of the distance between the maxima of the electron density of the two bonded atoms and, therefore, reflects the covalent character of the bond, with the majority of the electron density from the hydrogen 1s atomic orbital being displaced toward the bonded atom. One might also expect a similar situation to exist for terminally bound hydrogen atoms in transition-metal hydrides.[5] In contrast, the corresponding bond distance obtained by neutron diffraction reflects the actual internuclear separation since neutrons are scattered by the nuclei, which to a first approximation behave as point scatterers. A "neutron-determined" bond distance is primarily affected by the thermal motion of the nuclei in the crystal lattice rather than the electron distribution. Consequently, for transition-metal hydride complexes, the x-ray-determined M–H bond length(s), and the corresponding bond angle(s), may deviate substantially from their true values. The extent of these deviations can only be determined by a comparison of the structural parameters obtained by x-ray and neutron diffraction studies of a suitable hydride complex.

In the majority of transition-metal hydrides of current interest, the hydrogen atom has been shown to behave as a μ_2-bridging ligand. With the availability of high-quality x-ray diffractometry data, the bridging hydrogen atom position can usually be found directly from weak areas of electron density by difference Fourier methods. However, in even the most precise x-ray diffraction studies where the hydrogen atom is unambiguously located and refined using least-squares techniques, a physically meaningless isotropic thermal model for the hydrogen atom must be assumed and the esd's for the metal–hydrogen distance(s) are generally at least 0.05–0.10 Å.

Although neutron diffraction is well suited for structural studies of transition-metal hydrides, only a relatively small number of them have been characterized. We have recently reported the outcome of a precise neutron diffraction investigation of the bent Mo–H–Mo bond in $Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}H)(\mu\text{-}P(CH_3)_2)$.[8] In order to evaluate the differences between the "x-ray-determined" and "neutron-determined" structural parameters of the bridging hydrogen atom, we have obtained x-ray diffractometry data[9,10] for this complex. With a suitably corrected set of x-ray data, the position of the bridging hydrogen atom should be resolved since all of the necessary criteria previously outlined by Ibers[11] for the determination of the hydrogen atom position in a transition-metal complex are fulfilled. Since the x-ray-determined hydrogen position in the bent M–H–M bond is expected to represent the location of maximum electron density in the bond, this work also affords the opportunity (within the limitations of the x-ray data) to estimate the degree to which the overlap region in the bond deviates from the hydrogen's nuclear position.

Experimental Section

A red crystal suitable for data collection with dimensions of 0.32 mm × 0.24 mm × 0.56 mm was mounted on the end of a thin glass fiber such that the *a* axis was nearly parallel to the spindle axis of the goniometer. The crystal and goniometer were transferred to a Nova-automated Syntex $P\bar{1}$ diffractometer. The angular coordinates (2θ, ω, ϕ, and χ) of 15 peaks (2θ = 16–36°) were automatically centered with monochromatic Mo Kα radiation ($\lambda(K\alpha_1)$ 0.709 26 Å, $\lambda(K\alpha_2)$ 0.713 54 Å). The least-squares lattice parameters for the $C\bar{1}$ cell[12] are given in Table I and are in good agreement with the values used in the neutron diffraction study.

Table I. Lattice Parameters Corresponding to the $C\bar{1}$ Cell for $Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}H)(\mu\text{-}P(CCH_3)_2)$

Parameter	X-ray	Neutron
a, Å	9.180 (1)	9.192 (11)
b, Å	16.631 (3)	16.631 (20)
c, Å	11.593 (2)	11.592 (14)
α, deg	93.13 (1)	93.06 (6)
β, deg	97.52 (1)	97.56 (7)
γ, deg	90.65 (1)	90.68 (9)
V, Å^3	1751.9 (5)	1753.9

Intensity data corresponding to four independent octants of the reciprocal lattice were collected at 20 ± 2 °C via the θ–2θ scan mode with a scintillation counter and pulse-height analyzer set to accept 90% of the Mo Kα peak. The intensities of 3312 reflections ($5° \le 2\theta \le 45°$) were measured with the Bragg angle for the crystal–graphite monochromator $2\theta_M$ set at 12.16° and the takeoff angle at 4°. Variable scan speeds with a minimum of 2.0°/min and variable scan widths based on the overall intensity and width of each peak were employed. Stationary-crystal, stationary-counter background measurements for half of the total scan time were made on each side of a peak. After every 50 reflections, two standard reflections were measured to monitor the instrument's stability as well as the crystal's alignment and decay. During the course of data collection, the intensities of the standard reflections decreased monotonically by ca. 4%.

Since variable scan speeds were used, the calculated integrated intensities were normalized to be consistent with a scan rate of 1°/min by the expression $I = [S - B(t_s/t_b)](SR)$ where S designates the integrated scan count obtained in time t_s, B is the total background count otained in time t_b, and SR is the selected scan rate. The observed integrated intensity of each reflection was then corrected for crystal decay, Lorentz polarization, and absorption (μ = 15.098 cm^{-1}) effects. The *Lp* factor for the monochromator on the Syntex $P\bar{1}$ diffractometer is given by the expression[13]

$$Lp = \frac{0.5}{\sin 2\theta}\left[\frac{\cos^2 2\theta_M + \cos^2 2\theta}{1 + \cos^2 2\theta_M} + \frac{\cos 2\theta_M + \cos^2 2\theta}{1 + \cos 2\theta_M}\right]$$

which assumes that the graphite monochromator crystal is 50% mosaic and 50% perfect. The minimum and maximum transmission coefficients were 0.663 and 0.770, respectively. The standard deviation of each corrected intensity was obtained from the relationship

$$\sigma(I) = \{[S + B(t_s/t_b)^2](SR) + 0.04I^2\}^{1/2}$$

The duplicate reflections were averaged to produce a total of 3075 independent reflections of which 2850 were found to have $I \ge 1.0\sigma(I)$. The quality of the x-ray data is indicated by the "agreement factors"[14] calculated for equivalent reflections of $R_a(F_o) = 0.016$ and $R_a(F_o^2) = 0.014$.

Refinement of the Bridging Hydrogen Atom Position

Two different methods were employed to determine the bridging hydrogen atom position based upon our x-ray data. Since the atomic positions of all of the atoms in $Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}H)(\mu\text{-}P(CH_3)_2)$ were well established by the neutron diffraction study,[8] their values serve as a good initial model for the x-ray data analysis. The atom scattering factors[15-18] were corrected for anomalous dispersion and after three cycles (utilizing the neutron-determined positional and thermal parameters for all atoms) with only the scale factor varied, the discrepancy indices[19] were $R(F_o) = 0.054$, $R(F_o^2) = 0.085$, and $R_w(F_o^2) = 0.125$ for all the data. Full-matrix least-squares refinement of the atomic positions and temperature factors (with anisotropic factors for the nonhydrogen atoms and isotropic factors for the hydrogen atoms) further reduced the discrepancy indices for all of the data to their final values of 0.0402, 0.0611, and 0.0875, respectively, and the goodness-of-fit parameter[20] to $\sigma_1 = 1.41$. The final isotropic temperature factors of all the hydrogen atoms were positive (B = 3.2–10.4 Å^2); the x-ray-determined nonhydrogen atom positions and the corresponding bond distances and angles were essentially identical with their neutron-determined values. *The only major difference is with regard to the Mo–H–Mo molecular fragment.* The distances from the Mo atoms to the x-ray-determined bridging hydrogen position differ by 0.30 (10) Å (i.e., 3.0σ) with Mo(1)–H(17) = 1.94 (6) Å and Mo(2)–H(17) = 1.64 (6) Å; the resultant Mo–H–Mo bond angle

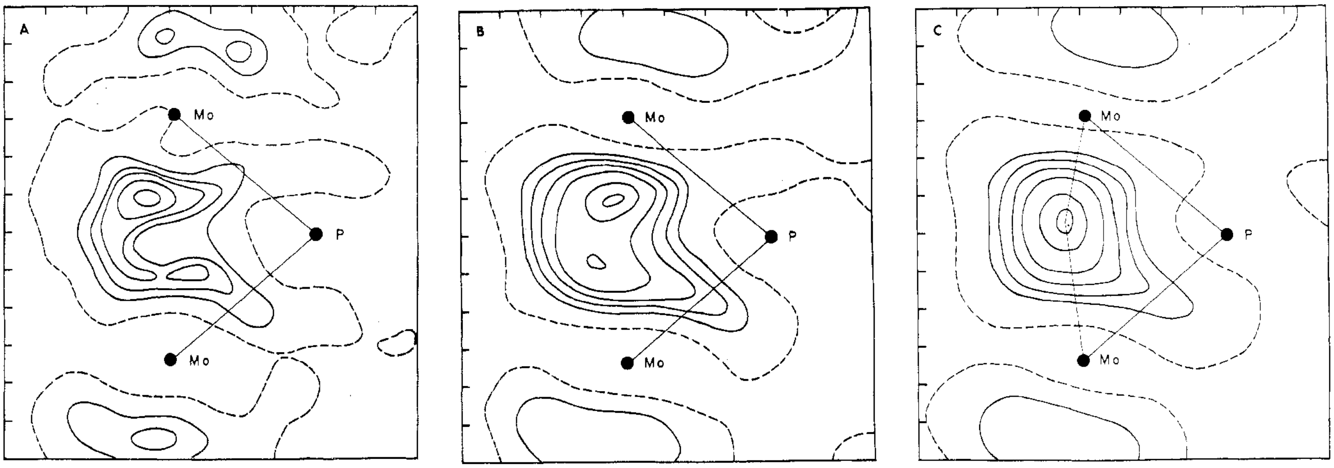

Figure 1. Difference Fourier sections through the $Mo_2(\mu\text{-}H)(\mu\text{-}P)$ plane calculated with (A) all of the x-ray data, (B) only data with $(\sin\theta)/\lambda$ less than 0.43 $Å^{-1}$, and (C) only data with $(\sin\theta)/\lambda$ less than 0.33 $Å^{-1}$. The dashed contour represents 0 $e/Å^3$ with each successive contour drawn at 0.3, 0.4, 0.5, 0.6, 0.7, and 0.75 $e/Å^3$.

Table II. Positional Parameters[a,b,c] and Temperature Factors for the $Mo_2(\mu\text{-}H)(\mu\text{-}P)$ Fragment in $Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}H)(\mu\text{-}P(CH_3)_2)$

Atom		x	y	z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$	B, $Å^2$
Mo(1)	(a)	0.4852 (2)	0.3362 (1)	0.2455 (2)	52 (2)	21 (1)	42 (1)	−3 (1)	4 (1)	5 (1)	
	(b)	0.48467 (4)	0.33618 (2)	0.24546 (3)	65 (1)	21 (0)	45 (0)	−2 (0)	6 (0)	3 (0)	
	(c)	0.48466 (4)	0.33618 (2)	0.24546 (3)	65 (1)	21 (0)	45 (0)	−2 (0)	6 (0)	3 (0)	
Mo(2)	(a)	0.8258 (2)	0.3686 (1)	0.2045 (1)	60 (2)	19 (1)	40 (1)	0 (1)	14 (1)	3 (1)	
	(b)	0.82576 (4)	0.36856 (2)	0.20437 (3)	67 (1)	19 (0)	43 (0)	0 (1)	12 (0)	2 (0)	
	(c)	0.82576 (4)	0.36856 (2)	0.20437 (3)	67 (1)	19 (0)	43 (0)	0 (1)	12 (0)	2 (0)	
P	(a)	0.6693 (3)	0.4356 (1)	0.3303 (2)	64 (3)	18 (1)	47 (2)	−4 (1)	11 (2)	−2 (1)	
	(b)	0.66934 (12)	0.43582 (7)	0.33042 (10)	79 (1)	21 (0)	49 (1)	−2 (1)	15 (1)	−2 (0)	
	(c)	0.66934 (12)	0.43582 (7)	0.33042 (10)	79 (1)	21 (0)	49 (1)	−2 (1)	15 (1)	−2 (0)	
H(17)	(a)	0.6490 (4)	0.3102 (3)	0.1741 (4)	94 (5)	35 (2)	86 (4)	−10 (2)	24 (4)	24 (4)	3.85 (8)
	(b)	0.669 (6)	0.319 (3)	0.184 (5)							5.8 (1.4)
	(c)	0.669 (6)	0.319 (3)	0.184 (5)							6.0 (1.4)

[a] (a), (b), and (c) represent the positional and temperature factor parameters for the neutron study, the first x-ray refinement, and the second x-ray refinement, respectively. [b] The estimated standard deviations in parentheses refer to the least significant figures. [c] The form of the temperature factor is $\exp\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\}$.

is 132 (3)°. At this point, it was not evident whether these differences were due to our refinement procedure, the x-ray data, or both. As a consequence, we decided to refine the hydrogen atom position using more or less what has become the standard procedure for the determination of hydrogen atoms bonded to transition metals. This procedure is based on the fact that the hydrogen atom scattering contribution is greater for low-angle reflections. Since the ratio of the peak height of an atom to the standard deviation of the electron density goes through a maximum as a function of scattering angle, Ibers[21] has pointed out that an optimum number of low-angle data can be used to locate light atoms. A difference Fourier map was first calculated in a conventional manner with all of the x-ray-determined atom positions except for the bridging hydrogen atom included. The section through the $Mo_2(\mu\text{-}P)(\mu\text{-}H)$ plane (Figure 1A) shows two promising peaks superimposed on a broad area of positive electron density. Following a procedure similar to that outlined by Bau and co-workers,[3d] two additional difference Fourier maps were calculated. The map (Figure 1B) calculated with a $(\sin\theta)/\lambda$ cutoff of 0.43 $Å^{-1}$ (1140 reflections) shows considerable improvement in resolution, but two peaks ($x_1 = 0.718$, $y_1 = 0.351$, $z_1 = 0.209$; $x_2 = 0.620$, $y_2 = 0.330$, $z_2 = 0.214$) of nearly equal magnitude remain. Finally, the third difference Fourier map (Figure 1C) calculated with a $(\sin\theta)/\lambda$ cutoff of 0.33 $Å^{-1}$ (528 reflections) clearly resolves one peak[22] ($\rho = 0.78$ $e/Å^3$) at $x = 0.691$, $y = 0.342$, and $z = 0.207$ which is the largest peak in the entire three-dimensional map.

The subsequent refinement of the bridging hydrogen atom position and its isotropic temperature factor, as resolved in the difference Fourier map, was accomplished in three steps. By use of only low-angle data ($(\sin\theta)/\lambda$ cutoff 0.33 $Å^{-1}$, 528 reflections), the positional parameters of all of the atoms were refined. Then, with all of the hydrogen atoms fixed, the nonhydrogen atoms were refined anisotropically with all of the data. In the final step all parameters were refined to give final discrepancy indices for all of the data of $R(F_o) = 0.0402$, $R(F_o^2) = 0.0611$, and $R_w(F_o^2) = 0.874$ with $\sigma_1 = 1.41$, which are essentially the same as the values obtained from the refinement which utilized the neutron results.

Since this paper is primarily concerned with the x-ray-determined and neutron-determined parameters associated with the $Mo_2(\mu\text{-}H)(\mu\text{-}P)$ group, the corresponding positional and thermal parameters from the output of the last least-squares cycle in each case[23] are listed in Table II. Interatomic distances and bond angles with esd's calculated from the variance–covariance matrix are given in Table III.[24]

Comparison of X-Ray and Neutron Parameters

The agreement between the derived parameters from the x-ray and neutron diffraction data was tested by means of a half-normal probability plot,[25-27] which is depicted in Figure 2. Δj is equal to $||P_x(j)| - |P_n(j)||$, where $P_x(j)$ and $P_n(j)$ are the final values for parameters j obtained from the x-ray and neutron data, respectively, while $\sigma(j)$ is equal to $\{\sigma^2(P_x(j)) + \sigma^2(P_n(j))\}^{1/2}$, where $\sigma(P_x(j))$ and $\sigma(P_n(j))$ are the corresponding variances in these parameters. For the positional and thermal parameters of all of the nonhydrogen atoms, the slope of the plot is essentially linear but slightly larger than an ideal value of 1.0 for a normal distribution. The fact that the slope in this case is larger than unity indicates that the standard deviations from the least-squares matrix are underestimated by a factor of approximately 1.6. The zero intercept reflects the absence of any systematic errors. The observation that all of the points corresponding to the positional and thermal parameters fall on the same line suggests that the corre-

Table III. Interatomic Distances (Å) and Bond Angles (deg) for $Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}H)(\mu\text{-}P(CH_3)_2)$[a,b]

(A) Interatomic Distances					
Mo(1)-Mo(2)	(a)	3.267 (2)	Mo(1)-H(17)	(a)	1.851 (4)
	(b)	3.2714 (5)		(b)	1.94 (6)
	(c)	3.2715 (5)		(c)	1.94 (6)
Mo(1)-P	(a)	2.432 (3)	Mo(2)-H(17)	(a)	1.869 (4)
	(b)	2.431 (1)		(b)	1.64 (6)
	(c)	2.431 (1)		(c)	1.63 (6)
Mo(2)-P	(a)	2.411 (3)	Mo-H(17) (av)	(a)	1.86 (1)
	(b)	2.420 (1)		(b)	1.79 (15)
	(c)	2.420 (1)		(c)	1.78 (15)
(B) Bond Angles					
Mo(1)-H(17)-Mo(2)	(a)	122.9 (2)	P-Mo(1)-H(17)	(a)	76.0 (1)
	(b)	132 (3)		(b)	69 (2)
	(c)	133 (3)		(c)	69 (2)
Mo(1)-P-Mo(2)	(a)	84.8 (1)	P-Mo(2)-H(17)	(a)	76.3 (1)
	(b)	84.81 (4)		(b)	74 (2)
	(c)	84.81 (4)		(c)	73 (2)

[a] (a), (b), and (c) represent the interatomic distances and bond angles calculated from the neutron study, the first x-ray refinement and the second x-ray refinement, respectively. [b] The estimated standard deviations which are shown in parentheses for the average values are calculated from the formula $\sigma_{\bar{l}} = [\Sigma(\bar{l} - l_m)^2/(m^2 - m)]^{1/2}$, where m is the number of "equivalent" bonds, l_m is the length of the mth bond, and $\bar{l}$ is the mean length.

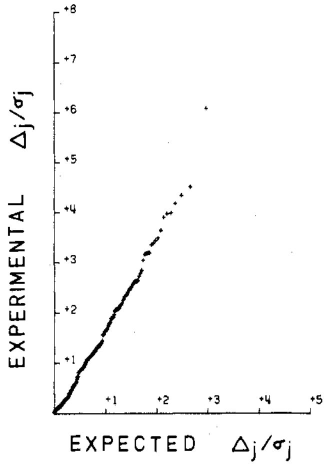

Figure 2. Half-normal probability plot comparing positional and thermal parameters derived from x-ray and neutron diffraction studies of $Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}H)(\mu\text{-}P(CH_3)_2)$.

sponding parameters from the two diffraction studies are in equally good agreement.

A comparison of the x-ray-determined and neutron-determined structural parameters for the $Mo_2(\mu\text{-}H)(\mu\text{-}P)$ molecular fragment in Tables II and III clearly illustrates that while the respective values for the P and Mo atoms are essentially identical within experimental error, the x-ray-determined and neutron-determined hydrogen positions do not coincide. This difference is due partially to the low x-ray scattering power of the hydrogen atom, which leads to a broad convergence minimum in the least-squares refinement, but also reflects to some degree the premise that the x-ray-determined hydrogen position in this case represents the location of the electron density maximum in the Mo-H-Mo bond, which does not coincide with the position of the hydrogen nucleus.

Discussion of Results

Since the neutron study has shown that the hydrogen atom is centered in the M-H-M hydrogen bond and resides within a symmetric potential well, the hydrogen atom experiences equivalent electronic environments from the two phosphido-bridged $Mo(\eta^5\text{-}C_5H_5)_2(CO)_2$ groups. The electron density maximum within the Mo-H-Mo bond (due to the overlap of the Mo hybrid orbitals with the H 1s atomic orbital) is expected to be equidistant from the two Mo atoms. Although the two x-ray-determined distances are not equal, an estimate of the region of common overlap can be made from the average x-ray-determined Mo-H distance of 1.79 (15) Å. On the basis of the assumption that the average x-ray-determined distance is a reasonable measure of the metal-overlap distance, Figure 3 illustrates, with respect to nuclear positions of the atoms in the $Mo_2(\mu\text{-}H)(\mu\text{-}P)$ core, that the electron density maximum is displaced nearly 0.2 Å toward the Mo-Mo internuclear vector from the bridging hydrogen atom. The consequence of this displacement is an apparent shortening of ca. 0.1 Å in the average x-ray-determined Mo-H distance compared to the average neutron-determined Mo-H distance of 1.86 (1) Å. This shortening is accompanied by a corresponding increase in the Mo-H-Mo bond angle from 123° to an estimated 133°, which is comparable to the x-ray-determined values of 132 (3) and 133 (3)° from the two least-squares refinements.

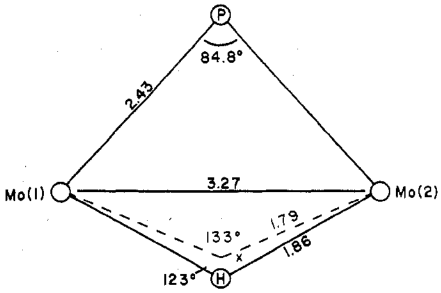

Figure 3. Location of the "x-ray-determined" hydrogen position, represented by x, with respect to the "neutron-determined" positions in the $Mo_2(\mu\text{-}H)(\mu\text{-}P)$ plane. The average x-ray-determined Mo-H distance of 1.79 Å indicates that the electron density in the Mo-H-Mo bond is located along the Mo-H-Mo bisector near the centroid of the Mo-H-Mo triangle.

The estimated location of the electron density maximum in the Mo-H-Mo bond in Figure 3 is consistent with a qualitative bonding representation of the overlap region for closed-type, bent W-H-W bonds, recently discussed by Bau and co-workers.[28] Their structural results[28,29] on several hydrogen-bridged tungsten dimers ($W_2(CO)_2(NO)(\mu\text{-}H)$, $W_2(CO)_8(NO)(P(OCH_3)_3)(\mu\text{-}H)$, $[(PPh_3)_2N]^+[W_2(CO)_{10}(\mu\text{-}H)]^-$, and $[Et_4N]^+[W_2(CO)_{10}(\mu\text{-}H)]^-$) imply that a significant amount of metal-metal interaction is present in the bent W-H-W system. Since the W-W overlap distance appears to remain fairly constant in the complexes which have been studied, the region of maximum overlap is located near the centroid of the W-H-W triangle. Our recent neutron diffraction study[30] of the tetraethylammonium salt of the $[Cr_2(CO)_{10}(\mu\text{-}H)]^-$ monoanion similarly has shown that the estimated overlap region in the slightly bent Cr-H-Cr bond (viz., 158.9 (6)°) does not coincide with the position of the hydrogen nucleus but is displaced from it by ca. 0.3 Å. From these structural studies it has been concluded that the bridging hydrogen atoms in bent M-H-M bonds are unlike terminal hydrogen atoms in that they do not occupy regular metal coordination sites. Consequently, the x-ray-determined position for the bridging hydrogen atom in a bent, closed-type M-H-M bond is expected to reflect the covalent character of the bond. Similarly, on the basis of our assumption that the average x-ray-determined hydrogen position provides a reasonable estimate of the electron density in a bent M-H-M bond, a comparison of our x-ray and neutron diffraction results for $Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}H)(\mu\text{-}P(CH_3)_2)$ demonstrates that the region of maximum overlap is displaced from the hydrogen nucleus toward the centroid of the Mo-H-Mo triangle.

In general, x-ray diffraction methods when applied to transition-metal hydrides containing bent M–H–M bonds will give shorter average M–H distances and larger M–H–M bond angles than neutron diffraction. The best x-ray-determined hydrogen position is not only extremely sensitive to the quality of the x-ray data and analysis but reflects the covalent nature of the metal–hydrogen–metal bond. Consequently, although a reasonable position for the bridging hydrogen atom in a transition-metal hydride can be "refined" with x-ray data in some cases, the inherent limitations of the x-ray diffraction experiment prevent a detailed analysis of the metal–hydrogen interaction.

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Registry No. $Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}H)(\mu\text{-}P(CH_3)_2)$, 12092-01-2.

Supplementary Material Available: A listing of the x-ray-determined atom positions and temperature factors, a table comparing the x-ray- and neutron-determined interatomic distances and bond angles, and a listing of the observed and calculated x-ray structure factors for $Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}H)(\mu\text{-}P(CH_3)_2)$ (17 pages). Ordering information is given on any current masthead page.

References and Notes

(1) This work was performed under the auspices of the Division of Basic Energy Sciences of the U.S. Department of Energy.

(2) (a) West Virginia University. (b) Argonne National Laboratory.

(3) For example: (a) M. R. Churchill and S. W.-Y. Ni, *J. Am. Chem. Soc.*, **95**, 2150 (1973); (b) M. R. Churchill and S. W.-Y. Chang, *Inorg. Chem.*, **13**, 2413 (1974); (c) M. R. Churchill, B. G. DeBoer, and F. J. Rotella, *ibid.*, **15**, 1843 (1976); (d) S. W. Kirtley, J. P. Olsen, and R. Bau, *J. Am. Chem. Soc.*, **95**, 4532 (1973).

(4) M. R. Churchill, *Inorg. Chem.*, **12**, 1213 (1973).

(5) Initial attempts to determine the metal–hydrogen distance[6] for a terminally bonded hydrogen atom such as $Mn(CO)_5H$ generally gave rather short internuclear separations and led earlier investigators to believe the hydrogen atom was buried in the electronic core of the metal atom. However, the outcome of a neutron diffraction study[7] of the β form of $Mn(CO)_5H$ provided conclusive evidence that the terminal hydride ligand behaves as a typical ligand with a normal Mn–H distance of 1.601 (16) Å. Although their x-ray data for β-$Mn(CO)_5H$ were not sufficient to refine the position of the terminal hydrogen atom, one might anticipate that the x-ray-determined bond length should be shorter than its neutron-determined value.

(6) (a) T. C. Farrar, F. E. Brinkman, T. D. Doyle, A. Davison, and J. W. Faller, *Inorg. Chem.*, **6**, 161 (1967); (b) A. G. Robiette, G. M. Sheldrick, and R. N. F. Simpson, *J. Mol. Struct.*, **4**, 221 (1969).

(7) S. J. LaPlaca, W. C. Hamilton, J. A. Ibers, and A. Davison, *Inorg. Chem.*, **8**, 1928 (1969).

(8) J. L. Petersen, L. F. Dahl, and J. M. Williams, *J. Am. Chem. Soc.*, **96**, 6610 (1974).

(9) The original x-ray structural analysis of $Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}H)(\mu\text{-}P(CH_3)_2)$ utilized three-dimensional equiinclination Weissenberg data.

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

(11) B. A. Frenz and J. A. Ibers in "Transition Metal Hydrides", E. L. Muetterties, Ed., Marcel Dekker, New York, N.Y., 1971. To refine the x-ray-determined position of the hydrogen atom in a transition-metal complex (within the inherent limitations of the x-ray experiment), the following conditions must be satisified: (a) the data must be of high quality and appropriate corrections for crystal decay, absorption effects, Lorentz–polarization effects, and anomalous dispersion must be included in the structural analysis; (b) the unit cell must be large to provide a sufficient number of low-angle diffraction data; (c) the thermal motion should be minimal; and (d) the compound should crystallize in a centrosymmetric point group. One additional factor of reasonable importance which has not been mentioned is that if the hydrogen atom is located on a symmetry element, the errors in the refinement found in the vicinity of the hydrogen atom may be magnified and contribute to the formation of a false electron density maximum. Since $Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}H)(\mu\text{-}P(CH_3)_2)$ does not exhibit any excessive amount or unusual type of thermal motion (as indicated by the reasonable anisotropic thermal ellipsoids from the neutron diffraction study[8]) and the bridging H atom is not constrained to lie on a symmetry element, this molecule is well suited for our purpose.

(12) The original x-ray[10] and later neutron diffraction[8] studies were made with a nonstandard *C*-centered triclinic cell of centrosymmetric symmetry $C\bar{1}$ rather than the reduced primitive triclinic cell due to the three interaxial angles being much closer to 90°.

(13) Private communication with J. C. Calabrese; R. A. Sparks et al., "Operations Manual, Syntex $P\bar{1}$ Diffractometer", Syntex Analytical Instrument, Cupertino, Calif., 1970.

(14) $R_a(F_o) = \sum||F_{av}| - |F_o||/\sum F_o$ and $R_a(F_o^2) = \sum|F_{av}^2 - F_o^2|/\sum F_o^2$.

(15) The scattering factor tables used for all nonhydrogen atoms were of Cromer and Mann.[16] The hydrogen atom scattering table was that of Stewart et al.[17] Real and imaginary corrections for anomalous dispersion (viz., $\Delta f' = -1.825$, $\Delta f'' = 0.688$ for Mo; $\Delta f' = 0.090$, $\Delta f'' = 0.095$ for P; $\Delta f' = 0.008$, $\Delta f'' = 0.006$ for O; $\Delta f' = 0.002$, $\Delta f'' = 0.002$ for C[18]) were included in the structure factor calculation.

(16) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).

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

(18) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).

(19) All least-squares refinements were based on the minimization of $\sum w_i|F_o^2 - S^2F_c^2|^2$ with the individual weights $w_i = 1/\sigma^2(F_o^2)$ and S the scale factor. $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$, $R(F_o^2) = \sum|F_o^2 - F_c^2|/\sum F_o^2$, and $R_w(F_o^2) = [\sum w_i|F_o^2 - F_c^2|^2/\sum w_iF_o^4]^{1/2}$.

(20) σ_1, the standard deviation of an observation of unit weight, is defined by the expression $[\sum w_i|F_o^2 - F_c^2|/(n-p)]^{1/2}$ where $w_i^{-1} = \sigma^2(F_o^2) = \sigma_c^2(F_c^2) + (0.04F_o^2)^2$, where σ_c is determined by counting statistics, n is the number of observations, and p is the number of parameters varied (viz., 276) during the least-squares refinement. For suitably weighted data and normally distributed errors the value of σ_1 is expected to be unity.

(21) S. J. LaPlaca and J. A. Ibers, *Acta Crystallogr.*, **18**, 511 (1965).

(22) The positional coordinates for the one peak on the difference Fourier map calculated with $(\sin\theta)/\lambda = 0.33$ Å^{-1} is roughly equal to a weighted average of the positional coordinates of the two peaks observed on the map calculated with $(\sin\theta)/\lambda = 0.43$ Å^{-1}. Since only one bridging hydrogen position is present, the observation of two peaks in the latter difference Fourier map is not clear.

(23) For a listing of the observed and calculated structure factors and the x-ray-determined and neutron-determined structural parameters, see the supplementary material.

(24) The computer programs which were used to perform the necessary calculations are as follows: data reduction and absorption correction, DATALIB; data averaging and sort, DATASORT; Fourier summation, CNTFOR, modification of FORDAP; least-squares refinement, ORXFLS3; error analysis of distances and angles, ORFFE3; and structural drawings, ORTEPII. A modification to DATASORT to calculate agreement factors between equivalent reflections was obtained from Fred K. Ross.

(25) "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974.

(26) S. C. Abrahams and E. T. Keve, *Acta Crystallogr.*, **23**, 971 (1967).

(27) The half-normal probability plot was obtained from a recent version of the program NORMPLOT, written by G. Christoph.

(28) R. A. Love, H. B. Chin, T. F. Koetzle, S. W. Kirtley, B. R. Wittlesey, and R. Bau, *J. Am. Chem. Soc.*, **98**, 4491 (1976).

(29) (a) J. P. Olsen, T. F. Koetzle, S. W. Kirtley, M. Andrew, D. L. Tipton, and R. Bau, *J. Am. Chem. Soc.*, **96**, 6621 (1974); (b) R. D. Wilson, S. A. Graham, and R. Bau, *J. Organomet. Chem.*, **91**, C49 (1975).

(30) J. Roziere, J. M. Williams, R. P. Stewart, Jr., J. L. Petersen, and L. F. Dahl, *J. Am. Chem. Soc.*, **99**, 4497 (1977).