mated P=O bond orders in a series of phosphoryl compounds of the basis of an internally consistent LCAO–MO method. A plot of P=O stretching frequency *vs.* P=O π-bond order based on these calculations reveals that trimethyl phosphate possesses a P=O π-bond order of 1.0, whereas this bond order in bicyclic phosphates such as II and IV is 1.4. These results substantiate the argument that the unusually high π-bond order in II and IV is associated with a withdrawal of electron density from the oxygen atom into available d orbitals on phosphorus. On the basis of Burger's observation that a decreasing extractant power of organophosphorus compounds for uranyl nitrate follows an increase in P=O stretching frequency for the ligand,[10] our results are not surprising. However, it is not clear at this time why unusually high P=O stretching frequencies are observed for polycyclic phosphates as opposed to the lower values associated with open-chain phosphates.

It is worthy of note that the increment in moment from I to II as shown in Table III is 2.95 D,[11] whereas this increase from open-chain phosphites to phosphates is about 1.2 D. On the basis of the infrared evidence a smaller P=O link moment for II than for an open-chain phosphate might be expected. However, these increments are only *apparent* values for the P=O link moments since they include other contributions, such as changes in bonding of phosphorus to the alkoxy oxygens, which cannot be separately evaluated on the basis of the dipole moment data alone.[11] The results of an X-ray structural analysis of II and electron diffraction studies on the bicyclic phosphite $P(OCH_2)_3CH$ and trimethyl phosphite now in progress will undoubtedly shed some light on the question of the bonding of phosphorus in these compounds.

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[9] E. L. Wagner, *J. Am. Chem. Soc.*, **85**, 161 (1963).

[10] L. L. Burger, U. S. Atomic Energy Commission Report HW-44888, 1957.

[11] T. L. Brown, J. G. Verkade, and T. S. Piper, *J. Phys. Chem.*, **65**, 2051 (1961).

Correspondence

The Molybdenum–Hydrogen Distance in Dihydridodi-π-cyclopentadienylmolybdenum

Sir:

The nature of the metal–hydrogen bond and the M–H distance in transition metal hydride complexes have given rise to considerable discussion. The point in dispute is whether the M–H distance is abnormally short in some of these compounds, that is, much less than a sum of covalent radii. The work relevant to this dispute has recently been reviewed in detail,[1,2] and it has been shown that the original arguments for a short M–H distance are no longer valid. The available evidence suggests that a normal M–H distance, that is, a distance consistent with the ordinary radii sum rules, is characteristic of the transition metal hydride complexes. The recent X-ray structure determination[3] of $(\pi\text{-}C_5H_5)_2MoH_2$, which reports an Mo–H distance of 1.2 ± 0.3 A, is in disagreement with this conclusion. We therefore felt that a reexamination of Gerloch and Mason's data[3] was in order. We demonstrate below that it is not possible to locate the metal-bonded hydrogen atom from the published X-ray data on $(\pi\text{-}C_5H_5)_2MoH_2$. It is also shown that these data do not support the reported[3] differences in carbon–carbon bond lengths.

Analysis of Gerloch and Mason's X-Ray Scattering Data.—The magnitudes of 274 observed structure factors in the $\{h0l\}$, $\{h1l\}$, $\{hk0\}$, and $\{0kl\}$ zones, on the "absolute" scale ×50, are listed in Gerloch and Mason's Table III. Of these, $F(40\bar{2}) = 0$ and presumably was included in error; it was omitted from the following analysis. It is necessary, with such a group of F_o values, to choose the method of analysis with care in order to avoid introduction of serious error. Thus, the proportion of the total number of independent $F(hkl)$ contained in this table is too small for three-dimensional Fourier series to be used. Further, two-dimensional Fourier series, with either F_o or ΔF (used by Gerloch and Mason) as coefficients, are unreliable especially in projection down axes of 10 A or greater as in the present crystal. The method of least squares was therefore selected as that best suited for analysis of Gerloch and Mason's scattering data.

In the correct use of the least-squares method, each observation must be weighted by the inverse variance in that observation. For investigations in which direct[4] estimation of this variance is not possible, a recent study[5] has demonstrated the Hughes' scheme[6] of $\sigma(F) \propto 4|F_{\min}|$ for $|F| \leq 4|F_{\min}|$, and $\sigma(F) \propto |F|$ for $|F| > 4|F_{\min}|$ to be the most acceptable alternative of the various empirical weighting schemes. Accordingly, Hughes' empirical weights were used, taking $|F_{\min}| = 375$ and the proportionality constant as 0.1. The approach to unity of S in Table I may be regarded as a demonstration that these weights are close to being correct. Neutral atomic scattering factors for C and

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[1] A. P. Ginsberg, "Transition Metal Chemistry," Vol. 1, R. L. Carlin, Ed., Marcel Dekker, Inc., New York, N. Y., 1965, Chapter 3.

[2] J. A. Ibers, *Ann. Rev. Phys. Chem.*, **16**, 375 (1965).

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[5] S. C. Abrahams and J. M. Reddy, *J. Chem. Phys.*, **43**, 2533 (1965).

[6] E. W. Hughes, *J. Am. Chem. Soc.*, **63**, 1737 (1941).

TABLE I

AGREEMENT FACTORS[a]

Parameters varied	R	wR	S
S.F., Mo(y, β_{ij}), 5C(xyz, β_{ij}), 6H	0.087	0.1170	1.132
S.F., Mo(y, β_{ij}), 5C(xyz, β_{ij}), 5H	0.089	0.1183	1.144
S.F., Mo(y, β_{ij}), 5C(xyz, β_{ij}), H(6)(xyz)5H	0.088	0.1172	1.142

[a] S.F. is the scale factor, parameters varied are given in parentheses, $wR = [\Sigma(\sqrt{w}||F_o| - |F_c||)^2/\Sigma(\sqrt{w}|F_o|)^2]^{1/2}$, and S is the standard deviation of an observation of unit weight.

H were taken directly from the International Tables.[7] A new Mo^+ atomic scattering factor[8] based on Hartree–Fock self-consistent field wave functions, with appropriate dispersion corrections,[7] was used for Mo. The actual least-squares calculations were performed with the Busing–Martin–Levy ORFLS program[9] modified[10] to accept $\Delta f'$ and $\Delta f''$.

Preliminary calculations were made in which the xyz coordinates of all 12 atoms in the asymmetric unit (see Gerloch and Mason's Table I) were included, but only Mo and the five C atoms were varied. This showed the F_o to be fitted best by anisotropic temperature factors. The best value for $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.119$ for the isotropic *vs.* 0.087 for the anisotropic temperature model. The isotropic Debye–Waller factor for each of the H atoms was taken as 3.5 A^2.

The crucial test was now made of allowing the atomic coordinates of H(6), the metal-bonded H atom, to vary, in addition to all of the coordinates of the six heavier atoms. Refinement was complete within three cycles and placed H(6) at −0.2505, 0.9368, 0.2599 as compared with Gerloch and Mason's assumed position —0.033, 0.5, 0.2. Attempts at refining the temperature factors of H(6), assuming either isotropic or anisotropic values, were unsuccessful. Large negative temperature coefficients (*e.g.*, $B > -15$ A^2) caused overflow in the IBM 7090 computer storage registers. An additional set of least-squares refinement was now computed, in which H(6) was completely omitted from the calculations. The three sets of least-squares refinement, using anisotropic temperature factors, can be quantitatively compared using Hamilton's[11] $\mathcal{R}$-ratio criterion. The necessary data for this test are given in Table I.

The information contained in Table I may be used to test the validity of two hypotheses relevant to Gerloch and Mason's postulate of H(6) being located at −0.033, 0.5, 0.2. Hypothesis a is: Gerloch and Mason's list of F_o contains a component caused by coherent X-ray scattering from H(6). Hypothesis b is: Gerloch and Mason's list of F_o is fitted better by H(6) at their postulated position than by H(6) at −0.2505, 0.9368, 0.2599. If hypothesis a is correct, the value of $R_{3,222,0.10}$ at the 0.10 significance level is 1.014, and at the 0.25 level it is 1.009. The experimental value of $\mathcal{R} = 0.1183/0.1170 = 1.011$. Hence, hypothesis a is rejected at the 10% but is accepted at the 25% significance level. If hypothesis b is true, $\mathcal{R}_{3,222,0.50}$ has the value 1.005. The experimental value is $\mathcal{R} = 0.1172/0.1170 = 1.002$. Hence, hypothesis b must be rejected, even at the 50% significance level.

The results obtained by the method of least squares should be, in principle, identical with those derivable by Fourier series analysis. Hydrogen atom positions have been successfully determined, by three-dimensional difference Fourier series, in the presence of atoms as heavy as rhodium.[12] In the present case, however, the Fourier series method is not comparable with the analysis used above, for the reasons indicated at the beginning of this section. It is nevertheless of interest to note the results of a two-dimensional difference Fourier series along the shortest (5.90 A) axis, based on the coordinates in Table II: The maximum and minimum features in $D(x0z)$, using the 80 $F(h0l)$ in Gerloch and Mason's Table III, are about 1 e A^{-2}. The maximum is associated with the Mo position, and the position of H(6) assumed by Gerloch and Mason lies within this maximum. The temperature factors given in Table III for Mo are uniformly and significantly lower by about 63% than Gerloch and Mason's values. Use of their temperature factors would produce an even larger feature at the Mo position. Numerous other features ascribable to noise, of ±0.5 e A^{-2}, appear throughout $D(x0z)$.

TABLE II

ATOMIC COORDINATES[a]

Atom	x	y	z
Mo(1)	0	0.3315 ± 5	$^1/_4$
C(1)	−0.1012 ± 16	0.0610 ± 43	0.2700 ± 32
C(2)	−0.1469 ± 16	0.1833 ± 67	0.1618 ± 40
C(3)	−0.1671 ± 17	0.4079 ± 77	0.2003 ± 36
C(4)	−0.1285 ± 16	0.4101 ± 69	0.3453 ± 29
C(5)	−0.0898 ± 21	0.1945 ± 50	0.3890 ± 35

[a] The standard deviations correspond to the least significant digit in the coordinate.

TABLE III

THERMAL VIBRATION PARAMETERS[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo(1)	29 ± 1	165 ± 8	78 ± 3	0	13 ± 1	0
C(1)	37 ± 8	180 ± 62	179 ± 38	−5 ± 24	18 ± 19	−102 ± 73
C(2)	28 ± 8	409 ± 138	214 ± 47	−29 ± 36	22 ± 18	61 ± 98
C(3)	34 ± 10	394 ± 117	207 ± 44	56 ± 45	7 ± 18	282 ± 77
C(4)	39 ± 10	304 ± 93	143 ± 29	38 ± 44	44 ± 15	18 ± 78
C(5)	59 ± 14	166 ± 72	171 ± 39	9 ± 34	64 ± 20	−80 ± 63

[a] All values ×10^4; see Table II regarding standard deviations. The values for C(3) are nonpositive definite, although not by a significant amount.

Restating, there is no significant evidence that Gerloch and Mason's scattering data either contain a component due to H(6) or can distinguish between H(6) at widely different positions in the unit cell.

Bond Lengths.—The atomic coordinates obtained by least-squares calculation, with all six hydrogen atoms constrained to occupy the positions given by Gerloch and Mason, are contained in Table II. If the position coordinates of H(6) are varied, the maximum

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(7) "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, pp 202, 216.

(8) A. J. Freeman and R. E. Watson, private communication, 1964.

(9) W. R. Busing, K. O. Martin, and H. A. Levy, ORNL Report TM-305, 1962.

(10) J. A. Ibers and W. C. Hamilton, *Acta Cryst.*, **17**, 781 (1964).

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(12) S. J. La Placa and J. A. Ibers, *ibid.*, **18**, 511 (1965).

change in any coordinate in Table II is half a standard deviation.

The bond lengths calculated from the atomic coordinates of Table II and Gerloch and Mason's lattice constants, using the Busing and Levy ORFFE program[13] to compute the standard deviations directly from the variance–covariance matrix, are given in Table IV.

TABLE IV

BOND LENGTHS[a]

Bond	Length, A	Bond	Length, A
Mo–C(1)	2.20 ± 26	C(1)–C(2)	1.36 ± 50
Mo–C(2)	2.25 ± 39	C(2)–C(3)	1.44 ± 60
Mo–C(3)	2.36 ± 30	C(3)–C(4)	1.48 ± 48
Mo–C(4)	2.34 ± 35	C(4)–C(5)	1.41 ± 48
Mo–C(5)	2.30 ± 39	C(5)–C(1)	1.44 ± 42

[a] See Table II regarding standard deviations.

The Mo–H distance, between Mo at 0, 0.3315, $^1/_4$ and H(6) at −0.2505, 0.9368, 0.2599, is 6.04 A as compared with the 1.2-A distance derived by Gerloch and Mason. H(6) at this position is closer to the symmetry-related Mo at $+(^1/_2{}^1/_2 0)$, with Mo–H = 2.98 A. The validity of Gerloch and Mason's H(6) position assumption has been discussed above.

The standard deviations given in Table IV are uniformly higher than those estimated by Gerloch and Mason. It should be pointed out here that the values in Table IV are indicators of precision, not accuracy, and, in the presence of systematic error such as is almost certainly present in Gerloch and Mason's list of F_o values, the true standard deviations are probably even larger than those given above. The Mo–C bond distances in Table IV agree with those of Gerloch and Mason, within one standard deviation. The C–C bond distances differ by up to 0.08 A, for C(4)–C(5).

We now show that the variation in C–C distance in the cyclopentadienyl ring is not significant. The average C–C bond length is 1.424 A; the maximum difference of a single observation from the average is 0.067 A, for C(1)–C(2). The Student t distribution indicates that we may reject the hypothesis that C(1)–C(2) is different from the average C–C length, at the 95% confidence level. Further, the C–C bond length distribution that Gerloch and Mason had found to be in apparent agreement with their metal–cyclopentadienyl bonding scheme[14] is now in disagreement. It is concluded that Gerloch and Mason's data[3] are not sufficiently accurate to distinguish small differences in C–C bond length.

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(13) W. R. Busing and H. A. Levy, ORNL Report 59-12-3, 1959.

(14) M. J. Bennett, M. B. Churchill, M. Gerloch, and R. Mason, *Nature*, **201**, 1318 (1964).

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Book Review

Organic Complexing Agents: Structure, Behavior, and Application to Inorganic Analysis. By D. D. PERRIN. Interscience Publishers, 605 Third Ave., New York, N. Y. 1964. v + 365 pp. 15 × 23 cm. $12.00.

This volume, the eighteenth in the series on analytical chemistry and its applications edited by P. J. Elving and I. M. Kolthof, "... attempts to present a picture of current chemical theory, more particularly as it relates to reaction between inorganic species and organic reagents. Applications to familiar analytical procedures will be discussed. ... (but) no attempt will be made to encompass practical details of the processes involved." To this end the chapters are concerned with "Chemical Bonds," "Stereochemistry and Stability of Metal Complexes," "Effects of Complex Formation on Oxidation–Reduction Potentials," "Factors Governing the Rates of Formation and Dissociation of Complexes," "Effects of Complex-Forming Species on Cation Concentrations," "Surface Phenomena," "Visible and Ultraviolet Absorption Spectra of Metal Complexes," "Solubility of Complexes," "Extraction into Organic Solvents," "Reactions of Organic Reagents with Inorganic Anions," "Procedures for Detecting and Determining Inorganic Neutral Molecules," "Analytical Properties of the Elements," and finally "On Seeking New Organic Reagents for Use in Inorganic Analysis."

A book of this nature is potentially valuable not only to the analytical chemist, but also to the coordination chemist, whether his interest is purely synthetic or kinetic and mechanistic. Most of the book reads well and is commendably referenced (through 1963). Unfortunately some sections lack the textual cohesiveness which would have resulted from critical comment concerning what is presented as only loosely related experimental evidence. There are also areas in which material is only sketchily referenced, or no references are cited at all. The pedagogical usefulness of the sections on theories of bonding and the spectra of complexes is questionable inasmuch as they are too briefly covered for someone not already familiar with the material, and their inclusion is superfluous for someone who is. It seems that the author had not quite determined to which level of competence he was directing his book when he, in the space of a few pages, introduces without comment the Jahn–Teller effect, defines coordination number, then poorly describes the origin of the Jahn–Teller effect.

In summary, however, the defects are minor in comparison with the value inherent in the fresh approach of this book, containing as it does a large amount of well correlated data.

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January 1966

H. EMELÉUS and A. G. SHARPE, Editors. "Advances in Inorganic Chemistry and Radiochemistry." Volume 7. Academic Press Inc., 111 Fifth Ave., New York, N. Y. 10003. 1965. vii + 449 pp. $15.50.

P. A. S. SMITH. "Open-Chain Nitrogen Compounds." W. A. Benjamin, Inc., 1 Park Ave., New York, N. Y. 10016. 1965. vii + 356 pp. Domestic $19.50; foreign $12.50.

W. E. DASENT. "Nonexistent Compounds." Marcel Dekker, Inc., 95 Madison Ave., New York, N. Y. 10016. 1965. vii + 182 pp. $8.50.