

# Structure of and Bonding in $[(C_5H_5)_2Mo_2H\{P(CH_3)_2\}(CO)_4]$ . Evidence for a Symmetrical, Bent, Three-Center Metal–Hydrogen–Metal Bond<sup>1</sup>

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A three-dimensional X-ray structural investigation of  $[(C_5H_5)_2Mo_2H\{P(CH_3)_2\}(CO)_4]$  has provided definite evidence for a symmetrical, localized, bent, three-center metal–hydrogen–metal bond. The molecular crystals are triclinic with reduced cell parameters  $a = 9.16$ ,  $b = 9.44$ ,  $c = 11.57$  Å.,  $\alpha = 84^\circ 01'$ ,  $\beta = 82^\circ 28'$ , and  $\gamma = 61^\circ 32'$ . The space group is  $P\bar{1}$  with two molecules per unit cell. A full matrix anisotropic–isotropic least-squares refinement has resulted in discrepancy factors  $R_1 = 10.5\%$  and  $R_2 = 12.5\%$ . The molecular configuration of approximate  $C_2$  symmetry consists of two essentially identical  $C_5H_5Mo(CO)_2$  fragments linked at the two molybdenum atoms, which are 3.26 Å. apart, by a symmetrically bridging  $P(CH_3)_2$  group. On the basis that the metal-coordinated hydrogen occupies a distinct coordination site (as has been found with other hydride transition metal complexes), the similar localized metal environments strongly imply equal association of the hydrogen with both molybdenum atoms. The probable location of the hydrogen at a regular coordination site which is 1.8 Å. from each molybdenum atom has been obtained from the close resemblance of the geometry of  $[(C_5H_5)_2Mo_2H\{P(CH_3)_2\}(CO)_4]$  to that of the related compounds  $[(C_5H_5)_2Mo(CO)_3]_2$  and  $(C_5H_5)_2Nb(CO)_4$ . The bent, three-center Mo–H–Mo bond involving one electron from the two molybdenum atoms and one from the hydrogen accounts for the compound's diamagnetism without the invoking of a separate Mo–Mo bond. The structural features and bonding of  $[(C_5H_5)_2Mo_2H\{P(CH_3)_2\}(CO)_4]$  are discussed with respect to the other phosphorus-bridged binuclear hydride complexes  $[(C_5H_5)_2Fe_2H\{PR_2\}(CO)_2]$  and  $[Mn_2H\{P(C_6H_5)_2\}(CO)_8]$ , for each of which the probable configuration involving a symmetrically bridging hydrogen atom (a localized, bent, three-center bond without a metal–metal bond) is proposed.

## Introduction

A large number of phosphorus- and arsenic-bridged binuclear compounds of metal carbonyls and their cyclopentadienyl derivatives recently have been prepared by Hayter and co-workers.<sup>3–10</sup> Among the most

interesting of these are the two hydrido complexes  $[(C_5H_5)_2Mo_2H\{P(CH_3)_2\}(CO)_4]$ <sup>4</sup> and  $[(C_5H_5)_2Fe_2H\{PR_2\}(CO)_2]$ <sup>3</sup> ( $R = CH_3$  or  $C_6H_5$ ) whose proton n.m.r. solution spectra showed the presence of metal-bonded hydrogen atoms. The absence of infrared absorption in the bridging carbonyl region indicated that these presumed dimeric molecules are held together in the solid state by a bridging dimethylphosphido group. Hayter<sup>3,4</sup> suggested the possibility that the metal-coordinated hydrogen atom may be associated equally with the two metal atoms, either by undergoing rapid intramolecular exchange between equivalent positions on the two metal atoms in solution or by participation in a bent, three-centered metal–hydrogen–metal bond possibly involving also the electrons of a metal–metal bond. The latter interaction was postulated<sup>3</sup> because of the diamagnetism of the compounds. A similar proposal of a rapid intramolecular exchange of a hydrogen between two metal atoms (although a bridging hydrogen was not excluded) was made earlier by Davison, *et al.*,<sup>11</sup> from their n.m.r. solution investigations of several protonated binuclear cations including  $[(C_5H_5)_2Fe_2H(CO)_4]^+$  and  $[(C_5H_5)_2W_2H(CO)_6]^+$ .

A three-dimensional single crystal X-ray structural examination of  $[(C_5H_5)_2Mo_2H\{P(CH_3)_2\}(CO)_4]$  has been carried out in order to investigate the coordination of the metal atoms and thereby to determine what inferences could be drawn concerning the position of the unique hydrogen.

## Experimental

Crystals of  $[(C_5H_5)_2Mo_2H\{P(CH_3)_2\}(CO)_4]$  were generously supplied to us by Dr. R. G. Hayter of Mellon Institute (now at Shell Development Co.). The density was determined by the flotation method. An irregularly shaped fragment of approximate dimensions  $0.2 \times 0.35 \times 0.2$  mm. was cut from a larger rod-shaped crystal, oriented about a 0.2-mm. direction, and used for gathering intensity data.

Multiple-film equi-inclination Weissenberg data were obtained for reciprocal levels  $0kl$  through  $12kl$ . Two sets of intensity data were taken for all levels except  $0kl$  in order to record the entire reciprocal lattice level on the top half of the Weissenberg film. This procedure eliminates the variations in reflection spot area due to spot compaction (but not spot extension).<sup>12</sup> On the basis of reflections common to both halves, these two sets were merged by least squares to give a single scale factor for each layer. A total of 4008 independent diffraction maxima were obtained in this

(1) Presented in part at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

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(3) R. G. Hayter, *J. Am. Chem. Soc.*, **85**, 3120 (1963).

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

(5) R. G. Hayter, *J. Am. Chem. Soc.*, **86**, 823 (1964).

(6) W. R. Cullen and R. G. Hayter, *ibid.*, **86**, 1030 (1964).

(7) R. G. Hayter and L. F. Williams, *Inorg. Chem.*, **3**, 613 (1964).

(8) R. G. Hayter, *ibid.*, **3**, 711 (1964).

(9) R. G. Hayter and L. F. Williams, *ibid.*, **3**, 717 (1964).

(10) R. G. Hayter and L. F. Williams, *J. Inorg. Nucl. Chem.*, **26**, 1977 (1964).

(11) A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3653 (1962).

(12) Cf. M. J. Buerger, "X-Ray Crystallography," John Wiley and Sons, Inc., New York, N. Y., 1942, pp. 227–229.

manner. In addition, timed-exposure precession photographs were taken for the  $hk0$ ,  $hkl$ , and  $hk2$  levels. The precession and Weissenberg data were merged by least squares onto a common scale before the anisotropic-isotropic part of the refinement was carried out.

All photographs were taken with Zr-filtered Mo  $K\alpha$  radiation. The intensities were estimated visually by comparison with a calibrated set of intensities taken from the same crystal. Lattice constants were determined from  $hk0$  and  $h0l$  precession photographs which were calibrated by superimposing a zero-level NaCl exposure on the same film. Corrections for Lorentz polarization effects and spot extension<sup>13</sup> were applied to all data, but absorption corrections were neglected owing to the small absorption coefficient ( $\mu R_{\max} = 0.25$ ). The atomic scattering factors were taken from the International Tables.<sup>14</sup> The standard deviations of the individual structure amplitudes were estimated as shown below.

$$\text{If } I(hkl)_0 < \sqrt{10}I_{\min}$$

$$\sigma(F(hkl)_0) = [F(hkl)_0/20][\sqrt{10}I_{\min}/I(hkl)_0]^2$$

$$\text{If } I(hkl)_0 \geq \sqrt{10}I_{\min}$$

$$\sigma(F(hkl)_0) = |F(hkl)_0|/20$$

## Results

**Crystal Data.** The lattice parameters for the reduced triclinic cell are  $a = 9.16 \pm 0.02$ ,  $b = 9.44 \pm 0.02$ ,  $c = 11.57 \pm 0.025 \text{ \AA}$ ,  $\alpha = 84^\circ 01' \pm 10'$ ,  $\beta = 82^\circ 28' \pm 10'$ , and  $\gamma = 61^\circ 32' \pm 10'$ . This reduced cell was determined<sup>15</sup> from the originally chosen C-centered cell which, because of its near-orthogonality, was used throughout the structural determination. The parameters for this nonprimitive cell are  $a_c = 9.16 \pm 0.02$ ,  $b_c = 16.59 \pm 0.03$ ,  $c_c = 11.57 \pm 0.025 \text{ \AA}$ ,  $\alpha_c = 92^\circ 39' \pm 10'$ ,  $\beta_c = 97^\circ 32' \pm 10'$ , and  $\gamma_c = 90^\circ 34' \pm 10'$ . All results are reported in terms of the C-centered cell, to which the reduced cell is related by the following transformation:  $a = a_c$ ,  $b = 1/2(a_c + b_c)$ , and  $c = -c_c$ . The experimental density of 1.89 g./ml. agrees with the value of 1.89 g./ml. calculated on the basis of four molecules per C-centered cell (or two molecules per primitive cell). The C-centered space group was chosen to be  $C\bar{1}$  (*i.e.*,  $P\bar{1}$  for the primitive cell) and the subsequent structural analysis verified this choice. The asymmetric unit consists of one molecule comprised of two molybdenum, one phosphorus, four oxygen, sixteen carbon, and seventeen hydrogen atoms.

**Determination of the Structure.** The atomic positions were found by the usual combination of three-dimensional Patterson and Fourier syntheses computed with the Blount program.<sup>16</sup> The resulting atomic parameters were refined with a modified version of the Busing-Martin-Levy full-matrix least-squares program.<sup>17</sup> After seven cycles of isotropic refinement, with

(13) D. C. Phillips, *Acta Cryst.*, **7**, 746 (1954).

(14) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962.

(15) L. V. Azaroff and M. J. Buerger, "The Powder Method in X-Ray Crystallography," McGraw-Hill Book Co., Inc., New York, N. Y., 1958, pp. 134-136.

(16) J. F. Blount, "A Three-Dimensional Crystallographic Fourier Summation Program for the CDC 1604 Computer," University of Wisconsin, 1962.

(17) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, A For-

individual atomic temperature factors and with a separate scale factor for each reciprocal layer of data, the discrepancy factors

$$R_1 = [\sum |F_o| - |F_c|]/[\sum |F_o|] \times 100$$

and

$$R_2 = [\sum w|F_o| - |F_c|]/[\sum w|F_o|]^{1/2} \times 100$$

stood at 10.9 and 13.7%, respectively. Since a three-dimensional difference Fourier map based on the isotropic refinement revealed some residual electron density around the positions of the heavy atoms, refinement was continued with individual anisotropic temperature coefficients for the molybdenum and phosphorus atoms, and with individual isotropic temperature factors for the light atoms. The precession-scaled data were used for this portion of the refinement (with one over-all scale factor being varied) to minimize interactions between the anisotropic temperature factor coefficients and the scale factors. The refinement was terminated with discrepancy factors  $R_1 = 10.5\%$  and  $R_2 = 12.5\%$ . During the last cycle, no parameter changed by more than half of its standard deviation.<sup>18</sup> The final positional parameters agreed well with the corresponding ones from the isotropic refinement. Of the 69 positional parameters, 55 differed by less than one standard deviation, 11 by one to two standard deviations, and only 3 (all coordinates of the cyclopentadienyl carbons) by two to three standard deviations.

A three-dimensional difference Fourier synthesis based on the final parameters confirmed the structure, but gave no positive indication of the position of the unique hydrogen atom (*vide infra*). Further attempts to locate this atom from difference maps based only on low angle reflections were also unsuccessful. No attempt was made to determine the coordinates of the other hydrogen atoms. A close examination of a final three-dimensional electron density map as well as the difference maps revealed no indication of a disordered structure involving the nonhydrogen atoms. The absence of any order-disorder phenomena also is in agreement with the refined molecular parameters. Hence, any possibility of the asymmetric molecule occupying more than one orientation in the unit cell can be ruled out.

Bond lengths and angles were calculated with the Busing-Martin-Levy function and error program.<sup>19</sup> Standard deviations assigned to individual distances and angles were obtained from the full inverse error matrix and consequently include the effects of correlation between the variables; estimated lattice constant errors also were included in the calculations. The final positional and thermal parameters are given in Table I, and the intramolecular bond lengths and angles are given in Tables II and III, respectively.

tran Crystallographic Least Squares Program," ORNL-TM-305, Oak Ridge National Laboratory, 1962.

(18) Calculated and observed structure factors are deposited as Document No. 8365 with the American Documentation Institute, Auxiliary Publication Project, Photoduplication Service, Library of Congress, Washington 25, D.C. A copy may be secured by citing the document number and remitting \$1.25 for photoprints or \$1.25 for 35-mm. microfilm in advance payable to: Chief, Photoduplication Service, Library of Congress.

(19) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, A Fortran Crystallographic Function and Error Program," ORNL-TM-306, Oak Ridge National Laboratory, 1964.

**Table I.** Final Atomic Parameters and Standard Deviations

| Atom            | x             | y             | z             | $B_i$ ,<br>Å. <sup>2</sup> | $10^4\sigma$<br>(x) | $10^4\sigma$<br>(y) | $10^4\sigma$<br>(z) | $\sigma(B_i)$ ,<br>Å. <sup>2</sup> |
|-----------------|---------------|---------------|---------------|----------------------------|---------------------|---------------------|---------------------|------------------------------------|
| Mo <sub>1</sub> | 0.4848        | 0.3363        | 0.2456        | a                          | 0.9                 | 0.5                 | 0.8                 | a                                  |
| Mo <sub>2</sub> | 0.8256        | 0.3686        | 0.2044        | a                          | 0.9                 | 0.5                 | 0.8                 | a                                  |
| P               | 0.6690        | 0.4357        | 0.3300        | a                          | 3                   | 2                   | 2                   | a                                  |
| C <sub>1</sub>  | 0.3742        | 0.4350        | 0.2417        | 2.54                       | 14                  | 8                   | 11                  | 0.19                               |
| O <sub>1</sub>  | 0.3116        | 0.4939        | 0.2400        | 3.49                       | 11                  | 6                   | 9                   | 0.18                               |
| C <sub>2</sub>  | 0.4281        | 0.3468        | 0.0815        | 2.61                       | 14                  | 8                   | 11                  | 0.19                               |
| O <sub>2</sub>  | 0.3935        | 0.3498        | -0.0189       | 4.08                       | 13                  | 7                   | 10                  | 0.21                               |
| C <sub>3</sub>  | 0.9587        | 0.3863        | 0.3507        | 2.55                       | 14                  | 7                   | 11                  | 0.19                               |
| O <sub>3</sub>  | 1.0386        | 0.3979        | 0.4325        | 3.98                       | 13                  | 7                   | 10                  | 0.20                               |
| C <sub>4</sub>  | 0.8693        | 0.2603        | 0.2489        | 2.50                       | 14                  | 8                   | 11                  | 0.19                               |
| O <sub>4</sub>  | 0.8963        | 0.1948        | 0.2770        | 3.60                       | 12                  | 6                   | 9                   | 0.19                               |
| C <sub>5</sub>  | 0.7098        | 0.4394        | 0.4890        | 3.01                       | 16                  | 8                   | 12                  | 0.22                               |
| C <sub>6</sub>  | 0.6502        | 0.5460        | 0.3127        | 3.28                       | 16                  | 9                   | 13                  | 0.24                               |
| C <sub>7</sub>  | 0.2958        | 0.2595        | 0.2924        | 4.80                       | 22                  | 11                  | 17                  | 0.36                               |
| C <sub>8</sub>  | 0.3859        | 0.2042        | 0.2416        | 4.16                       | 20                  | 10                  | 15                  | 0.30                               |
| C <sub>9</sub>  | 0.5190        | 0.2015        | 0.3015        | 3.65                       | 18                  | 10                  | 14                  | 0.26                               |
| C <sub>10</sub> | 0.5167        | 0.2524        | 0.4068        | 4.94                       | 23                  | 12                  | 18                  | 0.36                               |
| C <sub>11</sub> | 0.3804        | 0.2871        | 0.3963        | 4.44                       | 21                  | 11                  | 16                  | 0.32                               |
| C <sub>12</sub> | 1.0046        | 0.3881        | 0.0870        | 3.32                       | 17                  | 9                   | 13                  | 0.24                               |
| C <sub>13</sub> | 0.8903        | 0.3481        | 0.0160        | 3.33                       | 16                  | 9                   | 13                  | 0.24                               |
| C <sub>14</sub> | 0.7688        | 0.3977        | 0.0034        | 3.32                       | 17                  | 9                   | 13                  | 0.24                               |
| C <sub>15</sub> | 0.8104        | 0.4709        | 0.0690        | 3.71                       | 18                  | 9                   | 14                  | 0.27                               |
| C <sub>16</sub> | 0.9507        | 0.4638        | 0.1215        | 3.68                       | 18                  | 10                  | 14                  | 0.26                               |
|                 | $10^6 B_{11}$ | $10^6 B_{22}$ | $10^6 B_{33}$ | $10^6 B_{12}$              | $10^6 B_{13}$       | $10^6 B_{23}$       |                     |                                    |
| Mo <sub>1</sub> | 461 (9)       | 179 (3)       | 371 (7)       | 19 (4)                     | 79 (6)              | 51 (4)              |                     |                                    |
| Mo <sub>2</sub> | 474 (9)       | 155 (3)       | 344 (7)       | 24 (4)                     | 120 (6)             | 25 (3)              |                     |                                    |
| P               | 435 (25)      | 155 (9)       | 315 (18)      | -21 (12)                   | 165 (17)            | 0 (10)              |                     |                                    |

<sup>a</sup> For the molybdenum and phosphorus atoms temperature factors of the form  $\exp\{-h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkB_{12} + 2hlB_{13} + 2klB_{23}\}$  were used; the resulting thermal coefficients (with standard deviations in parentheses) are given in the lower part of the table.

## Discussion

The over-all configuration of the  $\mu$ -(dimethylphosphido)hydridodi- $\pi$ -cyclopentadienyltetracarbonyldimolybdenum molecule is shown in Figure 1. The two  $C_5H_5Mo(CO)_2$  fragments are essentially identical and are linked by a symmetrically bridging dimethylphos-

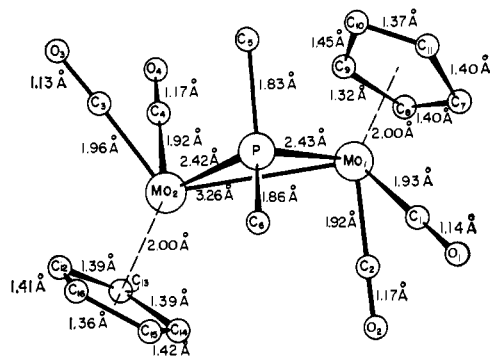


Figure 1. Molecular configuration of  $[(C_5H_5)_2Mo_2H\{P(CH_3)_2\}(CO)_4]$ .

phine group. A pseudo-twofold axis is defined by the phosphorus and the midpoint of the two molybdenum atoms. The Mo-Mo bond length of 3.26 Å. is that expected for a covalent  $\sigma$ -type metal-metal bond (later to be shown not to be needed to account for the "closed-shell" electronic configuration) and compares favorably with the value of 3.22 Å. found in the dimer,  $[(C_5H_5)Mo(CO)_3]_2$ ,<sup>20</sup> in which the two halves of the

(20) F. C. Wilson and D. P. Shoemaker, *J. Chem. Phys.*, **27**, 809 (1957).

Table II. Bond Lengths and Standard Deviations (Å.)

|                                  |               |                                  |               |
|----------------------------------|---------------|----------------------------------|---------------|
| Mo <sub>1</sub> -P               | 2.426 ± 0.006 | Mo <sub>2</sub> -P               | 2.416 ± 0.006 |
| Mo <sub>1</sub> -C <sub>1</sub>  | 1.934 ± 0.013 | Mo <sub>2</sub> -C <sub>4</sub>  | 1.960 ± 0.013 |
| Mo <sub>1</sub> -C <sub>2</sub>  | 1.918 ± 0.014 | Mo <sub>2</sub> -C <sub>8</sub>  | 1.923 ± 0.013 |
| Mo <sub>1</sub> -C <sub>7</sub>  | 2.276 ± 0.020 | Mo <sub>2</sub> -C <sub>12</sub> | 2.292 ± 0.016 |
| Mo <sub>1</sub> -C <sub>8</sub>  | 2.359 ± 0.018 | Mo <sub>2</sub> -C <sub>13</sub> | 2.344 ± 0.015 |
| Mo <sub>1</sub> -C <sub>9</sub>  | 2.369 ± 0.017 | Mo <sub>2</sub> -C <sub>14</sub> | 2.389 ± 0.016 |
| Mo <sub>1</sub> -C <sub>10</sub> | 2.367 ± 0.021 | Mo <sub>2</sub> -C <sub>15</sub> | 2.356 ± 0.017 |
| Mo <sub>1</sub> -C <sub>11</sub> | 2.275 ± 0.019 | Mo <sub>2</sub> -C <sub>16</sub> | 2.263 ± 0.017 |
| C <sub>1</sub> -O <sub>1</sub>   | 1.137 ± 0.015 | C <sub>2</sub> -O <sub>3</sub>   | 1.126 ± 0.016 |
| C <sub>2</sub> -O <sub>2</sub>   | 1.167 ± 0.016 | C <sub>4</sub> -O <sub>4</sub>   | 1.168 ± 0.016 |
| C <sub>7</sub> -C <sub>8</sub>   | 1.399 ± 0.025 | C <sub>12</sub> -C <sub>13</sub> | 1.386 ± 0.020 |
| C <sub>8</sub> -C <sub>9</sub>   | 1.323 ± 0.023 | C <sub>13</sub> -C <sub>14</sub> | 1.386 ± 0.021 |
| C <sub>9</sub> -C <sub>10</sub>  | 1.453 ± 0.025 | C <sub>14</sub> -C <sub>15</sub> | 1.424 ± 0.020 |
| C <sub>10</sub> -C <sub>11</sub> | 1.373 ± 0.026 | C <sub>15</sub> -C <sub>16</sub> | 1.356 ± 0.022 |
| C <sub>11</sub> -C <sub>7</sub>  | 1.398 ± 0.025 | C <sub>16</sub> -C <sub>12</sub> | 1.412 ± 0.021 |
| P-C <sub>6</sub>                 | 1.827 ± 0.015 | P-C <sub>6</sub>                 | 1.858 ± 0.015 |
| Mo <sub>1</sub> -Mo <sub>2</sub> | 3.262 ± 0.007 |                                  |               |

molecule are held together only by a Mo-Mo bond. The Mo-P bond lengths of 2.42 and 2.43 Å., which are equivalent within their standard deviations, are approximately 0.3 Å. shorter than the sum of the covalent radii of Mo (1.62 Å., based on one-half of the single bond Mo-Mo distance)<sup>21</sup> and P (1.10 Å.) and thereby

(21) The single bond covalent radii given by Pauling<sup>22</sup> for the transition metals are not applicable to the nonionic zerovalent metal carbonyls, their derivatives, and related compounds, especially for the earlier members of the third, fourth, and fifth row transition metal series. Instead, Bennett and Mason<sup>23</sup> from the length of the  $\sigma$ -bond Mo-C<sub>2</sub>H<sub>5</sub> in  $(C_5H_5)Mo(C_2H_5)(CO)_3$  and Dahl, *et al.*,<sup>24</sup> from the length of the presumed  $\sigma$ -bond in  $C_5H_5Mn(CO)_5$  have shown that a more meaningful covalent radius is obtained if one-half the metal-metal bond length is used. The following approximate values based on X-ray work are recommended for nonionic complexes (in Å.): Cr (1.50),<sup>25</sup> Mo (1.61),<sup>20</sup> Mn (1.46),<sup>26</sup> Tc (1.51),<sup>27</sup> Re (1.51).<sup>28</sup> The dependence of covalent radii on such factors as the effective nuclear charge, metal coordination number, and metal hybridization is ignored here. The variation of iron-iron distances in carbonyl compounds with metal-metal bonds is con-

**Table III. Bond Angles in Degrees**

|  |             |   |             |
|--|-------------|---|-------------|
| P-Mo <sub>1</sub> -C <sub>1</sub>                | 77.6 ± 0.4  | P-Mo <sub>2</sub> -C <sub>3</sub>                 | 77.7 ± 0.4  |
| P-Mo <sub>1</sub> -C <sub>2</sub>                | 112.9 ± 0.4 | P-Mo <sub>2</sub> -C <sub>4</sub>                 | 112.0 ± 0.4 |
| C <sub>1</sub> -Mo <sub>1</sub> -C <sub>2</sub>  | 77.6 ± 0.6  | C <sub>3</sub> -Mo <sub>2</sub> -C <sub>4</sub>   | 77.6 ± 0.6  |
| Mo <sub>2</sub> -Mo <sub>1</sub> -C <sub>1</sub> | 111.6 ± 0.4 | Mo <sub>1</sub> -Mo <sub>2</sub> -C <sub>3</sub>  | 112.9 ± 0.4 |
| Mo <sub>2</sub> -Mo <sub>1</sub> -C <sub>2</sub> | 88.5 ± 0.4  | Mo <sub>1</sub> -Mo <sub>2</sub> -C <sub>4</sub>  | 88.7 ± 0.4  |
| Mo <sub>2</sub> -Mo <sub>1</sub> -P              | 47.5 ± 0.1  | Mo <sub>1</sub> -Mo <sub>2</sub> -P               | 47.8 ± 0.1  |
| Mo <sub>1</sub> -C <sub>1</sub> -O <sub>1</sub>  | 178.7 ± 1.2 | Mo <sub>2</sub> -C <sub>3</sub> -O <sub>3</sub>   | 177.5 ± 1.2 |
| Mo <sub>1</sub> -C <sub>2</sub> -O <sub>2</sub>  | 177.1 ± 1.2 | Mo <sub>2</sub> -C <sub>4</sub> -O <sub>4</sub>   | 179.3 ± 1.1 |
| Mo <sub>1</sub> -P-C <sub>5</sub>                | 115.7 ± 0.5 | Mo <sub>2</sub> -P-C <sub>6</sub>                 | 115.1 ± 0.5 |
| Mo <sub>1</sub> -P-C <sub>6</sub>                | 123.7 ± 0.5 | Mo <sub>2</sub> -P-C <sub>5</sub>                 | 122.6 ± 0.5 |
| C <sub>7</sub> -C <sub>8</sub> -C <sub>9</sub>   | 112.2 ± 1.6 | C <sub>12</sub> -C <sub>13</sub> -C <sub>14</sub> | 109.1 ± 1.3 |
| C <sub>8</sub> -C <sub>9</sub> -C <sub>10</sub>  | 106.7 ± 1.5 | C <sub>13</sub> -C <sub>14</sub> -C <sub>15</sub> | 106.8 ± 1.3 |
| C <sub>9</sub> -C <sub>10</sub> -C <sub>11</sub> | 105.9 ± 1.6 | C <sub>14</sub> -C <sub>15</sub> -C <sub>16</sub> | 108.2 ± 1.4 |
| C <sub>10</sub> -C <sub>11</sub> -C <sub>7</sub> | 110.4 ± 1.6 | C <sub>15</sub> -C <sub>16</sub> -C <sub>12</sub> | 108.8 ± 1.4 |
| C <sub>11</sub> -C <sub>7</sub> -C <sub>8</sub>  | 104.5 ± 1.7 | C <sub>16</sub> -C <sub>12</sub> -C <sub>13</sub> | 107.0 ± 1.4 |
| Mo <sub>1</sub> -P-Mo <sub>2</sub>               | 84.7 ± 0.2  | C <sub>5</sub> -P-C <sub>6</sub>                  | 97.3 ± 0.7  |

indicate significant Mo-P  $\pi$ -bonding. The sum of Pauling's covalent radii for Mo and P is 2.40 Å.<sup>22</sup> The average metal-carbonyl carbon and carbon-oxygen distances of 1.93 and 1.15 Å., respectively, agree well with those found for other molybdenum carbonyl complexes.<sup>20, 23, 30</sup> The perpendicular distance of 2.00 Å. from the molybdenum atoms to the cyclopentadienyl rings is also very close to that found in other cyclopentadienyl molybdenum complexes.<sup>20, 23</sup> The Mo-C-O angles are all linear within experimental error. The bonds to the phosphorus form a somewhat compressed tetrahedron, as can be seen from the C-P-C and Mo-P-Mo angles of 97 and 85°, respectively.

The interesting question of the probable location of the hydridic hydrogen atom in this molecule can best be approached by considering the coordination of the metal atoms. Recent structural work on a number of transition metal hydride complexes including K<sub>2</sub>ReH<sub>6</sub>,<sup>31</sup> HMn(CO)<sub>5</sub>,<sup>32</sup> HRh(CO){P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>}<sub>3</sub>,<sup>33</sup> HOsBr(CO){P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>}<sub>3</sub>,<sup>34</sup> and HPt{P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>}<sub>2</sub>Br<sup>35</sup> indicates that in such compounds a hydridic hydrogen atom invariably occupies a distinct site in the coordination sphere of the metal to which it is bonded. Thus, the similar localized environments of the two metal atoms in [(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Mo<sub>2</sub>H{P(CH<sub>3</sub>)<sub>2</sub>}(CO)<sub>4</sub>] strongly imply that the hydrogen is symmetrically placed between the two metal atoms. If it were associated with only one metal atom, the two metals would have different coordination numbers and hence considerably different arrangements of their ligands.

siderable and can be rationalized in terms of the amount of negative charge localized on the metal atom through coordination with other ligands.<sup>29</sup>

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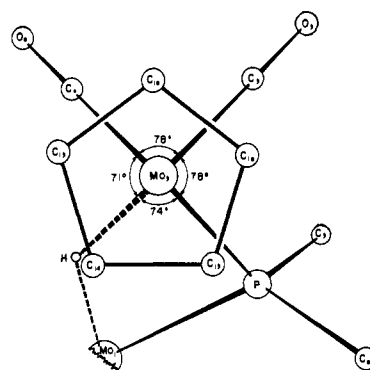


Figure 2. Localized environment of one molybdenum atom in [(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Mo<sub>2</sub>H{P(CH<sub>3</sub>)<sub>2</sub>}(CO)<sub>4</sub>], viewed perpendicular to the cyclopentadienyl ring, with the probable hydrogen position indicated.

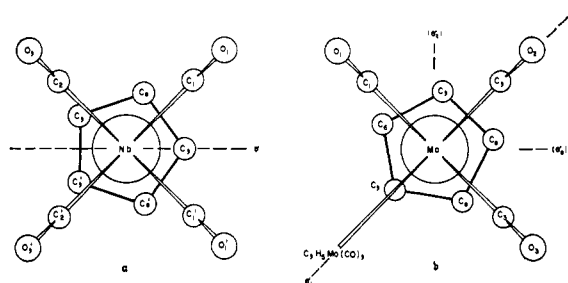


Figure 3. Views down the principal axis of (C<sub>5</sub>H<sub>5</sub>)Nb(CO)<sub>4</sub> and [(C<sub>5</sub>H<sub>5</sub>)Mo(CO)<sub>3</sub>]<sub>2</sub> (reprinted from the Ph.D. Thesis of H. W. Baird, University of Wisconsin, 1963).

A view of the environment of one of the metal atoms projected down a line perpendicular to its cyclopentadienyl ring is shown in Figure 2. This figure is very similar to corresponding views of the two closely related compounds [(C<sub>5</sub>H<sub>5</sub>)Mo(CO)<sub>3</sub>]<sub>2</sub><sup>20</sup> and (C<sub>5</sub>H<sub>5</sub>)Nb(CO)<sub>4</sub><sup>36</sup> (Figure 3). The C<sub>3</sub>-Mo-C<sub>4</sub> and C<sub>3</sub>-Mo-P angles of 77.6 and 77.7° in the phosphorus-bridged complex agree well with the average C-M-C angles for adjacent carbonyls of 76 and 74° in [(C<sub>5</sub>H<sub>5</sub>)Mo(CO)<sub>3</sub>]<sub>2</sub> and (C<sub>5</sub>H<sub>5</sub>)Nb(CO)<sub>4</sub>, respectively. The dihedral angle between the mean plane of the cyclopentadienyl ring and the plane determined by the carbonyl carbons is 5° in the niobium compound and 13° in the molybdenum dimer. In the phosphorus-bridged compound, the equivalent angle (between the mean cyclopentadienyl plane and the plane determined by C<sub>3</sub>, C<sub>4</sub>, and a point 1.94 Å. along the Mo-P bond) is 6°. All of the angles mentioned for the phosphorus-bridged complex are essentially identical in the two halves of the molecule. This close resemblance of the orientations of the cyclopentadienyl ring, the carbonyl groups, and the phosphorus atom of [(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Mo<sub>2</sub>H{P(CH<sub>3</sub>)<sub>2</sub>}(CO)<sub>4</sub>] (Figure 2) with those of the corresponding groups in the molecular molybdenum and niobium complexes (Figure 3) leads to the proposal that the hydrogen atom occupies the remaining regular coordination site and is symmetrically disposed between the two metal atoms (Figure 2). The bonding of [(C<sub>5</sub>H<sub>5</sub>)Mo(CO)<sub>3</sub>]<sub>2</sub> and (C<sub>5</sub>H<sub>5</sub>)Nb(CO)<sub>4</sub> has been interpreted<sup>36</sup> in terms of seven-coordinated metal atoms having the NbF<sub>7</sub><sup>2-</sup> configuration with the cyclopentadienyl groups occupying three coordination sites. The similarities men-

(36) H. W. Baird and L. F. Dahl, to be published.

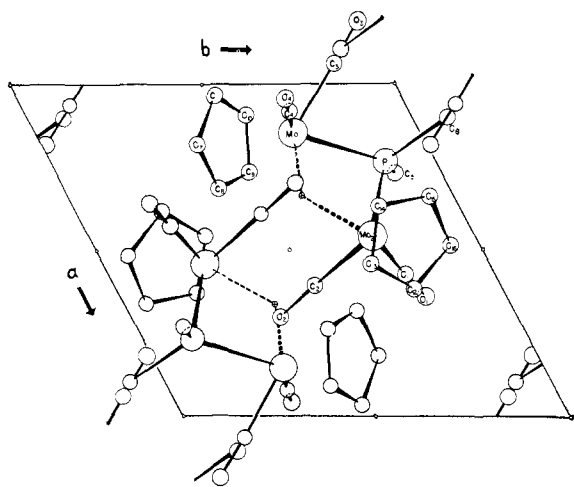


Figure 4. [001] projection of the primitive unit cell; the probable hydrogen positions are denoted.

tioned above suggest that the same type of coordination is involved in the phosphorus-bridged compound.

On the basis of these considerations, the approximate position of the hydrogen atom was obtained by calculating the point of intersection of the molecular pseudo-twofold axis defined by the phosphorus atom and the midpoint of the two molybdenum atoms with the plane which is perpendicular to the mean plane of the cyclopentadienyl ring and which passes through  $\text{Mo}_2$  and  $\text{C}_3$ . The fractional coordinates of this presumed hydrogen position were found to be  $x = 0.65$ ,  $y = 0.32$ , and  $z = 0.18$ , with the point being located at 1.8 Å. from each of the molybdenum atoms. The same point was found when the calculation was based on the other cyclopentadienylmolybdenum dicarbonyl fragment. Although a reinvestigation of the final difference maps revealed a positive residual of electron density at this point, it was not sufficiently great to identify the peak as due to the hydrogen atom. A bridged Mo-H distance of 1.8 Å. is a reasonable value based on comparison, for example, with the average terminal  $\text{Re-H}$  distance of  $1.68 \pm 0.01$  Å. observed in  $\text{K}_2\text{ReH}_3$ .<sup>31</sup> The Mo-H distance should be greater than 1.7 Å., since the covalent radius of rhenium is approximately 0.1 Å. shorter than that of molybdenum,<sup>21</sup> and since it is expected that a bridged Mo-H distance would be longer than a terminal Mo-H distance. This assumed position of the hydrogen also gives a  $\text{C}_4\text{-Mo-H}$  angle of  $71^\circ$  and a  $\text{P-Mo-H}$  angle of  $74^\circ$  (Figure 2), both of which are quite close to the corresponding angles in the molybdenum and niobium complexes. The Mo-H-Mo angle based on this assumed position is  $131^\circ$ .

A projection of the primitive unit cell onto a plane perpendicular to the [001] direction is shown for  $[(\text{C}_5\text{H}_5)_2\text{Mo}_2\text{H}\{\text{P}(\text{CH}_3)_2\}(\text{CO})_4]$  in Figure 4. The shortest intermolecular distances of 3.25 Å. indicate no abnormal interactions between molecules. The proposed positions for the hydridic hydrogen atoms of the two molecules have been included in the projection in order to show that there are no packing considerations which would rule out the location of hydrogen atoms in the vicinity of these points. The two predicted positions shown are separated from each other by a distance of 5.2 Å.

A qualitative analysis of the electronic structure of the proposed symmetrically bridging Mo-H-Mo system in  $[(\text{C}_5\text{H}_5)_2\text{Mo}_2\text{H}\{\text{P}(\text{CH}_3)_2\}(\text{CO})_4]$  has particular significance with regard to a metal-metal interaction no longer being necessary to account for the observed diamagnetism of this and other binuclear hydrido complexes. Since a cyclopentadienyl radical, two terminal carbonyl groups, and the bridging dimethylphosphine group can be considered as "effectively" donating  $10\frac{1}{2}$  electrons to each of the zerovalent molybdenum atoms (atomic no. 42), the Mo-H-Mo delocalized interaction may be described in terms of localized, bent, three-center MO's (with the three resulting MO's requiring as basis functions one  $\sigma$ -type orbital for each of the two molybdenum atoms and the one bridging 1s orbital for the hydrogen), of which only the bonding one is occupied with  $\frac{1}{2}$  electron contributed from each of the two molybdenum atoms and one from the hydrogen atom. This bonding representation with the two electrons delocalized over both molybdenum atoms (as well as the hydrogen) enables each molybdenum to attain a "closed-shell" electronic configuration without the need for a separate metal-metal bond. It is of interest whether this and other phosphorus-bridged binuclear hydrido complexes could be deprotonated without further degradation by suitable Lewis bases to give monobridged anionic complexes which then would be stabilized by a metal-metal bond in place of the bridging hydrogen system. The similarity of the Mo-Mo distances in  $[(\text{C}_5\text{H}_5)_2\text{Mo}_2\text{H}\{\text{P}(\text{CH}_3)_2\}(\text{CO})_4]$  (3.26 Å.) and  $[(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$ <sup>20</sup> (3.22 Å.) indicates that the Mo-H-Mo system in the former compound may be considered as arising from the protonation of a Mo-Mo single bond such that the geometry of the deprotonated species would remain essentially unaltered.

The proposed electron delocalized bonding of the bridged system is not without parallel, since delocalized systems involving bridged olefinic carbons bonded to two metals by delocalized  $\mu$ -type bonds have been demonstrated from X-ray studies of  $\text{Co}_4(\text{CO})_{10}$ - $(\text{C}_2\text{H}_5\text{C}_2\text{C}_2\text{H}_5)$ <sup>37</sup> and the black isomer of  $\text{Fe}_3(\text{CO})_8$ - $(\text{C}_6\text{H}_5\text{C}_2\text{C}_6\text{H}_5)_2$ .<sup>38</sup>

These results suggest that each of the binuclear hydrido complexes  $[(\text{C}_5\text{H}_5)_2\text{Fe}_2\text{H}\{\text{PR}_2\}(\text{CO})_2]$ <sup>3</sup> and  $[\text{Mn}_2\text{H}\{\text{P}(\text{C}_6\text{H}_5)_2\}(\text{CO})_3]$ <sup>5,39</sup> also possesses a symmetrically bridged hydrogen atom. No doubt the basic configuration for these two complexes can be considered as formed by the junction of two octahedra at a common edge along the phosphorus and hydrogen atoms which are equally shared between the two metals. The iron complex with each cyclopentadienyl group occupying three octahedral coordination sites (either *trans* or *cis* to each other) is thereby structurally similar to  $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ .<sup>40</sup> The manganese complex can be formally derived from the general three-electron donor bridging complex,  $[\text{XMn}(\text{CO})_4]_2$  ( $\text{X} = \text{Cl},$ <sup>41-43</sup>  $\text{Br},$ <sup>41-43</sup>

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I,<sup>41-43</sup> SR,<sup>44</sup> TeR,<sup>45</sup> PR<sub>2</sub>,<sup>5,39,46</sup> AsR<sub>2</sub>,<sup>5,6,47</sup>), which for the bromine-bridged derivative was characterized both by X-ray diffraction<sup>48</sup> and by detailed infrared spectral studies<sup>43</sup> to possess D<sub>2h</sub> symmetry.

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It is hoped that a neutron diffraction study of this compound can be undertaken in the near future in order to verify our proposed configuration.

*Acknowledgments.* We are deeply indebted to Dr. Roy Hayter for the sample and for helpful discussions of the chemistry. We also wish to thank the National Science Foundation for their financial support of this work. The calculations were performed on the CDC 1604 computer at the University of Wisconsin Computing Center and on the IBM 704 computer at MURA.

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## Structure of IrO<sub>2</sub>Cl(CO)(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>, the Oxygen Adduct of a Synthetic Reversible Molecular Oxygen Carrier<sup>1</sup>

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*The structure of IrO<sub>2</sub>Cl(CO)(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>, which is the oxygen adduct of the synthetic molecular oxygen carrier IrCl(CO)(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>, has been determined from three-dimensional X-ray data collected from a single crystal. The material crystallizes in space group C<sub>2</sub><sup>h</sup>-P $\bar{1}$  of the triclinic system with two molecules in a cell of dimensions  $a = 19.02$ ,  $b = 9.83$ ,  $c = 9.93$  Å.;  $\alpha = 94.0$ ,  $\beta = 64.9$ ,  $\gamma = 93.2^\circ$ ;  $V = 1676$  Å.<sup>3</sup>. The crystal structure consists of the packing of discrete, monomeric molecules. The molecular structure surmised by Vaska from spectroscopic data has been confirmed, and, in addition, details of the attachment of molecular oxygen to iridium have been obtained. The iridium may be described as either five- or six-coordinated: the iridium, the two oxygen atoms, the carbonyl group, and the chlorine atom lie in the basal plane, with phosphorus atoms above and below this plane. The two oxygen atoms are equidistant from the iridium atom, with an average Ir-O distance of 2.07 Å. The O-O bond length of  $1.30 \pm 0.03$  Å. is intermediate between those characteristic of O<sub>2</sub> (1.21 Å.) and O<sub>2</sub><sup>-2</sup> (1.49 Å.) and corresponds closely to O<sub>2</sub><sup>-</sup> (1.28 Å.).*

### Introduction

Knowledge of the manner in which oxygen is attached in natural molecular oxygen carriers, such as hemoglobin and hemocyanin, is obviously of great importance to our understanding of the molecular bases for such properties as reversibility of oxygen uptake and oxygen transport. No direct information on the mode of attachment is available at present, and the prospects for a direct determination by diffraction methods, though not altogether bleak, are at least not immediate. On the basis of indirect spectroscopic and magnetic measurements, several models for the mode of attachment of molecular oxygen to the iron in hemoglobin have been put forward.<sup>2-5</sup> These run the gamut from a

linear bonding arrangement<sup>2</sup> through a bent configuration<sup>3,4</sup> to the triangular, or  $\pi$ -bonding, arrangement<sup>5</sup> in which both oxygens are equidistant from the iron. There has also been recent speculation and discussion concerning the disposition of the electrons in the bonding scheme.<sup>4,6-8</sup>

The synthetic molecular oxygen carriers offer advantages over the natural ones in simplicity and variety. It is evident that by studying the physical and structural properties of synthetic carriers and their oxygen adducts one should be able to increase the understanding of the molecular bases for such phenomena as reversibility. Yet very few studies of a definitive nature have been carried out on these synthetic carriers or their oxygen adducts, probably because most of them are unstable or poorly characterized.<sup>9</sup> Vaska's discovery<sup>10</sup> of the 1:1 reversible molecular oxygen carrier IrCl(CO)(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub> is thus of great importance, for the oxygen adduct IrO<sub>2</sub>Cl(CO)(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub> may be crystallized and is extremely stable and well characterized in comparison with previously known oxygen adducts. In a preliminary report<sup>11</sup> we gave some details of our study of the molecular structure of this remarkable compound. In this paper we present our results in full.

### Collection and Reduction of the X-Ray Data

Excellent light orange crystals of IrO<sub>2</sub>Cl(CO)(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub> were very kindly supplied by L. Vaska. These crystals were stable in air during the X-ray photography,

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(1) Research performed under the auspices of the U. S. Atomic Energy Commission.