

# The Crystal and Molecular Structure of $\mu$ -Hydrido- $\mu$ -diphenylphosphido-bis(tetracarbonylmanganese), $(\text{CO})_4\text{Mn}(\text{H})(\text{P}(\text{C}_6\text{H}_5)_2)\text{Mn}(\text{CO})_4$

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**Abstract:** The crystal and molecular structure of  $\mu$ -hydrido- $\mu$ -diphenylphosphido-bis(tetracarbonylmanganese),  $(\text{CO})_4\text{Mn}(\text{H})(\text{P}(\text{C}_6\text{H}_5)_2)\text{Mn}(\text{CO})_4$ , has been determined from three-dimensional X-ray data collected by counter methods at room temperature. The material crystallizes in space group  $\text{C}_{2h}^6\text{-I2/c}$  of the monoclinic system with four molecules in a cell of dimensions  $a = 16.76$ ,  $b = 8.15$ ,  $c = 17.03$  Å,  $\beta = 110^\circ 46'$ . The structure has been refined by least-squares techniques to a final  $R$  factor on  $F$  of 7.2%. The average position of the bridging hydrogen atom was successfully included in this refinement. Twofold molecular symmetry is imposed on the well-separated molecular units. The geometry about the independent manganese atom is distorted octahedral, and the molecular structure results from the sharing of an edge of two manganese octahedra at the twofold axis. Each manganese atom is coordinated to four carbonyl groups, to the bridging phosphorus atom, and to the bridging hydrogen atom. Although the molecule is required to have symmetry 2, it has nearly symmetry  $\text{mm}$ . It is shown that from diffraction results alone it is not possible here, or in previous similar studies, to distinguish between the symmetric placement of the hydrogen atom between the two metal atoms in a single-minimum potential well and the placement of the hydrogen atom between the two metal atoms in a symmetric double-minimum potential well. The former description is consistent with a bonding scheme involving a symmetric, bent, three-center, two-electron bond between  $\text{Mn-H-Mn}$ ; the latter is consistent with a  $\text{Mn-H}$   $\sigma$  bond and a  $\text{Mn-Mn}$  metal-metal bond. A model involving an asymmetric potential well in which the hydrogen is preferentially associated with one manganese atom can be eliminated.

Considerable speculation about the nature of the bonding in transition metal hydride complexes containing a metal-hydrogen-metal linkage has occurred since their recent discovery.<sup>1-10</sup> Three types of complexes are known: those in which the hydrogen atom is the single bridging group, as in  $(\text{CO})_5\text{M-H-M}'(\text{CO})_5$ ,<sup>8-10</sup> where  $\text{M} = \text{M}' = \text{Cr}$  and  $\text{M} = \text{Cr}$ ,  $\text{M}' = \text{W}$ ; those in which the hydrogen atom is presumably part of a double bridge, as in  $(\text{C}_5\text{H}_5)(\text{CO})_2\text{Mo}(\text{H})(\text{P}(\text{CH}_3)_2)\text{Mo}(\text{CO})_2(\text{C}_5\text{H}_5)^3$  and the present compound  $(\text{CO})_4\text{Mn}(\text{H})(\text{P}(\text{C}_6\text{H}_5)_2)\text{Mn}(\text{CO})_4$ ,<sup>1,4</sup> and those in which the hydrogen atom is part of a multiple bridge, as in  $\text{Fe}_3\text{H}(\text{CO})_{11}$ <sup>7</sup> and  $\text{Mn}_3\text{H}(\text{B}_2\text{H}_6)(\text{CO})_{10}$ .<sup>6</sup> A linear symmetric  $\text{Cr-H-Cr}$  linkage is consistent with the spectroscopic and diffraction data on the  $(\text{CO})_5\text{Cr-H-Cr}(\text{CO})_5^-$  ion,<sup>8-10</sup> although a  $\text{Cr-H-Cr}$  linkage in which the hydrogen is in a symmetric double-minimum potential well of appropriate barrier height to yield a suitable tunneling frequency cannot be excluded. Data on the  $\text{Cr-H-W}$  linkage are not as plentiful,<sup>8,10</sup> although it is reasonable to assume here that the potential function for the hydrogen atom is asymmetric so that the hydrogen is associated unequally with  $\text{Cr}$  and  $\text{W}$ . In  $(\text{C}_5\text{H}_5)(\text{CO})_2\text{Mo}(\text{H})(\text{P}(\text{CH}_3)_2)\text{Mo}(\text{CO})_2(\text{C}_5\text{H}_5)$  no positive indication of the position of the bridging hydrogen atom was obtained,<sup>11</sup> but

because of the similar coordination around each of the crystallographically independent molybdenum atoms there is strong support for the equivalence of the hydrogen interaction with both molybdenum atoms, either through a single-minimum or a symmetric double-minimum potential function. Doedens and Dahl<sup>11</sup> adopted the description in terms of a single-minimum potential function, in which the  $\text{Mo-H-Mo}$  linkage may then be described as a symmetric, bent, three-center, two-electron bond, and no  $\text{Mo-Mo}$  bond is required. A similar type of bond has been postulated for an  $\text{Mn-H-Mn}$  linkage in  $\text{Mn}_3\text{H}(\text{B}_2\text{H}_6)(\text{CO})_{10}$ .<sup>6</sup>

An alternative description of these bent  $\text{M-H-M}$  bonds would involve a metal-metal bond and one metal-hydrogen  $\sigma$  bond. Yet as Doedens and Dahl<sup>11</sup> indicate the hydrogen atom cannot be preferentially associated with one metal atom. This model is also excluded by the various nuclear magnetic resonance studies on these types of compounds, for example, on  $(\text{C}_5\text{H}_5)_2\text{W}_2\text{H}(\text{CO})_6^{+2}$  and by the Mössbauer study on  $\text{Fe}_3\text{H}(\text{CO})_{11}$ .<sup>12</sup> Yet the time scale of these experiments is around  $10^{-6}$  sec, and so a description in terms of a metal-metal bond and a metal-hydrogen  $\sigma$  bond is appropriate if the hydrogen atom is located in a symmetric, double-minimum potential function of such a barrier that the tunneling frequency through the barrier is greater than  $10^6 \text{ sec}^{-1}$ . Such tunneling could be very slow in relation to the time scale of the X-ray diffraction experiment ( $\approx 10^{-18}$  sec) and so such a model would be compatible with "static" disorder of  $\text{Mn-H}\cdots\text{Mn}$  and  $\text{Mn}\cdots\text{H-Mn}$  configurations in the solid state.

In order to gain additional insight into the bonding in compounds containing the bent  $\text{M-H-M}$  linkage, the present study of  $(\text{CO})_4\text{Mn}(\text{H})(\text{P}(\text{C}_6\text{H}_5)_2)\text{Mn}(\text{CO})_4$  was undertaken. Our objectives were to obtain direct

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(11) R. J. Doedens and L. F. Dahl, *ibid.*, **87**, 2576 (1965).

(12) N. E. Erickson and A. W. Fairhall, *Inorg. Chem.*, **4**, 1320 (1965).

information on the position of the unique hydrogen atom and to assess the probability of success of a neutron diffraction study on this or a related system. The present compound is far more suitable for such a neutron diffraction study than is the Mo complex studied by Doedens and Dahl. That compound contains 29 nonhydrogen atoms and 16 hydrogen atoms in addition to the one of interest. The present compound contains 16 crystallographically independent nonhydrogen atoms and 5 hydrogen atoms in addition to the one of interest.

Our objectives have indeed been realized in this study. With the use of counter data it has proved possible to determine and refine the average position of the unique hydrogen atom.

### Collection and Reduction of the Intensity Data

Crystals of  $(\text{CO})_4\text{Mn}(\text{H})(\text{P}(\text{C}_6\text{H}_5)_2)\text{Mn}(\text{CO})_4$  were prepared in the manner previously described<sup>4</sup> and were kindly supplied by Dr. R. G. Hayter. Suitable crystals were grown by vacuum sublimation and were mounted in capillary tubes. The crystal chosen for the intensity measurements was an irregular rhombic plate of approximate dimensions  $0.04 \times 0.02 \times 0.01$  cm. From preliminary precession and Weissenberg X-ray photographs the material was found to crystallize in the monoclinic system. The lattice parameters at  $25^\circ$ , obtained from a least-squares refinement<sup>13</sup> of the setting angles of 13 reflections, which had been accurately centered on a Picker four-circle, automatic X-ray diffractometer, are  $a = 16.76 \pm 0.02$ ,  $b = 8.15 \pm 0.01$ ,  $c = 17.03 \pm 0.02$  Å;  $\beta = 110^\circ 46' \pm 2'$  ( $\lambda(\text{Mo K}\alpha_1) = 0.70926$  Å). The systematic absences observed are  $hkl$  for  $h + k + l$  odd, and  $h0l$  for  $l$  odd. These absences are consistent with the space groups  $\text{C}_{2h}^6\text{-I2/c}$  and  $\text{C}_s^4\text{-Ic}$ . A density of  $1.59$  g/cm<sup>3</sup> calculated for four molecules in the unit cell is a reasonable one for this type of compound. Owing to various difficulties, no experimental density was determined. If the space group is Ic, then no crystallographic symmetry is imposed on the molecule. If the space group is I2/c, then either a center of symmetry or a twofold rotation axis is imposed on the molecule. A center of symmetry is only possible if disorder occurs; a twofold rotation axis is compatible with the formulation of the complex as a symmetric bridging of two  $\text{Mn}(\text{CO})_4$  groups by  $\text{P}(\text{C}_6\text{H}_5)_2$ . The crystal habit has symmetry  $2/m$ , which tends to support the centrosymmetric space group. In addition, no piezoelectric effect could be observed. The structure has been solved successfully in I2/c.

Intensity data were collected at room temperature on a Picker diffractometer in the manner detailed previously.<sup>13,14</sup> The  $b^*$  axis of the crystal was inclined about  $5^\circ$  to the axis of the goniometer head, and so the effects of multiple reflection should be minimal.<sup>15</sup> Owing to the high absorption coefficient for Cu  $\text{K}\alpha$  radiation ( $\mu = 172$  cm<sup>-1</sup>), Mo  $\text{K}\alpha$  radiation was employed ( $\mu = 13.4$  cm<sup>-1</sup>). The diffracted beams were filtered through 3.0-mil Zr foil. The pulse height ana-

lyzer was set to admit about 90% of the Mo  $\text{K}\alpha_1$  peak. A rectangular counter aperture  $3.5 \times 4.5$  mm was placed 21 cm from the crystal. The intensities of the diffracted beams were sufficiently low so that attenuators were not required. Checks of the crystal mosaicity were satisfactory. A take-off angle of  $1.3^\circ$  was chosen as a compromise between intensity and width of the reflections. Data were collected by the  $2\theta$ - $\theta$  scan technique with a symmetric scan of  $1^\circ/\text{min}$  from  $-0.9$  to  $+0.9^\circ$  in  $2\theta$  from the peak center. Stationary-counter, stationary-crystal background counts of 20 sec each were taken at each end of the scan range. Three standard intensities were measured at intervals during the data collection. These were observed to fall off uniformly to about 87% of their initial values during the course of the run. A simple linear correction factor was applied to take into account the decrease in the intensities of the standards. All four forms ( $hkl$ ,  $h\bar{k}l$ ,  $\bar{h}kl$ , and  $\bar{h}\bar{k}l$ ) from this monoclinic crystal were measured out to  $2\theta_{\text{Mo K}\alpha}$  of  $40^\circ$ . Beyond this point, and even between  $35$  and  $40^\circ$ , very few intensities were above background. In all, the intensities of 3838 reflections were measured.

An absorption correction was applied by numerical methods, using the accurately measured dimensions of the crystal and a linear absorption coefficient of  $13.4$  cm<sup>-1</sup>. The transmission factors varied between about 1.10 and 1.25, so that the absorption correction is a relatively small one.

The data were then processed and averaged and yielded 1011 independent reflections. Standard deviations on  $F^2$ ,  $\sigma(F^2)$ , were estimated both from the range of equivalent forms and from the individual standard deviations. For these individual standard deviations a value of  $p$  of  $0.04^{13}$  was used. The larger of these two estimates was taken as  $\sigma(F^2)$ , after adjustment for the number of reflections in the given equivalent set. Of the 1011 reflections, the range estimate was larger than the individual estimate for 490 reflections. The predicted value of the weighted  $R$  factor on  $F^2$ ,  $R_2(F^2)$ , is 12.8%.<sup>14</sup> Of the 1011 independent reflections, only 612 had  $F^2 > \sigma(F^2)$ , and these will henceforth be referred to as being above background. The relatively large number of intensities below background results from the low scattering power of the crystal. A better data set undoubtedly would have been obtained, even with the necessity of a larger absorption correction, had a larger crystal been available.

### Solution and Refinement of the Structure

With four molecules in space group I2/c, the coordinates of the phosphorus, one manganese, one phenyl ring, and four carbonyl groups and the unique hydrogen atom must be determined. Initial values of the coordinates of the Mn and P atoms were obtained from a three-dimensional Patterson<sup>16</sup> function. These parameters were refined by usual least-squares

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

(14) R. J. Doedens and J. A. Ibers, *ibid.*, **6**, 204 (1967).

(15) W. H. Zachariasen, *Acta Cryst.*, **18**, 705 (1965).

(16) The computer programs for the CDC 3400 used in this work include local modifications of Zalkin's FORDP for Fourier calculations, Hamilton's GONO9 for absorption corrections, the Busing-Levy ORFFE error function program, Johnson's ORTEP for thermal ellipsoid plotting, as well as various local programs including PICK for setting reflections on the diffractometer, PICKOUT for processing the diffractometer data, and NUGLS for least-squares refinement of rigid groups.

procedures, use being made of the 612 reflections whose intensities were above background. In all least-squares calculations, the function minimized was  $\sum w(F_o - F_c)^2$ , where  $F_o$  and  $F_c$  are the observed and calculated structure amplitudes and where the weights  $w$  are taken as  $4F_o^2/\sigma^2(F_o^2)$ . The usual tabulation of atomic scattering factors for Mn, P, C, and O was used;<sup>17</sup> the atomic scattering factor for H was that of Stewart, Davidson, and Simpson.<sup>18</sup> The effects of anomalous dispersion were included in  $F_c$ ;<sup>19</sup> the  $f'$  and  $f''$  values for Mn were taken from Cromer's tabulation.<sup>20</sup> The usual agreement factor,  $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$ , was 29% after refinement of the Mn and P atomic positions and isotropic thermal parameters and an over-all scale factor. In a subsequent difference Fourier map the carbon atoms of the phenyl ring and two of the four carbonyl groups were located. These were refined together with the Mn and P atomic positions in the group refinement program NUGLS<sup>13</sup> to a value of  $R_1$  of 24%. The other two carbonyl groups were located on a second difference Fourier map. Subsequent refinement of all the nonhydrogen atoms, with individual isotropic thermal parameters on the nonring atoms and a single isotropic thermal parameter for the ring, yielded an  $R_1$  value of 8.9% and a value of the weighted  $R$  factor

$$R_2 = [\sum w(F_o - F_c)^2 / \sum w F_o^2]^{1/2} = 7.6\%$$

In the next round of calculations the model for thermal motion was changed to the extent that the Mn and P atoms were allowed to vibrate anisotropically and the carbon atoms of the phenyl group individually. In addition the contributions of the H atoms on the ring were included, an isotropic thermal parameter of  $9 \text{ \AA}^2$  being assigned to each hydrogen atom. This refinement converged to values of  $R_1$  and  $R_2$  of 8.3 and 6.9%. At this stage the data were carefully examined for possible effects of secondary extinction. Twenty-four reflections with the largest values of  $\beta(\theta)I$ , where  $\beta(\theta)$  is Zachariasen's<sup>21</sup> angle factor and  $I$  is the raw intensity corrected for background, were omitted and the refinement was repeated. There were no significant changes in parameters, and in particular the scale and temperature factors did not change. Had these reflections been diminished through secondary extinction, then changes in scale and thermal parameters would have been expected. In a final round of calculations on the 612 reflections above background, the thermal model was again changed to allow complete anisotropic refinement of all non-group atoms and individual isotropic thermal parameters on the carbon atoms of the group. (The fixed value of  $9 \text{ \AA}^2$  for the hydrogen atoms of the group was maintained.) This refinement of 99 variables led to values of  $R_1$  and  $R_2$  of 7.5 and 5.9%. We take both this significant improvement<sup>22</sup> in  $R_2$  and the physical reasonableness of the vibrational ellipsoids (*vide infra*) as justification for the anisotropic refinement of the carbonyl groups.

(17) J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1962, Table 3.3.1A.

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

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

(20) D. T. Cromer, *ibid.*, **18**, 17 (1965).

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(22) W. C. Hamilton, *ibid.*, **18**, 502 (1965).

## Location and Refinement of the Hydrogen Atom

Structure factors were computed for all 1011 observed reflections, and a difference Fourier map was then calculated. (The values of  $F_o$  for those reflections for which  $F_o^2$  was less than  $\sigma(F_o^2)$  were put in as observed, unless  $F_o^2$  was negative, in which case we set  $F_o = 0$ .) This difference Fourier map had its highest peak ( $0.8 \text{ e/\AA}^3$ ) on the twofold axis  $2.7 \text{ \AA}$  away from the P atom and therefore near to a plausible position for the unique H atom. The next highest peak, of height  $0.65 \text{ e/\AA}^3$ , was at the centroid of the Mn-P-Mn triangle. Using a procedure described previously,<sup>23</sup> we next computed a difference Fourier map for those 500 inner reflections for which  $\lambda^{-1} \sin \theta \leq 0.4 \text{ \AA}^{-1}$ . The highest peak, again of height  $0.8 \text{ e/\AA}^3$ , shifted slightly to a position  $2.91 \text{ \AA}$  from the P atom. The next highest peak was only  $0.31 \text{ e/\AA}^3$ . Use of Cruickshank's method<sup>24</sup> led to the following estimates of errors in electron density for the complete data set:  $\sigma(\rho(x, y, z)) = 0.12 \text{ e/\AA}^3$ ;  $\sigma(\rho(0, y, 1/4)) = 0.17 \text{ e/\AA}^3$ . Consequently the highest peak on these maps is significantly above background. Moreover, it alone is unaffected when reflections for which  $\lambda^{-1} \sin \theta > 0.4 \text{ \AA}^{-1}$  are omitted. These facts, coupled with the reasonableness of the position for the hydrogen atom, encouraged us to attempt to refine a hydrogen atom in this position.

Our previous experience led us to believe that the position of the unique hydrogen atom, as obtained from the inner difference Fourier map, would be the most reliable. Many unsuccessful attempts were made to refine a hydrogen atom in this position. In retrospect we see that our estimates of starting parameters, particularly the isotropic thermal parameter, were too inexact. The following procedure led to a successful refinement of the hydrogen atom position. A series of structure factor calculations was carried out for different values of  $y_H$  and  $B_H$  (where  $y_H$  is the positional parameter and  $B_H$  the isotropic thermal parameter of the H atom). From these structure factor calculations we located a minimum value of the weighted  $R$  factor  $R_2$  in  $(R_2, y_H, B_H)$  space. Then with these particular values of  $y_H$  and  $B_H$  fixed, we refined the other 99 variable parameters to allow their values to adjust to a hydrogen atom that had been placed approximately correctly. Finally we carried out six cycles of least-squares refinements in which all 101 parameters (99 as described above together with  $y_H$  and  $B_H$ ) were allowed to vary. This refinement, as opposed to early ones involving the hydrogen atom, did not diverge. Rather this refinement converged to the parameters given in Table I. (The hydrogen atom parameters showed some oscillation, but this oscillation was far less than the estimated standard deviations on these parameters.) The final values of  $R_1$  and  $R_2$  for this refinement are 7.2 and 5.6%. In particular, this improvement in  $R_2$  over the refinement without the hydrogen atom is highly significant.<sup>22</sup> To our knowledge this is the first successful least-squares refinement of a hydrogen atom in the presence of an atom as heavy as manganese with the use of X-ray diffraction data. It is particularly pleasing to

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

(24) D. W. J. Cruickshank, *ibid.*, **2**, 65 (1949); D. W. J. Cruickshank and J. S. Rollett, *ibid.*, **6**, 705 (1953).

Table I. Positional and Thermal Parameters for  $(\text{CO})_4\text{Mn}(\text{H})(\text{P}(\text{C}_6\text{H}_5)_2)_2\text{Mn}(\text{CO})_4$ 

Atom	x	y	z	$\beta_{11}^a$	$\beta_{22}^a$	$\beta_{33}^a$	$\beta_{12}^a$	$\beta_{13}^a$	$\beta_{23}^a$		
Mn	0.05748 (15) <sup>b</sup>	0.01594 (38)	0.20194 (14)	0.00492 (12)	0.02092 (64)	0.00387 (11)	-0.00030 (33)	0.00147 (10)	-0.00031 (30)		
P	0 <sup>c</sup>	0.23054 (84)	1/4 <sup>c</sup>	0.00407 (32)	0.0160 (16)	0.00312 (29)	0 <sup>c</sup>	0.00079 (25)	0 <sup>c</sup>		
C <sub>1</sub>	0.1517 (10)	0.0080 (26)	0.3001 (9)	0.0053 (9)	0.0201 (39)	0.0038 (9)	-0.0001 (24)	0.0010 (8)	-0.0007 (22)		
O <sub>1</sub>	0.2094 (6)	0.0057 (20)	0.3587 (7)	0.0050 (6)	0.0376 (33)	0.0061 (7)	0.0008 (18)	-0.0014 (5)	-0.0002 (18)		
C <sub>2</sub>	-0.0325 (9)	0.0197 (27)	0.1022 (10)	0.0052 (9)	0.0266 (47)	0.0046 (10)	0.0006 (23)	0.0017 (8)	-0.0001 (22)		
O <sub>2</sub>	-0.0858 (7)	0.0166 (20)	0.0378 (6)	0.0055 (9)	0.0480 (42)	0.0044 (8)	-0.0059 (21)	0.0007 (7)	-0.0047 (20)		
C <sub>3</sub>	0.1179 (11)	0.1363 (20)	0.1554 (11)	0.0072 (13)	0.0044 (37)	0.0054 (11)	-0.0001 (16)	0.0017 (7)	-0.0021 (14)		
O <sub>3</sub>	0.1553 (7)	0.2238 (16)	0.1270 (8)	0.0075 (8)	0.0250 (35)	0.0085 (8)	-0.0018 (14)	0.0037 (6)	0.0021 (14)		
C <sub>4</sub>	0.0872 (12)	-0.1800 (25)	0.1733 (11)	0.0074 (12)	0.0167 (48)	0.0063 (11)	-0.0002 (20)	0.0029 (9)	-0.0019 (19)		
O <sub>4</sub>	0.1106 (8)	-0.3012 (18)	0.1521 (8)	0.0118 (11)	0.0210 (36)	0.0108 (10)	0.0014 (16)	0.0061 (8)	-0.0048 (16)		
H	0 <sup>c</sup>	-0.125 (12)	1/4 <sup>c</sup>	-1.0 (2.5) <sup>d</sup>							
Group	$x_e^e$	$y_e$	$z_e$	$\delta$	$\eta$	$B_1$	$B_2$	$B_3$	$B_4$	$B_5$	$B_6$
$\text{C}_6\text{H}_5$	0.1226 (4)	0.4878 (8)	0.3818 (4)	2.436 (7)	1.216 (6)	3.9 (3)	7.4 (5)	9.2 (5)	6.8 (5)	8.0 (5)	6.3 (4)

<sup>a</sup> The form of the anisotropic thermal ellipsoid is  $\exp(-\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$ . <sup>b</sup> Numbers in parentheses here and in succeeding tables are standard deviations in the least significant digits. <sup>c</sup> Parameter fixed by symmetry. <sup>d</sup> Isotropic thermal parameter (in  $\text{\AA}^2$ ). <sup>e</sup>  $x_e$ ,  $y_e$ , and  $z_e$  are the fractional coordinates of the ring center. The angles  $\delta$ ,  $\epsilon$ , and  $\eta$  (in radians) which bring about alignment (except for translation) of an internal coordinate system with a fixed external coordinate system have been defined in previous papers: S. J. La Placa and J. A. Ibers, *Acta Cryst.*, **18**, 511 (1965); R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965).  $B_i$  is the isotropic thermal parameter (in  $\text{\AA}^2$ ) of carbon atom  $i$  in the ring. The atoms in the ring are numbered so that C<sub>1</sub> is attached to P; C<sub>4</sub> is *para* to C<sub>1</sub>. The isotropic thermal parameter of the five hydrogen atoms was fixed at  $9 \text{\AA}^2$ .

find that the least-squares and partial Fourier calculations of the hydrogen atom position agree so well. This adds support to the reliability of our previous location by partial Fourier methods of the hydrogen atom in  $\text{RhH}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_3$ .<sup>23</sup>

The final values of  $R_1$  and  $R_2$  for all 1011 reflections for a structure factor calculation based on the parameters of Table I are 12.0 and 6.2%. The good agreement between the  $R_2$  values for the entire data set and for those reflections above background suggests that the relative weighting scheme is a reasonable one. The error in an observation of unit weight is 1.04 for the 612 reflections above background; this suggests that the absolute weighting scheme is also very reasonable. The final value of  $R_2(F^2)$  for all 1011 reflections is 12.3%; this compares very favorably with the value of 12.8% predicted from the internal agreement among the various equivalent forms. It further suggests that the structure has been refined as far as is justified by the accuracy of the data.

Table I also includes the standard deviations of the parameters as estimated from the inverse matrix. In Table II we give the fractional coordinates of the

Table II. Derived Parameters for Group Atoms

Atom	x	y	z
C <sub>1</sub>	0.0714 (6) <sup>a</sup>	0.3723 (11)	0.3258 (6)
C <sub>2</sub>	0.0548 (6)	0.4142 (14)	0.3980 (7)
C <sub>3</sub>	0.1060 (7)	0.5298 (14)	0.4541 (5)
C <sub>4</sub>	0.1738 (7)	0.6034 (11)	0.4378 (6)
C <sub>5</sub>	0.1904 (6)	0.5614 (14)	0.3656 (7)
C <sub>6</sub>	0.1392 (6)	0.4459 (13)	0.3096 (5)
H <sub>1</sub>	0.0021 (9)	0.3571 (22)	0.4107 (11)
H <sub>2</sub>	0.0930 (10)	0.5623 (21)	0.5102 (6)
H <sub>3</sub>	0.2135 (9)	0.6930 (16)	0.4813 (9)
H <sub>4</sub>	0.2431 (9)	0.6186 (22)	0.3529 (11)
H <sub>5</sub>	0.1522 (9)	0.4134 (21)	0.2534 (6)

<sup>a</sup> The estimated standard deviations are derived from those of the group parameters and are meant to be used in error analyses on distances from this ring to other atoms in the structure. Intraring distances, of course, are fixed (C-C = 1.397  $\text{\AA}$ , C-H = 1.084  $\text{\AA}$ ).

carbon and hydrogen atoms of the phenyl group that may be derived from the data of Table I. In Table III we present values in electrons of  $10F_o$  and  $10F_c$  for all reflections measured. Those marked by an asterisk in front of  $10F_o$  were below background and were not used in the refinements. For none of these did  $F_c^2$  exceed  $\sigma(F_o^2)$ . In Table IV we give the root-mean-square amplitudes of vibration that may be derived from the data of Table I. An indication of the orientations of the thermal ellipsoids may be obtained from Figure 1. In general these vibrational amplitudes and directions seem reasonable.

### Description of the Structure

The crystal structure of  $(\text{CO})_4\text{Mn}(\text{H})(\text{P}(\text{C}_6\text{H}_5)_2)_2\text{Mn}(\text{CO})_4$  consists of the packing of monomeric units. Table V contains a listing of the pertinent distances and angles and their standard deviations as estimated from the parameter errors of Table I and the correlation matrix. Intermolecular distances are not listed, as they are normal. The molecules are well separated; thus the closest P...P distance is 8.15  $\text{\AA}$ . In Figure 1 the structure of one molecule is shown.



Table V. Selected Distances (Å) and Angles (Degrees)

— Intramolecular distance —		— Angle —	
Mn—Mn'	2.937 (5)	Mn—P—Mn'	80.04 (27)
Mn—P	2.284 (6)	Mn—H—Mn'	104.1 (4.8)
Mn—C <sub>1</sub>	1.850 (16)	H—Mn—P	87.9 (2.4)
Mn—C <sub>2</sub>	1.829 (16)	C <sub>1</sub> —Mn—C <sub>2</sub>	177.23 (74)
Mn—C <sub>3</sub>	1.785 (18)	C <sub>1</sub> —Mn—C <sub>3</sub>	89.03 (76)
Mn—C <sub>4</sub>	1.791 (20)	C <sub>1</sub> —Mn—C <sub>4</sub>	89.06 (83)
Mn—H	1.86 (6)	C <sub>2</sub> —Mn—C <sub>3</sub>	89.41 (76)
P—H	2.89 (10)	C <sub>2</sub> —Mn—C <sub>4</sub>	88.85 (84)
P—RC <sub>1</sub> <sup>a</sup>	1.827 (20)	C <sub>3</sub> —Mn—C <sub>4</sub>	96.51 (84)
P—C <sub>1</sub>	2.991 (19)	P—Mn—C <sub>1</sub>	92.10 (59)
P—C <sub>2</sub>	2.935 (18)	P—Mn—C <sub>2</sub>	90.36 (60)
P—C <sub>3</sub>	3.057 (17)	P—Mn—C <sub>3</sub>	96.65 (57)
C <sub>1</sub> —O <sub>1</sub>	1.116 (13)	P—Mn—C <sub>4</sub>	166.81 (62)
C <sub>2</sub> —O <sub>2</sub>	1.143 (14)	H—Mn—C <sub>1</sub>	89.44 (55)
C <sub>3</sub> —O <sub>3</sub>	1.161 (16)	H—Mn—C <sub>2</sub>	91.94 (57)
C <sub>4</sub> —O <sub>4</sub>	1.166 (17)	H—Mn—C <sub>3</sub>	175.2 (2.4)
C <sub>1</sub> —C <sub>3</sub>	2.548 (24)	H—Mn—C <sub>4</sub>	78.9 (2.5)
C <sub>1</sub> —C <sub>4</sub>	2.554 (25)	Mn—C <sub>1</sub> —O <sub>1</sub>	178.5 (1.9)
C <sub>1</sub> —RC <sub>1</sub>	3.352 (25)	Mn—C <sub>2</sub> —O <sub>2</sub>	175.9 (1.7)
C <sub>1</sub> —H	2.61 (4)	Mn—C <sub>3</sub> —O <sub>3</sub>	175.5 (1.6)
C <sub>2</sub> —C <sub>3</sub>	2.542 (23)	Mn—C <sub>4</sub> —O <sub>4</sub>	174.7 (1.8)
C <sub>2</sub> —C <sub>4</sub>	2.534 (26)	RC <sub>1</sub> —P—RC <sub>1</sub> '	101.6 (1.0)
C <sub>2</sub> —RC <sub>1</sub>	3.279 (25)	Mn'—Mn—C <sub>1</sub>	90.86 (45)
C <sub>2</sub> —H	2.65 (5)	Mn'—Mn—C <sub>2</sub>	91.70 (47)
C <sub>3</sub> —C <sub>4</sub>	2.668 (26)		
C <sub>4</sub> —H	2.32 (3)		
C <sub>1</sub> —C <sub>2</sub> '	3.021 (22)		

<sup>a</sup> RC<sub>1</sub> is the carbon atom of the phenyl group which is attached to P.

compared with a terminal Co—P distance of 2.20 Å in Co(P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>H)<sub>3</sub>Br<sub>2</sub>.<sup>27</sup> It thus appears that metal—P distances do not change significantly when the P is a bridging, rather than a terminal, group. The Mn—P distance of 2.28 Å in the present compound is toward the low end of the range of terminal metal—P distances found in the second- and third-row transition metals; these range from 2.22 Å in Ru(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub><sup>28</sup> to 2.49 Å in ReN(P(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub>.<sup>13</sup> However, the Mn radius is somewhat smaller than those of Ru and Re and hence the Mn—P distance of 2.28 Å appears to be about normal for a terminal Mn—P bond. However, if one takes the tetrahedral radius of P as 1.10 Å<sup>29</sup> and uses either of the estimates of the Mn single bond radius of 1.39<sup>30</sup> or 1.46 Å,<sup>11</sup> then one concludes that there is significant Mn—P multiple bonding in this structure. It would seem that the bond orders of metal—P linkages are poorly understood.

The P—C distance and the C—P—C angle of the P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> group agree well with those found for the P(CH<sub>3</sub>)<sub>2</sub> group in (C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>Mo(H)(P(CH<sub>3</sub>)<sub>2</sub>)Mo(CO)<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>)<sup>11</sup> and with those found in a variety of PR<sub>3</sub> linkages, where R is aryl or alkyl.

The Mn—C and C—O distances found here are consistent in that those bonds with the longest Mn—C distances have the shortest C—O distances. The Mn—C<sub>1</sub> and Mn—C<sub>2</sub> bonds, which are normal to the Mn—P—Mn—H plane, compare well with those found in Mn<sub>2</sub>(CO)<sub>10</sub><sup>31</sup> and HMn(CO)<sub>5</sub>.<sup>32</sup> The two Mn—C distances

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in the plane, namely Mn—C<sub>3</sub> and Mn—C<sub>4</sub>, are significantly shorter, and this is presumably indicative of increased multiple bonding between Mn and C. In Figure 1 we show the nonbonded C—C distances between the various carbonyl groups. The C<sub>3</sub>—C<sub>4</sub> distance of 2.67 Å is significantly longer than any of the others; in fact, the major distortion from octahedral symmetry around the Mn is the C<sub>3</sub>—Mn—C<sub>4</sub> angle of 96.5°. The C—C nonbonded interactions in Mn<sub>2</sub>(CO)<sub>10</sub> and HMn(CO)<sub>5</sub> average 2.62 Å with only very small variations. In these compounds the axial carbonyl groups are free to move away from the equatorial ones. In the present structure this is not possible: C<sub>1</sub> and C<sub>2</sub> are constrained by the phenyl group and C<sub>3</sub> by the P atom. Presumably the constraint of C<sub>4</sub> is less, since only the H is nearby to it.

### The Position of the Hydrogen Atom and the Nature of the Bonding

The essential argument that Doedens and Dahl<sup>11</sup> put forward in favor of a bonding scheme involving a symmetric, bent, three-center two-electron Mo—H—Mo bond and no Mo—Mo bond in (C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>Mo(H)(P(CH<sub>3</sub>)<sub>2</sub>)Mo(CO)<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>) was that the configurations around the two independent Mo atoms were indistinguishable. In the present compound there is certainly good evidence that the molecule contains an effective twofold symmetry axis, resulting in the equivalence of the two Mn atoms. This evidence arises from the agreement between *F*<sub>o</sub> and *F*<sub>c</sub>, which is as good as is to be expected on the basis of the statistical analysis of agreement of the *F*<sub>o</sub> values from equivalent forms. Accordingly the Mn atoms have the same configurations, even if the imposition of the twofold symmetry axis should be removed. We can thus eliminate with confidence a molecular structure in which the hydrogen atom is associated with only one of the Mn atoms, if such molecules pack in an ordered way in the cell. However, we do not feel that there is any direct evidence that enables us to separate the following two alternatives: (1) the H atom is symmetrically located with respect to the Mn atoms; (2) the H atom is preferentially associated with one of the Mn atoms, but the individual molecules pack in the cell so that the Mn atom with the H and the one without are statistically disordered. Neither the final difference map nor the atomic thermal parameters show any effects attributable to statistical disorder. However such effects, if present, would be expected to be small and could well be undetectable. This is particularly true because the hydrogen peak on the final difference Fourier map is most reasonably interpreted in terms of a Mn—H distance of at least 1.5 Å (*vide infra*). As we indicated in the introductory section, such a statistical disorder is compatible with the various spectroscopic measurements that indicate the hydrogen to be equally associated with the two metal atoms, provided that the tunneling frequency through the barrier is greater than 10<sup>6</sup> sec<sup>-1</sup>.

If one chooses to adopt the three-center two-electron bond model for the Mn—H—Mn interaction, it must be assumed that the steric effects of such a bond are comparable with those of a direct metal—metal interaction. Thus the Mn—Mn distance in the present compound is

2.937  $\pm$  0.005 Å, essentially the same as that of 2.92 Å in Mn<sub>2</sub>(CO)<sub>10</sub>.<sup>31</sup> Similarly the Mo–Mo distance in the H bridged compound of 3.26 Å compares favorably with that of 3.22 Å in ((C<sub>5</sub>H<sub>5</sub>)Mo(CO))<sub>2</sub>.<sup>33</sup> Thus the metal–metal distances in the hydrogen-bridged complexes are essentially equal to comparable metal–metal distances in complexes where the existence of a metal–metal bond is unequivocal. The geometry around the P atom also seems pertinent to this discussion. The Mn–P–Mn angle is 80°, whereas one normally expects the angles around P to be more nearly 100°. Thus consider the recent study of ((C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PM(C<sub>5</sub>H<sub>5</sub>))<sub>2</sub>, where M = Ni and Co. Coleman and Dahl<sup>26</sup> find that the Co–Co distance is 2.56 Å, whereas the Ni–Ni distance is 3.36 Å. In the former compound, which they describe as containing a Co–Co bond, the Co–P–Co angle is 73°; in the latter compound, which does not contain a Ni–Ni bond, the Ni–P–Ni angle is 102°.

This problem of attempting to separate a single-minimum from a symmetric double-minimum potential barrier is not a new one, and we have dealt with it at some length in the discussion of the F–H–F<sup>−</sup> ion.<sup>34–36</sup> In Figure 2 we show the electron density of the H atom in the Mn–P–Mn plane. Insofar as this electron density representation is reliable, the density is compatible either with the centered model or with the superposition of two half-hydrogens on either side of the twofold axis, although this superposition looks more reasonable if one chooses a Mn–H distance of at least 1.5 Å. No quantitative interpretation of the electron density map is possible for two reasons: (1) the map itself is not too reliable, because the scattering power of the hydrogen atom is low; (2) no information from spectroscopic studies is available. Even if the map shown in Figure 2 were the result of a neutron diffraction study, and one had determined the amplitudes of vibration of the hydrogen atom, interpretation would not be pos-

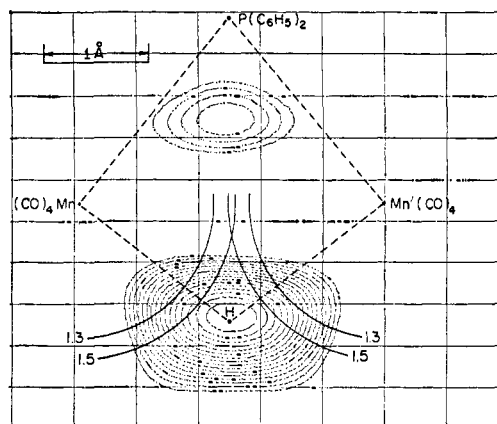


Figure 2. The residual electron density in the Mn–P–Mn'–H plane, computed from the 500 inner reflections and  $F_o$  values that did not contain the contribution of the unique hydrogen atom. The peak height of the hydrogen atom is 0.82 e/Å<sup>3</sup>. The lowest contour is 0.16 e/Å<sup>3</sup> and the contour interval is 0.04 e/Å<sup>3</sup>. The noise peak above the hydrogen atom, of height 0.31 e/Å<sup>3</sup>, is the second highest feature in the entire difference Fourier.

sible without such spectroscopic information. One needs to know the assignments and frequencies of the Mn–H modes.<sup>34</sup> Such information can only be obtained by suitable deuteration experiments, since the Mn–H region of the spectrum overlaps with the C–O stretching region. Thus we emphasize that if there is any hope of settling the question of the potential function of the hydrogen atom, it must come from the combination of very careful spectroscopic and neutron diffraction studies. Neither by itself will answer the question. Because the neutron diffraction study involves considerable effort and difficulties, it would seem appropriate not to carry it out until it is shown that the necessary spectroscopic information can be obtained.

**Acknowledgments.** We are indebted to Dr. R. G. Hayter for supplying the crystals used in this study. This work was supported in part by the National Science Foundation.

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