show that π-electron density from these groups is critical to the stability of the compounds.[2b]

A second important implication of this study, in conjunction with the chemical studies of Marks, pertains to the rearrangement pathway for the $(OC)_3Co(GeR_2)_2Co(CO)_3$ type molecules. Adams and Cotton[3] examined two possible pathways in the case of the $(CH_3)_2$ Ge-bridged molecule: (1) polytopal rearrangements about each cobalt atom with continuous retention of the bridges, and (2) bridge opening to an intermediate (or transition state) having a dimethylgermylene, $(CH_3)_2Ge$, group on each cobalt atom, followed by reclosing of the bridges. They expressed a preference for the first of these, one reason for which was the lack of any precedent for dialkylgermylene metal moieties. Subsequently, Muetterties has expressed the opinion that pathway 2 is more probable.[16] While definitive evidence is still lacking (although efforts are being made in this laboratory by R. D. Adams to obtain such evidence), our present findings militate against pathway 2. It appears that terminal $R_2Ge{=}$ and $R_2Sn{=}$ ligands are not stable as such, but only when rendered four-coordinate by the intervention of a donor molecule L, such as THF or pyridine, to give $R_2Ge(L)$– and $R_2Sn(L)$– ligands.

Acknowledgment. It is a pleasure to thank Professor Tobin J. Marks of Northwestern University for supplying the sample and for stimulating discussions.

(16) E. L. Muetterties, *MTP Int. Rev. Sci., Inorg. Ser. 1*, **9**, 77 (1972).

Location of the Hydrogen Atoms in $H_3Mn_3(CO)_{12}$. A Crystal Structure Determination

S. W. Kirtley,[1a] J. P. Olsen,[1a] and R. Bau*[1b]

Contribution from the Department of Chemistry,
New College, Sarasota, Florida 33578, and the Department of Chemistry,
University of Southern California, Los Angeles, California 90007.
Received January 22, 1973

Abstract: Difference Fourier techniques have been successfully applied to locate the hydrogen atoms in the metal cluster complex $H_3Mn_3(CO)_{12}$. The hydrogen atom positions are most clearly revealed when only low-angle data ($0 < \sin\theta/\lambda < 0.33$ Å^{-1}) are used to calculate the difference maps. The hydrogen atom parameters were successfully refined by least-squares methods. The molecular structure of $H_3Mn_3(CO)_{12}$ consists of an equilateral array of manganese atoms, each with four terminal carbonyl groups. The hydrogen atoms lie in the equatorial Mn_3 plane in symmetrically bridging positions. They are displaced from the centers of the Mn–Mn bonds by about 0.7 Å and are coplanar with the Mn_3 plane by within ±0.2 Å. Average distances and angles are Mn–Mn, 3.111 (2) Å; Mn–H, 1.72 (3) Å; Mn–H–Mn, 131 (7)°; H–Mn–H, 108 (6)°. Crystallographic data: unit cell triclinic; space group $P\bar{1}$; $a = 8.22$ (1), $b = 14.86$ (2), $c = 8.99$ (1) Å; $\alpha = 105.2$ (1), $\beta = 118.5$ (1), $\gamma = 96.9$ (1)°; final R factor = 5.8% for 1537 reflections.

The location of hydrogen atoms in metal cluster complexes remains one of the more difficult tasks for the structural chemist today. The problems normally encountered in trying to find a hydrogen atom bonded to a metal atom are compounded when that hydrogen atom is simultaneously attached to two or more metal atoms, a situation which often exists in metal cluster hydrides. We wish to report here the structure determination of $H_3Mn_3(CO)_{12}$. This, we believe, is the first time that the locations of bridging hydrogen atoms in a metal cluster compound[2] have been definitively established.

$H_3Mn_3(CO)_{12}$ was first prepared by Kaesz and coworkers in 1964.[3] The method used was the treatment of $Mn_2(CO)_{10}$ with $NaBH_4$, followed by acidification. An improved synthesis was later developed by Lewis and coworkers in which concentrated aqueous KOH was used in place of $NaBH_4$.[4] In their original paper Kaesz and coworkers assigned to $H_3Mn_3(CO)_{12}$ a D_{3h} structure in which the H atoms occupied symmetrically bridging positions in the Mn_3 plane. This conclusion was reached primarily on the basis of the compound's infrared spectrum,[5] which was very similar to that of the known $Os_3(CO)_{12}$.[6] Subsequent investigations provided further support for the D_{3h} model: the presence of a single nmr signal at τ 24.0 indicated the equivalence of all H atoms in the molecule[7a] and mass spectral work confirmed the total number of H atoms to be three.[4,7b]

---

(1) (a) New College; (b) University of Southern California.

(2) Metal cluster compounds are defined as "Groups of three or more metal atoms in which each is bound to all, or most, of the others." F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience, New York, N. Y., 1966, p 656.

(3) W. Fellmann, D. K. Huggins, and H. D. Kaesz, Proceedings of the Eighth International Conference on Coordination Chemistry, held in Vienna, Austria, Sept 1964, V. Gutmann, Ed, Springer-Verlag, Berlin, 1964, pp 255–257.

(4) (a) B. F. G. Johnson, R. D. Johnston, J. Lewis, and B. H. Robinson, *Chem. Commun.*, 851 (1966); (b) *J. Organometal. Chem.*, **10**, 105 (1967).

(5) The interpretation of the ir spectrum of the analogous $H_3Re_3(CO)_{12}$ is given in D. K. Huggins, W. Fellmann, J. M. Smith, and H. D. Kaesz, *J. Amer. Chem. Soc.*, **86**, 4841 (1964).

(6) E. R. Corey and L. F. Dahl, *Inorg. Chem.*, **1**, 521 (1962).

(7) (a) E. O. Fischer and R. Aumann, *J. Organometal. Chem.*, **10**, P1 (1967); (b) J. M. Smith, K. Mehner, and H. D. Kaesz, *J. Amer. Chem. Soc.*, **89**, 1759 (1967).

Experimental Section

A sample of $H_3Mn_3(CO)_{12}$ was prepared by published methods.[4] Recrystallization of the compound was extremely difficult, almost always leading to twinned or disordered crystals. We had previously encountered similar difficulties in trying to grow suitable crystals of the isostructural $H_3Re_3(CO)_{12}$.[8] Eventually, from slow recrystallization from a hot CH_2Cl_2 solution, it was possible to isolate a single crystal suitable for X-ray analysis.

The irregularly shaped crystal (approximate dimensions 0.1 × 0.2 × 0.5 mm) was mounted in a thin-walled glass capillary of diameter 0.2 mm such that the long axis of the crystal roughly coincided with the axis of the capillary. Weissenberg and precession photographs indicated that the crystal system is triclinic. The unit cell parameters, obtained by carefully measuring the setting angles of 22 reflections on a Nonius CAD-3 automated diffractometer, are given together with other relevant crystal data in Table I. The density was measured by flotation in a CCl_4–CH_3I mixture. One hemisphere of data was collected by the $\theta/2\theta$ scan technique using Zr-filtered Mo Kα radiation up to a 2θ limit of 45°. A total of 2282 reflections (including 120 check reflections) was collected in the following manner: (1) a scan speed of 10°/min was used; (2) the scan range was defined as $\Delta\theta = 1.2 + 0.15 \tan\theta$; (3) background counts were taken at the beginning and the end of each scan (the time taken for counting each background was precisely one-quarter of the time taken for the scan itself); (4) the number of scans for each reflection varied between two and six, depending on the intensity of the reflection (weak reflections were scanned more often than strong ones); (5) zirconium-foil attenuators were automatically inserted if the counting rate exceeded 2500 counts/sec; (6) a takeoff angle of 4° was used.

Table I. Crystal Data for $H_3Mn_3(CO)_{12}$

a = 8.215 (10) Å	Mol wt = 504.0
b = 14.864 (19) Å	Space group $P\bar{1}$
c = 8.990 (14) Å	$Z = 2$
α = 105.22 (10)°	$F(000) = 492$
β = 118.50 (11)°	D_{measd} = 1.886 (5) g cm^{-3}
γ = 96.95 (9)°	D_{calcd} = 1.879 g cm^{-3}
V = 890.8 Å^3	

Three check reflections were monitored at 20-reflection intervals and showed no significant variation in intensity. The standard deviation of each intensity reading, $\sigma(F_o^2)$, was estimated using the formula[12] $\sigma(F_o^2) = [(\text{total count}) + 0.04\,(\text{net intensity})^2]^{1/2}$. Reflections whose net intensities were less than 3σ were considered unobserved and were eliminated from the subsequent structure analysis. An empirical absorption correction was applied, based on the variation in intensity of an axial reflection with ϕ.[13] This gave correction factors (normalized to an average of unity) which varied between 0.90 and 1.11. The intensities were further corrected for Lorentz and polarization effects and placed on an approximately absolute scale by means of a Wilson plot.[14]

Solution and Refinement of the Structure. A three-dimensional Patterson map[15] was interpretable in terms of three independent heavy-atom positions in the centric space group $P\bar{1}$. A difference Fourier map phased by the three metal atoms revealed the positions of the carbonyl groups quite clearly. Exhaustive least-squares refinement[16] of all positional and anisotropic thermal parameters resulted in the agreement factors[17] R_1 = 6.1% and R_2 = 7.3% for the 1537 nonzero reflections.[18]

The structure of the molecule at this stage shows near-perfect D_{3h} symmetry, a fact which by itself is almost sufficient proof for the symmetrically bridging hydride model originally proposed.[3] Nevertheless, we were anxious to see if the hydrogen atoms could be located directly using crystallographic methods.

A difference Fourier map was first calculated in a conventional manner. This map (Figure 1a) shows promising peaks at likely positions, but is unfortunately marred by a large number of background peaks. We then tried a technique applied by Ibers and coworkers to $HRh(CO)(PPh_3)_3$[19] and $HMn_2(CO)_8PPh_2$.[20] This is to use only low-angle reflections in the calculation of difference Fourier maps. The rationale here is that, since the scattering from hydrogen atoms is largely confined to the low-angle reflections, the H atom peaks should be enhanced when some high-angle data are omitted. Consequently, a second difference Fourier map was calculated using approximately the inner two-thirds of the data (1102 reflections; $\sin\theta/\lambda$ cutoff = 0.43 Å^{-1}). This map (Figure 1b) shows considerable improvement, but some background peaks still remain. Finally, using approximately one-third of the data (553 reflections; $\sin\theta/\lambda$ cutoff = 0.33 Å^{-1}) a third difference Fourier map (Figure 1c) now reveals the hydrogen atom positions quite clearly. At this stage, these three remaining peaks are in fact the largest peaks in the entire three-dimensional difference Fourier map.

The subsequent refinement of the hydrogen atom positions and temperature factors was carried out in the following manner. (A) Using only the low-angle data (553 reflections), the positions and temperature factors of *all* the atoms were refined (the H atoms isotropically). This converged easily to reasonable hydrogen positions and temperature factors. (B) Keeping the hydrogen positions and temperature factors fixed, the other atoms were refined anisotropically using all the data. This is to allow the other atoms to "adjust" to the presence of the hydrogen atoms. (C) Finally, all the parameters were refined[16] using all the data, resulting in final agreement factors of R_1 = 5.8% and R_2 = 7.0%.

Discussion of the Structure

The final molecular geometry (now including the hydrogen atoms[21]) is given in Figure 2. The atomic positions are listed in Table II, the thermal parameters in Table III, the bond distances in Table IV, and the

---

(8) Difficulties in obtaining suitable crystals are quite commonly encountered when dealing with compounds of the type $M_3(CO)_{12}$ and $M_4(CO)_{12}$. The source of the problem is that the packing in these compounds is largely determined by the exterior array of oxygen atoms, which are often arranged in highly symmetrical and spheroidal geometrical forms such as the icosahedron (as in $Fe_3(CO)_{12}$, $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$)[9,10] or the cube octahedron (as in $H_6Re_4(CO)_{12}^{2-}$).[11] This makes it relatively easy for the molecules to pack in a variety of orientations, causing disorder.

(9) C. H. Wei and L. F. Dahl, *J. Amer. Chem. Soc.*, **88**, 1821 (1966); **91**, 1351 (1969).

(10) C. H. Wei, G. R. Wilkes, and L. F. Dahl, *J. Amer. Chem. Soc.*, **89**, 4792 (1967).

(11) H. D. Kaesz, B. Fontal, R. Bau, S. W. Kirtley, and M. R. Churchill, *J. Amer. Chem. Soc.*, **91**, 1021 (1969).

(12) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 6, 197 (1967). In the expression given in the text, "total count" means $[(\text{background})_1 + (\text{peak count}) + (\text{background})_2]$.

(13) T. C. Furnas, "Single Crystal Orientation Manual," General Electric Co., 1966. A more analytical absorption correction was not possible because of the irregular shape of the crystal.

(14) A. J. C. Wilson, *Nature (London)*, **150**, 151 (1942).

(15) The major computations in this work were performed using CRYM, an amalgamated set of crystallographic programs developed by Dr. Richard Marsh's groups at the California Institute of Technology.

(16) Throughout this work, in the least-squares refinement, the parameters were blocked such that the positional parameters were put in one matrix and the temperature factors and scale factor in the other.

(17) $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$, where the weights w are defined as $4F_o^2/[\sigma(F_o^2)]^2$.

(18) The form factors for Mn, O, C, and H were taken from Table 3.3.1A and the $\Delta f'$ and $\Delta f''$ dispersion correction factors for Mn were taken from Table 3.3.2C of the "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1968.

(19) S. J. LaPlaca and J. A. Ibers, *J. Amer. Chem. Soc.*, **85**, 3501 (1963); *Acta Crystallogr.*, **18**, 511 (1965).

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

(21) Throughout this paper, we will use the H atom positions derived from refinement step (A) (*i.e.*, using data with $\sin\theta/\lambda$ limit = 0.33 Å^{-1}). We feel that these positions should be more reliable because they were derived from data which had the greatest proportional amount of hydrogen atom contribution. For completeness, however, we list here the H parameters resulting from refinement step (C) (*i.e.*, using all data)

Atom	x	y	z	B
H_1	0.070 (9)	0.315 (5)	0.013 (9)	4.1 (1.7)
H_2	0.079 (11)	0.198 (6)	−0.251 (10)	6.8 (2.3)
H_3	0.246 (11)	0.199 (6)	0.096 (11)	4.8 (2.3)

These positions give the following M–H distances: Mn_1–H_1 = 1.49, Mn_2–H_1 = 1.72, Mn_2–H_2 = 1.81, Mn_3–H_2 = 1.73, Mn_3–H_3 = 1.50, Mn_1–H_3 = 1.83 Å. It is evident that these distances are not as self-consistent as those obtained from the other set of H atom positions (see Table IV).

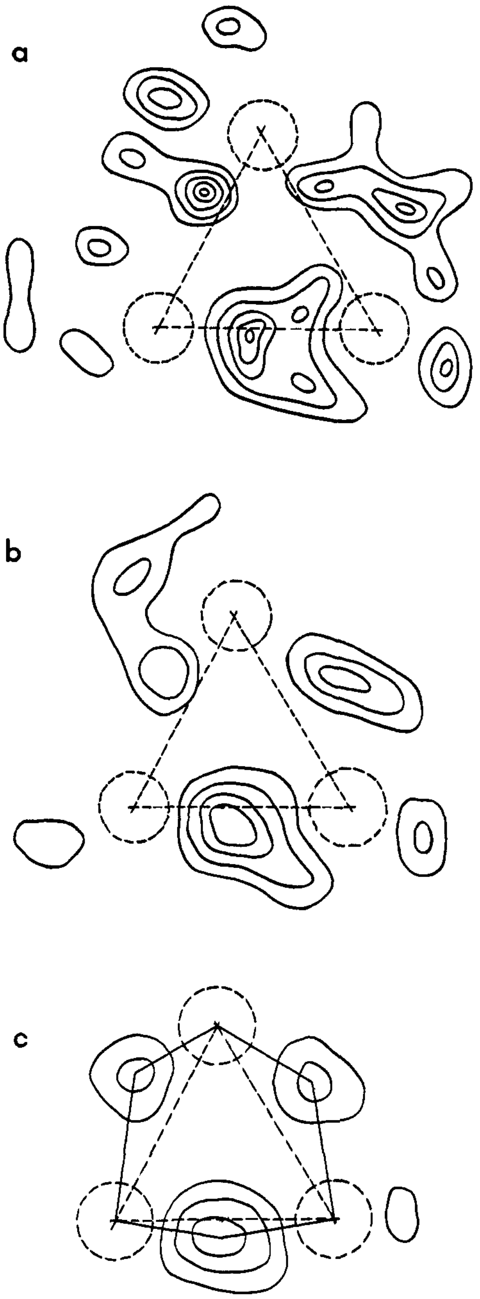

Figure 1. Difference Fourier maps sectioned onto the equatorial Mn_3 plane: (a) using all data, (b) using the inner two-thirds data, (c) using the inner one-third data. Contours are drawn at 0.2, 0.3, 0.4, 0.5, and 0.6 e/Å^3. The dotted circles represent the positions of the manganese atoms.

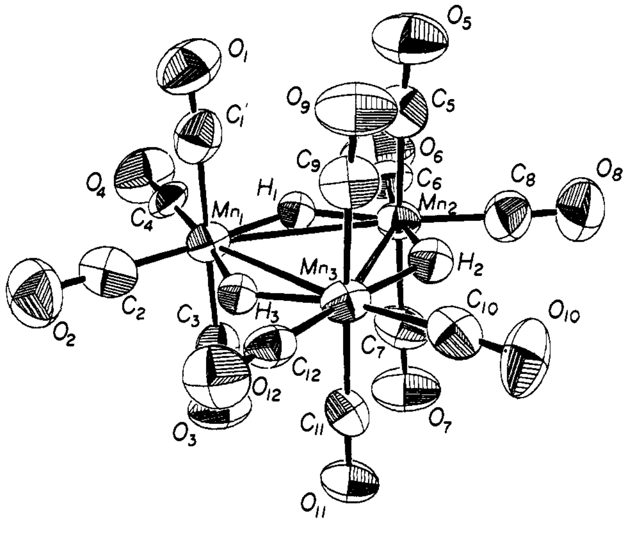

Figure 2. Molecular geometry of $H_3Mn_3(CO)_{12}$.

Table II. Final Atomic Positions for $H_3Mn_3(CO)_{12}$ (in fractional coordinates)[a]

Atom	x	y	z
Mn_1	0.1582 (2)	0.2933 (1)	0.1856 (2)
Mn_2	−0.0291 (2)	0.2845 (1)	−0.2151 (2)
Mn_3	0.2310 (2)	0.1527 (1)	−0.0847 (2)
C_1	0.3813 (17)	0.3856 (8)	0.2647 (14)
C_2	0.2726 (15)	0.2709 (8)	0.3885 (16)
C_3	−0.0628 (15)	0.1957 (8)	0.1011 (14)
C_4	0.0739 (14)	0.3873 (8)	0.2780 (13)
C_5	0.1817 (16)	0.3813 (9)	−0.1506 (15)
C_6	−0.1589 (17)	0.3720 (8)	−0.2073 (16)
C_7	−0.2408 (16)	0.1832 (8)	−0.2911 (15)
C_8	−0.1080 (16)	0.2633 (9)	−0.4438 (16)
C_9	0.4453 (15)	0.2495 (8)	−0.0229 (14)
C_{10}	0.2324 (14)	0.0807 (8)	−0.2806 (15)
C_{11}	0.0162 (14)	0.0552 (7)	−0.1563 (12)
C_{12}	0.3875 (14)	0.0988 (7)	0.0650 (14)
O_1	0.5217 (12)	0.4424 (6)	0.3195 (12)
O_2	0.3467 (14)	0.2557 (7)	0.5259 (12)
O_3	−0.1946 (12)	0.1379 (5)	0.0595 (12)
O_4	0.0209 (13)	0.4447 (6)	0.3354 (12)
O_5	0.3051 (13)	0.4404 (7)	−0.1226 (14)
O_6	−0.2386 (13)	0.4296 (6)	−0.1973 (15)
O_7	−0.3736 (11)	0.1228 (6)	−0.3430 (12)
O_8	−0.1650 (14)	0.2537 (8)	−0.5945 (11)
O_9	0.5747 (11)	0.3038 (6)	0.0076 (13)
O_{10}	0.2303 (11)	0.0317 (7)	−0.4036 (11)
O_{11}	−0.1105 (10)	−0.0080 (5)	−0.2022 (10)
O_{12}	0.4883 (11)	0.0664 (6)	0.1637 (11)
H_1[b]	0.063 (17)	0.319 (8)	0.005 (18)
H_2[b]	0.091 (15)	0.197 (7)	−0.259 (14)
H_3[b]	0.248 (14)	0.197 (8)	0.119 (14)

[a] Standard deviations in parentheses. [b] See footnote 21.

bond angles in Table V. A listing of the observed and calculated structure factors is available.[22]

We have confirmed, then, that the hydrogen atoms lie in the equatorial Mn_3 plane in positions that bridge pairs of metal atoms, probably in a symmetrical fashion.[23] The metal–hydrogen distances[21] (Mn_1–H_1 = 1.61 (13), Mn_2–H_1 = 1.64 (13), Mn_2–H_2 = 1.79 (12), Mn_3–H_2 = 1.79 (11), Mn_3–H_3 = 1.71 (11), Mn_1–H_3 = 1.78 (13) Å) average to 1.72 (3) Å,[24] in good agreement with the general trend of bond lengths found in bridging

---

(22) Listings of structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth Street, N.W., Washington, D. C. 20036, by referring to code number JACS-73-4532. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(23) We should comment, however, on the apparent asymmetry of the H atom positions as shown in Figure 1c (*i.e.*, the two upper peaks seem to be slightly asymmetrically disposed about the metal atoms and the lower peak seems to be larger than the other two). This, we believe, is an artifact. Given the accuracy of the data, it would have been unreasonable to expect perfect threefold symmetry in our difference maps; it is difficult enough even to *detect* the hydrogen atoms under the present circumstances. Because there is no chemical reason for believing otherwise, we tend to favor a symmetrically bridging D_{3h} model, even though an asymmetric model cannot be definitively rejected at this stage.

(24) The estimated error of the mean (±0.03 Å) is calculated using the formula $[\Sigma^n_{i=1}(d_i + \bar{d})^2/n(n - 1)]^{1/2}$, where d_i and $\bar{d}$ are the distances and the mean distance, respectively.

Table III. Final Temperature Factors[a] for $H_3Mn_3(CO)_{12}$

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Mn_1	182 (4)	44 (1)	182 (3)	43 (3)	194 (6)	47 (3)
Mn_2	160 (4)	46 (1)	189 (3)	34 (3)	167 (6)	72 (3)
Mn_3	171 (4)	45 (1)	204 (3)	47 (3)	217 (6)	50 (3)
C_1	305 (30)	60 (7)	195 (23)	70 (25)	242 (45)	36 (21)
C_2	198 (26)	70 (7)	332 (31)	87 (23)	253 (48)	111 (26)
C_3	244 (26)	56 (7)	236 (23)	86 (22)	355 (44)	55 (21)
C_4	198 (24)	53 (6)	172 (21)	−15 (20)	177 (37)	−9 (19)
C_5	231 (28)	76 (8)	276 (26)	84 (25)	258 (46)	142 (24)
C_6	315 (30)	43 (6)	289 (27)	34 (23)	271 (47)	86 (22)
C_7	230 (27)	59 (7)	310 (27)	106 (23)	299 (46)	154 (23)
C_8	253 (27)	81 (8)	212 (24)	6 (24)	224 (45)	69 (23)
C_9	194 (25)	55 (7)	280 (25)	62 (22)	256 (43)	101 (22)
C_{10}	155 (22)	76 (7)	245 (25)	49 (21)	195 (41)	114 (23)
C_{11}	178 (23)	56 (6)	200 (22)	78 (20)	243 (39)	99 (20)
C_{12}	232 (25)	39 (6)	219 (23)	50 (20)	279 (41)	27 (18)
O_1	226 (19)	90 (6)	354 (21)	−23 (17)	241 (34)	40 (18)
O_2	453 (26)	121 (7)	301 (20)	185 (22)	260 (38)	200 (20)
O_3	335 (22)	60 (5)	424 (22)	18 (17)	582 (39)	51 (18)
O_4	440 (24)	76 (5)	414 (23)	146 (19)	573 (41)	27 (18)
O_5	294 (23)	100 (7)	528 (27)	3 (20)	406 (42)	210 (23)
O_6	388 (24)	66 (5)	592 (29)	161 (19)	471 (44)	148 (21)
O_7	218 (20)	74 (6)	463 (24)	14 (16)	301 (36)	140 (19)
O_8	489 (28)	149 (8)	200 (18)	−56 (24)	286 (38)	74 (21)
O_9	206 (18)	80 (6)	472 (23)	−5 (16)	361 (35)	138 (19)
O_{10}	312 (20)	121 (7)	240 (18)	128 (19)	385 (33)	37 (17)
O_{11}	227 (18)	56 (4)	290 (17)	−3 (14)	291 (29)	95 (14)
O_{12}	267 (19)	80 (5)	340 (20)	153 (16)	262 (32)	160 (16)
H_1	3.1 (1.4)[b]					
H_2	4.0 (1.6)[b]					
H_3	3.2 (1.5)[b]					

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [b] Isotropic thermal parameters, see footnote 21.

Table IV. Bond Distances in $H_3Mn_3(CO)_{12}$ (in Å)

	(a) Mn–Mn Distances		
Mn_1–Mn_2	3.126 (2)	Mn_2–Mn_3	3.099 (2)
Mn_1–Mn_3	3.107 (2)		Av 3.111 (2)[a]
	(b) Mn–C Distances		
	Axial		Equatorial
Mn_1–C_1	1.839 (14)	Mn_1–C_2	1.755 (12)
Mn_1–C_3	1.855 (13)	Mn_1–C_4	1.816 (12)
Mn_2–C_5	1.846 (14)	Mn_2–C_6	1.787 (14)
Mn_2–C_7	1.857 (14)	Mn_2–C_8	1.757 (12)
Mn_3–C_9	1.874 (13)	Mn_2–C_{10}	1.811 (12)
Mn_3–C_{11}	1.854 (12)	Mn_3–C_{12}	1.808 (11)
	Av 1.854 (5)[a]		Av 1.789 (11)[a]
	(c) C–O Distances		
	Axial		Equatorial
C_1–O_1	1.136 (18)	C_2–O_2	1.187 (16)
C_3–O_3	1.128 (17)	C_4–O_4	1.121 (16)
C_5–O_5	1.134 (18)	C_6–O_6	1.150 (18)
C_7–O_7	1.127 (17)	C_8–O_8	1.162 (15)
C_9–O_9	1.121 (17)	C_{10}–C_{10}	1.144 (15)
C_{11}–O_{11}	1.133 (15)	C_{12}–O_{12}	1.150 (14)
	Av 1.130 (2)[a]		Av 1.152 (9)[a]
	(d) Mn–H Distances[b]		
Mn_1–H_1	1.61 (13)	Mn_3–H_3	1.71 (11)
Mn_2–H_1	1.64 (13)	Mn_1–H_3	1.78 (13)
Mn_2–H_2	1.79 (12)		Av 1.72 (3)[a]
Mn_3–H_2	1.79 (11)		

[a] The estimated errors of the average values are calculated, whenever meaningful (*i.e.*, for six or more observations), using the formula $[\Sigma^n_{i=1}(d_i - \bar{d})^2/n(n-1)]^{1/2}$, where d_i and $\bar{d}$ are the distances and mean distance, respectively. For less than six observations, the estimated errors are calculated by taking the average of the individual standard deviations. [b] See footnote 21.

metal hydrides.[25] The fact that this distance is slightly longer than the terminal Mn-H distance (1.60 (1) Å) found in $HMn(CO)_5$[27] might very well reflect the lower bond order (formally one-half) of the M-H bonds in bridging hydrides. Similar differences between terminal and bridging bond lengths are observed in B_2H_6 (the B-H distance is 1.19 (1) Å for terminal hydrogens and 1.33 (2) Å for bridging hydrogens).[28]

The H atoms are coplanar with the Mn_3 plane by within ±0.2 Å and are displaced from the centers of the Mn-Mn bonds by about 0.7 Å. In fact, they appear as though they are situated at octahedral coordination positions about the manganese atoms. This is illustrated in Figure 2, which shows the near-linearity of the H-Mn-C-O linkages quite clearly (also see Table V). The observed increase of the Mn-Mn distance upon protonation (average Mn-Mn distance in this compound is 3.111 (2) Å, Mn-Mn distance[29] in $Mn_2(CO)_{10}$ = 2.923 Å) lends support to our earlier contention[11,30] that the increased bond lengths in $H_2Re_3(CO)_{12}^-$ (Re-Re distance[30] = 3.177 Å) and $H_6Re_4(CO)_{12}^{2-}$ (Re-Re distance[11] = 3.160 Å, as compared with 3.02 (1) Å in $Re_2(CO)_{10}$[31]) were due to hydrogen bridging of this nature.

---

(25) For a recent tabulation of terminal and bridging metal hydride bond lengths, see Tables XV and XVI in H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, 72, 231 (1972). In particular, we would like to quote the M-H distance of 1.65 Å found for the Mn-H-Mn bridge in $HMn_3(CO)_{10}(BH_3)_2$[26] and the 1.86 Å found in $HMn_2(CO)_8PPh_2$.[20]

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

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

(28) W. N. Lipscomb, "Boron Hydrides," Benjamin, New York, N.Y., 1963.

(29) L. F. Dahl and R. E. Rundle, *Acta Crystallogr.*, **16**, 419 (1963).

(30) M. R. Churchill, P. H. Bird, H. D. Kaesz, R. Bau, and B. Fontal, *J. Amer. Chem. Soc.*, **90**, 7135 (1968).

(31) L. F. Dahl, E. Ishishi, and R. E. Rundle, *J. Chem. Phys.*, **26**, 1750 (1957).

Table V. Bond Angles in $H_3Mn_3(CO)_{12}$ (in degrees)

	(a) Mn–Mn–Mn Angles		
Mn_1–Mn_2–Mn_3	59.9 (1)	Mn_3–Mn_1–Mn_2	59.6 (1)
Mn_2–Mn_3–Mn_1	60.5 (1)		
	(b) Mn–C–O Angles		
Mn_1–C_1–O_1	177.6 (10)	Mn_1–C_2–O_2	178.7 (13)
Mn_1–C_3–O_3	176.1 (10)	Mn_1–C_4–O_4	179.3 (12)
Mn_2–C_5–O_5	175.5 (11)	Mn_2–C_6–O_6	178.1 (11)
Mn_2–C_7–O_7	177.2 (11)	Mn_2–C_8–O_8	176.1 (13)
Mn_3–C_9–O_9	176.2 (11)	Mn_3–C_{10}–O_{10}	177.1 (12)
Mn_3–C_{11}–O_{11}	176.3 (10)	Mn_3–C_{12}–O_{12}	178.3 (10)
	(c) C(ax)–Mn–C(ax) Angles		
C_1–Mn_1–C_3	177.3 (6)	C_9–Mn_3–C_{11}	177.5 (5)
C_5–Mn_2–C_7	176.8 (6)		
	(d) C(eq)–Mn–C(eq) Angles		
C_2–Mn_1–C_4	92.7 (5)	C_{10}–Mn_3–C_{12}	94.4 (5)
C_6–Mn_2–C_8	92.1 (6)		Av 93.1 (5)[a]
	(e) C(ax)–Mn–C(eq) Angles		
C_1–Mn_1–C_2	90.5 (6)	C_7–Mn_2–C_6	91.7 (6)
C_1–Mn_1–C_4	90.1 (6)	C_7–Mn_2–C_8	89.4 (6)
C_3–Mn_1–C_2	89.5 (6)	C_9–Mn_3–C_{10}	89.6 (5)
C_3–Mn_1–C_4	92.6 (6)	C_9–Mn_3–C_{12}	91.0 (5)
C_5–Mn_2–C_6	90.1 (6)	C_{11}–Mn_3–C_{10}	88.2 (5)
C_5–Mn_2–C_8	88.0 (6)	C_{11}–Mn_3–C_{12}	90.2 (5)
	(f) C(ax)–Mn–Mn Angles		
C_1–Mn_1–Mn_2	92.8 (3)	C_1–Mn_1–Mn_3	89.5 (4)
C_3–Mn_1–Mn_2	86.6 (3)	C_3–Mn_1–Mn_3	88.0 (4)
C_5–Mn_2–Mn_1	91.4 (4)	C_5–Mn_2–Mn_3	91.1 (4)
C_7–Mn_2–Mn_1	90.9 (4)	C_7–Mn_2–Mn_3	88.1 (4)
C_9–Mn_3–Mn_1	91.4 (4)	C_9–Mn_3–Mn_2	89.3 (4)
C_{11}–Mn_3–Mn_1	90.5 (3)	C_{11}–Mn_3–Mn_2	90.3 (4)
	(g) C(eq)–Mn–Mn Angles		
C_2–Mn_1–Mn_3	106.6 (4)	C_2–Mn_1–Mn_2	165.8 (4)
C_4–Mn_1–Mn_2	101.1 (3)	C_4–Mn_1–Mn_3	160.6 (3)
C_6–Mn_2–Mn_1	99.2 (4)	C_6–Mn_2–Mn_3	159.1 (4)
C_8–Mn_2–Mn_3	108.8 (5)	C_8–Mn_2–Mn_1	168.6 (5)
C_{10}–Mn_3–Mn_2	106.0 (4)	C_{10}–Mn_3–Mn_1	166.5 (4)
C_{12}–Mn_3–Mn_1	99.1 (4)	C_{12}–Mn_3–Mn_2	159.6 (4)
	Av 103.5 (17)[a]		Av 163.4 (17)[a]
	(h) H–Mn–Mn Angles[b]		
H_1–Mn_1–Mn_3	74 (5)	H_1–Mn_1–Mn_2	16 (5)
H_1–Mn_2–Mn_3	74 (5)	H_1–Mn_2–Mn_1	16 (5)
H_2–Mn_2–Mn_1	90 (3)	H_2–Mn_2–Mn_3	30 (3)
H_2–Mn_3–Mn_1	91 (4)	H_2–Mn_3–Mn_2	30 (4)
H_3–Mn_1–Mn_2	86 (4)	H_3–Mn_3–Mn_1	28 (4)
H_3–Mn_3–Mn_2	88 (4)	H_3–Mn_1–Mn_3	27 (4)
	Av 84 (3)[a]		Av 24 (3)[a]
	(i) H–Mn–C(eq) Angles[b]		
H_1–Mn_1–C_2	177 (5)	H_1–Mn_1–C_4	87 (5)
H_1–Mn_2–C_8	172 (5)	H_1–Mn_2–C_6	85 (5)
H_2–Mn_2–C_6	171 (3)	H_2–Mn_2–C_8	79 (3)
H_2–Mn_3–C_{12}	170 (4)	H_2–Mn_3–C_{10}	76 (4)
H_3–Mn_3–C_{10}	165 (4)	H_3–Mn_3–C_{12}	72 (4)
H_3–Mn_1–C_4	173 (4)	H_3–Mn_1–C_2	80 (4)
	171 (2)[a]		80 (2)[a]
	(j) Mn–H–Mn Angles[b]		
Mn_1–H_1–Mn_2	149 (9)	Mn_3–H_3–Mn_1	126 (7)
Mn_2–H_2–Mn_3	119 (6)		Av 131 (7)[a]
	(k) H–Mn–H Angles[b]		
H_1–Mn_2–H_2	104 (6)	H_3–Mn_1–H_1	101 (6)
H_2–Mn_3–H_3	118 (6)		Av 108 (6)[a]

[a] Average bond angles are calculated wherever meaningful. For six or more observations the formula $[\Sigma^{n}_{i=1}(\theta_i - \bar{\theta})^2/n(n-1)]^{1/2}$ is used to calculate the estimated errors of the averages, where θ_i and $\bar{\theta}$ are the angles and average angles, respectively. For less than six observations the estimated errors are calculated by taking the average of the individual standard deviations. [b] See footnote 21.

The difference between the average axial (1.854 (5) Å) and average equatorial (1.789 (11) Å) M–C bond lengths in $H_3Mn_3(CO)_{12}$ is in keeping with the general observation that M–L distances opposite π-bonding ligands (such as CO) are longer than M–L distances opposite σ-bonding ligands (such as H). This effect has been attributed to a greater competition for back-bonding electrons (and a concomitant weakening of the M–L bonds) when two π-bonding ligands are opposite one another.[27,32]

We have carefully considered alternative explanations for the presence of the peaks in the difference maps. Our argument that these do indeed represent H atoms can be summarized as follows. (1) Clearly, there is *some* electron density at the observed positions. The successful refinement of both positional and thermal parameters is good evidence for this. (2) The above conclusion is reinforced by the observed drop in R factor from 6.1 to 5.8% when the hydrogens are included in the least-squares refinement. According to Hamilton's R factor significance test,[33] and R factor ratio of 1.05 for 12 added parameters and an $(n - m)$ value[34] of approximately 1300 indicates that the probability that the electron density peaks are real is better than 99.5%. (3) Having established that the peaks are real, the remaining question is then whether the peaks are due to hydrogen atoms as claimed or to atoms of some other element. One possibility that particularly troubled us was whether the peaks could be attributed to a small amount of packing disorder. In other words, could the three peaks in Figure 1c be due to manganese atoms arising from a small percentage of the molecules (say 1–5%) packing in an orientation 60° from the rest of the molecules?[35] Probably our best argument against this hypothesis is the sequence of difference Fourier maps shown in Figure 1. The enhancement of peak positions upon elimination of high-angle data is a phenomenon characteristic of hydrogen atoms.[19,20] Moreover, the peak to peak distances of 2.7 Å are too short to be Mn–Mn bonds. (4) Lastly, and perhaps most importantly of all, there is the chemical reasonableness of the whole structure: the threefold symmetry of hydrogen peaks, the reasonable M–H bond lengths, the octahedral coordination of the manganese atoms. These observations, coupled with the unequivocal mass spectral evidence[4,7b] for the presence of three hydrogen atoms, provide as good a proof as any for the correctness of the structure.

Acknowledgments. We thank the National Institutes of Health, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Research Corporation for supporting this research. We are also grateful to the National Science Foundation for making the purchase of the diffractometer possible (through a Center of Excellence grant to the University of Southern California) and to the Computer Center of the University of Southern California for supplying the computer time used in this work. Special thanks are due to Professor H. D. Kaesz of the University of California, Los Angeles, for having originally suggested this problem.

---

(32) B. A. Coyle and J. A. Ibers, *Inorg. Chem.*, **11**, 1105 (1972).

(33) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

(34) n = number of reflections, m = total number of refineable parameters.

(35) We are referring to the "Star of David" disorder phenomenon found in $Fe_3(CO)_{12}$, see ref 9.