

Lawrence Berkeley National Laboratory

Recent Work

Title

THE CRYSTAL AND MOLECULAR STRUCTURE OF TRIPHENYLMETHYLPHOSPHONIUM 1,1,1-TRICARBONYL-4,6-DICARBA-I-MANGANA-CLOSO-NONABORATE(1-)

Permalink

<https://escholarship.org/uc/item/5bf865hf>

Authors

Hollander, Frederick J.
Tenpleton, David H.
Zalkin, Allan.

Publication Date

1973-04-01

Submitted to Inorganic Chemistry

RECEIVED
LAWRENCE
RADIATION LABORATORY

LBL-1661
Preprint c.)

LIBRARY AND
DOCUMENTS SECTION

THE CRYSTAL AND MOLECULAR STRUCTURE OF
TRIPHENYLMETHYLPHOSPHONIUM 1, 1, 1-TRICARBONYL-4, 6-
DICARBA-1-MANGANA-CLOSO-NONABORATE(1-)

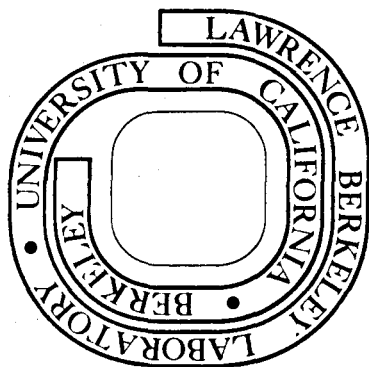
Frederick J. Hollander, David H. Templeton, and Allan Zalkin

April 1973

Prepared for the U. S. Atomic Energy Commission
under Contract W-7405-ENG-48

For Reference

Not to be taken from this room



LBL-1661
c.)

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

CONTRIBUTION FROM THE LAWRENCE BERKELEY LABORATORY
AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF
CALIFORNIA, BERKELEY, CALIFORNIA 94720

The Crystal and Molecular Structure of
Triphenylmethylphosphonium 1,1,1-tricarbonyl-4,6-dicarbonyl-1-
mangana-closo-nonaborate(1-)¹

By

Frederick J. Hollander, David H. Templeton, and Allan Zalkin

Crystals of $((C_6H_5)_3PCH_3)^+((B_6C_2H_8)Mn(CO)_3)^-$ are
triclinic, space group $P\bar{1}$, with $a = 11.216(5) \text{ \AA}$, $b = 11.285(4) \text{ \AA}$,
 $c = 11.464(5) \text{ \AA}$, $\alpha = 105.79(1)^\circ$, $\beta = 104.46(1)^\circ$, $\gamma = 98.04(1)^\circ$,
 $d_o = 1.25 \text{ g/cm}^3$, $d_c = 1.29 \text{ g/cm}^3$ for $Z = 2$. X-ray
diffraction intensities were collected by stationary-crystal,
stationary-counter technique using $MoK\alpha$ radiation. The
structure was refined to $R = 0.042$ for 2862 independent
reflections. The predicted structure of the anion is
confirmed; manganese is bonded to two carbon atoms (at 2.04 \AA)
and three boron atoms (two at 2.35 \AA and one at 2.23 \AA)
of the eight-atom carborane cage.

¹Work done under the auspices of the U.S.

Atomic Energy Commission.

Introduction

The $(B_6C_2H_8)Mn(CO)_3^-$ ion was synthesized by Hawthorne and Pitts,² and a tentative structure was assigned to it on the basis of IR and NMR spectroscopic data.³

(2) M. F. Hawthorne and A. D. Pitts, J. Am. Chem. Soc., 89, 7115 (1967).

(3) A. D. George and M. F. Hawthorne, Inorg. Chem., 8, 1801 (1969).

This study of the triphenylmethylphosphonium (TPMP) salt, undertaken to verify the structure by X-ray crystallographic means, confirms that it is triphenylmethylphosphonium 1,1,1-tricarbonyl-4,6-dicarbonyl-1-mangano-closo-nonaborate(1-).⁴

(4) Named according to Fig. 14, Inorg. Chem., 7, 1945 (1968).

Experimental Procedure

Clear, orange-red, needlelike crystals of the compound were supplied to us by M. Frederick Hawthorne as prepared by A. Denise Pitts. Optical extinction between crossed polarizers was very sharp. Precession photographs indicated that the unit cell was triclinic, and preliminary cell dimensions were obtained from $hk0$ and $h0l$ photographs. A crystal of approximate dimensions 0.18 mm x 0.14 mm x 0.19 mm was attached to a glass fiber and mounted on a General Electric XRD-5 single crystal diffractometer equipped with a manual

quarter-circle Eulerian cradle goniostat. A strong reflection, $(\bar{1} \bar{2} 1)$, was set at $\chi = 90^\circ$ to facilitate checking of the orientation of the crystal. Twenty-seven high-angle reflections were then accurately centered in χ , ϕ , and 2θ using molybdenum radiation ($K\alpha_1 = 0.709261 \text{ \AA}$, $K\alpha_2 = 0.713543 \text{ \AA}$, $K\beta = 0.632253 \text{ \AA}$), and a least-squares analysis yielded accurate cell dimensions and the crystal orientation matrix. The derived cell dimensions (and standard deviations) are $\underline{a} = 11.216(5) \text{ \AA}$, $\underline{b} = 11.285(4) \text{ \AA}$, $\underline{c} = 11.464(5) \text{ \AA}$, $\alpha = 105.79(1)^\circ$, $\beta = 104.46(1)^\circ$, $\gamma = 98.04(1)^\circ$. The density measured by flotation in a mixture of n-hexane and carbon tetrachloride was 1.25 g/cm^3 compared to 1.29 g/cm^3 calculated for two formula units in a unit cell volume of 1318 \AA^3 . The measured density is low due to difficulties in getting the solution to wet the crystals.

Intensity data were collected on the same crystal using filtered $\text{MoK}\alpha$ radiation ($0.003''$ Zr in the diffracted beam) with the distances from the source and receiving apertures to the crystal 14.5 and 17.8 cm, respectively. All reflections lying in a hemisphere in reciprocal space $\chi = 0^\circ$ - 90° , $\phi = 0^\circ$ - 360° from $2\theta = 0^\circ$ to $2\theta = 45^\circ$ ($\sin\theta/\lambda = 0.5385$) were counted for 10 sec each with both crystal and counter stationary at an X-ray tube takeoff angle of 4° . Background counts were taken from a plot of background vs. 2θ averaged over several

values of χ and ϕ . The background was measured individually for each reflection which was seriously affected by streaking. Periodic checks of three standard reflections showed only small ($\pm 1\%$) random fluctuations in intensity. The data included 3445 reflections, of which 583 had $I < \sigma(I)$.

Inspection of the intensity of $(\bar{1} \bar{2} 1)$ as a function of ϕ at $\chi = 90^\circ$ showed no significant variation, and the values of μ and μ_R are 5.9 cm^{-1} and 0.11 ; no absorption correction was made to the intensities. The intensities were corrected for Lorentz and polarization factors.

Atomic scattering factors of Cromer and Waber⁵ for

(5) D. T. Cromer and J. T. Waber, Acta Crystallogr., 18, 104 (1965).

the non-hydrogen atoms and those of Stewart, Davidson and Simpson⁶ for spherical hydrogen atoms were used. Real and

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

imaginary dispersion corrections of Cromer⁷ were used for

(7) D. T. Cromer, Acta Crystallogr., 18, 17 (1965).

manganese and phosphorus.

— The function minimized by least-squares was $\sum w(\Delta F)^2 / \sum w F_o^2$.

The weighting scheme used throughout the refinement was $w = 0.0$ for $F^2 < \sigma(F^2)$ and $w = 1/\sigma^2(F)$ otherwise; $\sigma(F^2)$ was calculated as previously described⁸ with the ignorance

(8) F. J. Hollander, D. H. Templeton, and A. Zalkin, Acta Crystallogr. in press (1973).

factor $p = 0.04$. The programs used in this study structure are listed in the same paper.⁸

Structure Determination and Refinement

The centric space group, $P\bar{1}$, was assumed because the unit cell contains two formula units. This group was confirmed by the successful structure determination.

A three-dimensional Patterson synthesis yielded the position of the Mn atom, and the remainder of the non-hydrogen atoms were found by successive refinements and Fourier syntheses. The expected structure of the anion was recognized, and the atoms expected to be carbon were labeled as such, but placed into least squares with boron scattering factors. Two cycles of full-matrix least-squares refinement in which the coordinates and isotropic thermal parameters of the atoms were varied brought the conventional R value ($R_1 = \sum |\Delta F| / \sum |F_o|$) to 0.12. The average thermal parameter for those atoms labeled "carbon" was 3.86 \AA^2 compared to the average for the

boron atoms of 6.43 \AA^2 and the bond distances to the "carbon" atoms were all shorter than boron-boron distances. In all further refinements the carbon atoms were given their proper scattering factor. The manganese atom was then allowed to refine with anisotropic thermal parameters, reducing R_1 to 0.098. A difference Fourier map showed peaks at all the positions where hydrogen atoms were expected. Two cycles of full-matrix least squares refined the coordinates of all the atoms, anisotropic thermal parameters for phosphorus and manganese, isotropic thermal parameters for all other non-hydrogen atoms, and one isotropic thermal parameter for each of three sets (cage, methyl, phenyl) of hydrogens; R_1 fell to 0.078.

Comparison of observed and calculated structure factors showed 55 pairs with large discrepancies. These reflections were remeasured using the same method as before and were incorporated into the data set. Some scaling was necessary to allow for a slight deterioration of the crystal.

All non-hydrogen atoms were then allowed to refine with anisotropic thermal parameters, and the individual isotropic thermal parameters of the hydrogens were allowed to refine. The refinement proceeded in two blocks, with the anion refined in one block and the cation in the other, while the scale factor was refined in both. Finally, two cycles of full-matrix least squares on all atoms brought the shifts of all parameters to less than 2% of their calculated standard deviations. The final

R_1 was 0.042 for 2862 reflections, the weighted $R_2 = [\sum w(\Delta F)^2 / \sum w F_o^2]^{1/2}$ was also 0.042, and the standard deviation of an observation of unit weight was 1.12. A difference Fourier map showed no peak greater than $0.21 \text{ e}^-/\text{\AA}^3$.⁹ The final atomic

(9) A table of observed structure factors, their e.s.d.'s and final differences is presented in the appendix following this paper.

parameters are given in Table 1 with their standard deviations as calculated by the least-squares program.

Results and Discussion

The compound consists of discrete cations and anions. A listing of the bond distances in both ions is given in Table 2.

Triphenylmethylphosphonium (TPMP) Ion.—The cation exhibits a pseudo-threefold axis of symmetry along the P-C(3) bond, the phenyl groups being tilted so as to form a propeller (Figure 1). The environment of the phosphorus is nearly regular tetrahedral, with C-P-C bond angles from 108.9° to 109.9° . The P-C(3) bond distance is shorter by three standard deviations than the average of the other three P-C bonds ($1.779(5) \text{ \AA}$ vs. $1.794(3) \text{ \AA}$), a difference that is barely significant. The hydrogens on the methyl group are staggered with respect to the carbons on the phosphorus as expected.

TABLE I

Coordinates and Thermal Parameters^{a, b}

(a) In this and the following table the standard deviation of the least significant digit is given in parentheses.

(b) The form of the temperature factor (B's in Å²) is:

$$T = \exp(-0.25B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)$$

for the anisotropic atoms and $T = \exp(-B \sin^2\theta/\lambda^2)$ for the isotropic atoms.

(Table to be reproduced photographically.)

TABLE I.

ATOM	X	Y	Z	811	822	833	812	813	823
MN	.30036(5)	.44937(5)	.17205(5)	4.35(3)	4.51(3)	3.97(3)	.73(2)	1.06(2)	.68(2)
B(1)	.3772(5)	.3197(5)	.2897(5)	5.8(3)	9.1(4)	5.8(3)	2.7(3)	2.2(2)	3.8(3)
B(2)	.3231(5)	.2421(4)	.0886(5)	5.5(2)	4.7(2)	5.2(2)	1.2(2)	.5(2)	.2(2)
B(3)	.4255(5)	.2026(6)	.2001(6)	6.7(3)	6.4(3)	8.2(3)	2.4(2)	1.5(3)	2.9(3)
B(4)	.5329(5)	.3362(5)	.2857(5)	5.0(2)	9.1(3)	5.0(2)	2.1(2)	.3(2)	2.4(2)
B(5)	.4865(5)	.2671(5)	.1072(5)	5.9(3)	7.9(3)	5.3(3)	3.0(2)	1.4(2)	1.3(2)
B(6)	.5015(4)	.4497(5)	.1832(4)	4.4(2)	6.5(3)	5.2(2)	.6(2)	1.4(2)	1.8(2)
C(1)	.4608(4)	.4503(4)	.3048(4)	4.7(2)	6.9(2)	3.8(2)	.7(2)	.5(2)	.7(2)
C(2)	.3959(4)	.3546(4)	.0604(4)	5.5(2)	6.7(2)	3.8(2)	2.2(2)	1.4(2)	1.4(2)
O(1)	.0498(3)	.3310(2)	.1695(3)	4.8(1)	5.4(1)	9.0(2)	.3(1)	2.3(1)	.6(1)
C(4)	.1486(4)	.3785(3)	.1695(3)	5.0(2)	4.0(2)	5.1(2)	1.0(2)	1.1(2)	.1(1)
O(2)	.2914(3)	.6865(3)	.3520(3)	6.5(2)	5.7(2)	8.8(2)	-.1(1)	3.4(1)	-1.2(1)
C(5)	.2952(3)	.5924(4)	.2812(4)	4.5(2)	5.4(2)	5.5(2)	-.2(2)	2.0(2)	.5(2)
O(3)	.1931(4)	.5405(3)	-.0393(3)	13.1(3)	10.5(2)	7.3(2)	6.1(2)	3.1(2)	4.5(2)
C(6)	.2350(4)	.5039(4)	.0435(4)	7.6(3)	5.9(2)	5.1(2)	2.6(2)	1.8(2)	1.4(2)
P	-.13721(8)	.08644(8)	-.29728(8)	3.71(4)	4.19(4)	3.67(4)	.76(3)	.96(3)	.69(3)
C(3)	-.2172(5)	.1414(5)	.1748(5)	5.0(2)	6.5(3)	4.8(2)	2.1(2)	1.3(2)	1.4(2)
C(7)	-.0363(3)	.2194(3)	.4275(3)	4.0(2)	3.7(2)	3.7(2)	.7(1)	1.5(1)	1.1(1)
C(8)	.0931(3)	.2334(4)	.4674(4)	4.4(2)	4.5(2)	4.4(2)	.7(2)	1.1(2)	.6(2)
C(9)	.1670(4)	.3359(4)	.5687(4)	4.4(2)	5.6(2)	5.3(2)	-.3(2)	.8(2)	1.0(2)
C(10)	.1128(5)	.4242(4)	.6300(4)	6.9(3)	4.3(2)	4.4(2)	-1.0(2)	1.4(2)	.6(2)
C(11)	-.0143(5)	.4125(4)	.5916(4)	7.0(3)	3.8(2)	5.0(2)	.9(2)	2.8(2)	.5(2)
C(12)	-.0894(4)	.3103(3)	.4898(4)	4.3(2)	4.7(2)	5.1(2)	.5(2)	2.0(2)	1.3(2)
C(13)	-.0441(3)	-.0176(3)	.2357(3)	3.8(2)	3.9(2)	3.0(1)	.4(1)	.7(1)	.6(1)
C(14)	-.0566(4)	-.1386(4)	.2413(3)	4.7(2)	4.7(2)	3.8(2)	.6(2)	1.3(2)	1.3(2)
C(15)	.0159(4)	-.2164(4)	.1922(4)	6.8(3)	4.0(2)	4.9(2)	1.4(2)	1.1(2)	1.2(2)
C(16)	.1016(4)	-.1727(4)	.1386(4)	6.7(2)	5.3(2)	4.8(2)	2.6(2)	1.8(2)	.8(2)
C(17)	.1149(4)	-.0529(4)	.1326(4)	5.4(2)	5.7(2)	5.1(2)	1.6(2)	2.7(2)	1.2(2)
C(18)	.0423(4)	.0251(4)	.1805(3)	5.6(2)	3.7(2)	4.4(2)	1.1(2)	1.7(2)	1.1(2)
C(19)	-.2502(3)	.0038(3)	.3499(3)	3.5(2)	4.1(2)	3.9(2)	.4(1)	.5(1)	.3(1)
C(20)	-.2393(4)	.0277(4)	.4776(4)	3.6(2)	4.6(2)	4.4(2)	.2(2)	.7(2)	.7(2)
C(21)	-.3266(4)	-.0390(4)	.5151(5)	4.6(2)	5.8(2)	5.4(2)	.5(2)	2.1(2)	1.6(2)
C(22)	-.4259(4)	-.1280(4)	.4268(5)	4.9(2)	6.5(2)	7.4(3)	.2(2)	2.9(2)	2.1(2)
C(23)	-.4392(4)	-.1538(4)	.3000(5)	4.6(2)	6.8(3)	7.1(3)	-1.5(2)	1.5(2)	-.0(2)
C(24)	-.3521(4)	-.0873(4)	.2611(5)	5.2(2)	7.0(3)	4.8(2)	-.2(2)	1.5(2)	.3(2)
H(1)	.338(3)	.309(3)	.356(4)	7.0(10)					
H(2)	.237(3)	.172(3)	.024(3)	6.2(8)					
H(3)	.427(3)	.111(4)	.203(4)	7.3(10)					
H(4)	.625(3)	.349(3)	.359(4)	7.4(9)					
H(5)	.538(3)	.225(3)	.047(4)	7.7(10)					
H(6)	.576(3)	.520(3)	.183(3)	5.7(8)					
H(7)	.498(3)	.516(3)	.380(3)	5.4(9)					
H(8)	.387(3)	.364(3)	-.016(4)	6.6(11)					
H(9)	-.167(4)	.188(4)	.141(4)	7.3(12)					
H(10)	-.263(3)	.189(3)	.205(3)	5.5(10)					
H(11)	-.276(3)	.084(3)	.116(3)	4.5(10)					
H(12)	.129(3)	.172(3)	.426(3)	3.9(8)					
H(13)	.254(4)	.344(3)	.596(4)	6.9(11)					
H(14)	.164(3)	.489(3)	.694(4)	5.9(10)					
H(15)	-.054(3)	.468(3)	.622(3)	4.5(9)					
H(16)	-.169(3)	.303(2)	.466(2)	2.1(7)					
H(17)	-.111(3)	-.165(2)	.274(3)	2.4(7)					
H(18)	.002(3)	-.294(3)	.191(3)	5.0(9)					
H(19)	.149(3)	-.224(3)	.109(3)	5.1(9)					
H(20)	.176(3)	-.024(3)	.097(3)	4.4(8)					
H(21)	.046(3)	.100(3)	.170(3)	3.1(7)					
H(22)	-.174(3)	.084(3)	.537(3)	2.8(7)					
H(23)	-.319(3)	-.024(3)	.597(4)	5.9(10)					
H(24)	-.483(3)	-.175(3)	.456(3)	5.8(9)					
H(25)	-.506(4)	-.210(4)	.236(4)	7.4(11)					
H(26)	-.358(3)	-.096(3)	.183(3)	4.8(9)					

TABLE II
Bond Distances (Å)

Anion		Cation	
Atoms	Distance	Atoms	Distance
Mn - C(1)	2.043(4)	P - C(3)	1.779(5)
Mn - C(2)	2.047(4)	P - C(7)	1.796(3)
Mn - B(1)	2.356(5)	P - C(13)	1.797(3)
Mn - B(2)	2.349(5)	P - C(19)	1.788(3)
Mn - B(6)	2.227(5)	C(7) - C(8)	1.380(5)
Mn - C(4)	1.765(4)	C(8) - C(9)	1.376(5)
Mn - C(5)	1.771(4)	C(9) - C(10)	1.364(6)
Mn - C(6)	1.780(5)	C(10) - C(11)	1.358(6)
C(1) - B(1)	1.573(7)	C(11) - C(12)	1.381(5)
C(1) - B(4)	1.607(6)	C(12) - C(7)	1.379(5)
C(1) - B(6)	1.571(6)	C(13) - C(14)	1.373(5)
C(2) - B(2)	1.565(6)	C(14) - C(15)	1.381(5)
C(2) - B(5)	1.609(6)	C(15) - C(16)	1.368(6)
C(2) - B(6)	1.589(6)	C(16) - C(17)	1.362(5)
B(1) - B(2)	2.122(7)	C(17) - C(18)	1.378(5)
B(1) - B(3)	1.683(8)	C(18) - C(13)	1.383(5)
B(1) - B(4)	1.743(7)	C(19) - C(20)	1.385(5)
B(2) - B(3)	1.695(7)	C(20) - C(21)	1.376(5)
B(2) - B(5)	1.764(7)	C(21) - C(22)	1.358(6)
B(3) - B(4)	1.668(8)	C(22) - C(23)	1.367(6)
B(3) - B(5)	1.667(8)	C(23) - C(24)	1.382(6)
B(4) - B(5)	1.885(7)	C(24) - C(19)	1.385(5)
B(4) - B(6)	1.971(7)	H(9) - C(3)	0.94(4)
B(5) - B(6)	1.971(7)	H(10) - C(3)	0.86(4)
C(4) - O(1)	1.162(4)	H(11) - C(3)	0.83(3)
C(5) - O(2)	1.161(4)	H(12) - C(8)	0.92(3)
C(6) - O(3)	1.157(4)	H(13) - C(9)	0.93(4)
H(1) - B(1)	1.00(4)	H(14) - C(10)	0.89(4)
H(2) - B(2)	1.10(4)	H(15) - C(11)	0.87(3)
H(3) - B(3)	1.05(4)	H(16) - C(12)	0.85(3)
H(4) - B(4)	1.12(4)	H(17) - C(14)	0.85(3)

TABLE II. (continued)

Anion		Cation	
Atoms	Distance	Atoms	Distance
H(5) - B(5)	1.07(4)	H(18) - C(15)	0.86(3)
H(6) - B(6)	1.06(3)	H(19) - C(16)	0.85(3)
H(7) - C(1)	0.92(3)	H(20) - C(17)	0.94(3)
H(8) - C(2)	0.90(4)	H(21) - C(18)	0.88(3)
		H(22) - C(20)	0.88(3)
		H(23) - C(21)	0.89(4)
		H(24) - C(22)	0.96(4)
		H(25) - C(23)	0.92(4)
		H(26) - C(24)	0.86(3)

The phenyl groups are very closely planar, with each atom less than one standard deviation from the mean plane. Two of the phenyls have the P-C bond bent slightly but significantly out of the plane, with P out of the plane by 0.025 Å.

All C-H distances are normal for X-ray crystallographic studies (average C-H = 0.89 Å uncorrected for thermal motion). The average C-C bond length in the phenyl groups is 1.374(2) Å, also uncorrected for thermal motion. There is a measurable discrepancy between the length of the bonds from the meta- to the para-carbons (e.g. C(9)-C(10), Figure 1) which average to 1.363 Å (range: 1.358—1.368 Å) and the other carbon-carbon bonds which average to 1.380 Å (range: 1.373—1.385 Å). The C—C—C angles also show a variation dependent on position, the angle adjacent to the phosphorus being reduced by about 1.5° with respect to the other angles. (Average for adjacent angles is 118.8°, range 118.4° to 119°; average for all other angles 120.2°, range 119.8° to 120.6°.)

The results from this study are consistent with the results of Fritchie¹⁰ on another TPMP salt. The average

(10) C. J. Fritchie, Jr., Acta Crystallogr., 20, 107 (1966).

values of chemically equivalent bonds are within the sum of their standard deviations of each other, but Fritchie's study is not precise enough to confirm or deny the small differences noted above. The primary difference between the TPMP ions in

the two studies is that in this study the ion assumes the expected propeller configuration, whereas in Fritchie's study packing forces distort it considerably.

The $(B_6C_2H_8)Mn(CO)_3$ Anion.—This work confirms the structure proposed for both the $B_6C_2H_8^{2-}$ ligand and for the entire anion.^{2,3} The anion possesses an almost exact non-crystallographic mirror plane running through the Mn, B(3) and B(6) (Figure 2). Variations from mirror symmetry for the carborane cage atoms, including hydrogens, are all less than twice the standard deviations of their positions. The carbons of the carbonyl groups also conform well to the mirror symmetry, but the oxygen atoms deviate from this symmetry by as much as five standard deviations. In addition, the carbonyl groups are very closely radial about the manganese. These observations confirm Hawthorne's spectroscopic conclusions,³ and the slight deviations of the oxygens can undoubtedly be attributed to crystal packing forces.

The manganese-carborane cage can be described as a tricapped trigonal prism, where C(1), C(2) and B(3) are the capping atoms. The prism can be seen in Figure 2, with B(1), B(2) and Mn defining one triangular face and B(4), B(5) and B(6) the other. The most nearly analogous carborane structure we have found is the $B_7H_7C_2(CH_3)_2$ molecule¹¹ in

(11) T. F. Koetzle, F. E. Scarbrough, and W. N. Lipscomb, Inorg. Chem., 7, 1076 (1968).

which a boron atom takes the place of manganese, and the variation of bond distances is very similar in these two substances. The B(1)—B(2) distance of 2.122 Å is longer than any B—B bond distance we are able to cite, but the average with B(4)—B(5) = 1.885 Å is 2.00 Å, which is close to the average 1.98 Å for the bonds in Koetzle's molecule¹¹ which correspond to these triangle edges. The other triangle edges, B(4)—B(6) and B(5)—B(6), are 1.97 Å and can be compared with an average of 1.96 Å for the other molecule. The prism edges B(1)—B(4) and B(2)—B(5) average 1.75 Å in our structure, 1.77 Å in the other one. The four B—B bonds to the capping atom B(3) average 1.68 Å, compared to 1.70 Å. The average of all the B—B bond distances in our structure (1.82 Å) is similar to values found in more symmetrical carboranes, for example 1.78 Å in a typical icosahedral carborane¹². The average B—C

(12) D. St. Clair, A. Zalkin, and D. H. Templeton, J. Amer. Chem. Soc., 92, 1173 (1970).

distance, 1.59 Å, is close to the average 1.60 Å found by Koetzle, Scarbrough, and Lipscomb.¹¹ In the anion $\text{Co}(\text{B}_7\text{C}_2\text{H}_9)_2^-$, an analogous carbon atom is bonded to three boron atoms and to cobalt; the average B—C bond length is also 1.60 Å.¹³

(13) D. St. Clair, A. Zalkin, and D. H. Templeton, Inorg. Chem., 11, 377 (1972).

Packing.—The packing of the cations and the anions can be seen in Figure 4. In a crude approximation it may be described as CsCl-type packing, but this approximation would be more accurate if the b axis were shorter and a and c were longer. The cations pack in rows on the c axis with the phenyl groups of one cation interleaving with the phenyl groups of another related by a center of symmetry at $0,0,1/2$. There is relatively close approach of parallel phenyl groups across the center of symmetry at $1/2,0,1/2$, and a very close one across the center of symmetry at $0,1/2,1/2$, with a distance C(11)—C(11) of only 3.29 Å (not shown in Figure 4). Other close inter-molecular contacts are: O(1)—C(3) (methyl carbon) 3.45 Å, O(2)—C(12) 3.24 Å, and O(2)—C(22) 3.31 Å. As can be seen from Figure 4, the carbonyl ends of two anions are opposed across the center of symmetry at $0,1/2,0$ and the carborane ends of anions are opposed across the centers at $1/2,0,0$, $1/2,1/2,0$ and $1/2,1/2,1/2$. None of these oppositions forces close contact between atoms of the two anions.

We thank Professor Hawthorne and Dr. Pitts for the crystals used in this research.

Figure Captions

Figure 1. Conformation and labeling of the cation.

Perspective view roughly down the pseudo-threefold axis.

Thermal ellipsoids have been scaled to enclose 50% probability. Hydrogen atoms have been given an artificial isotropic thermal parameter of 2.0 \AA^2 .

Figure 2. Conformation and labeling of the anion.

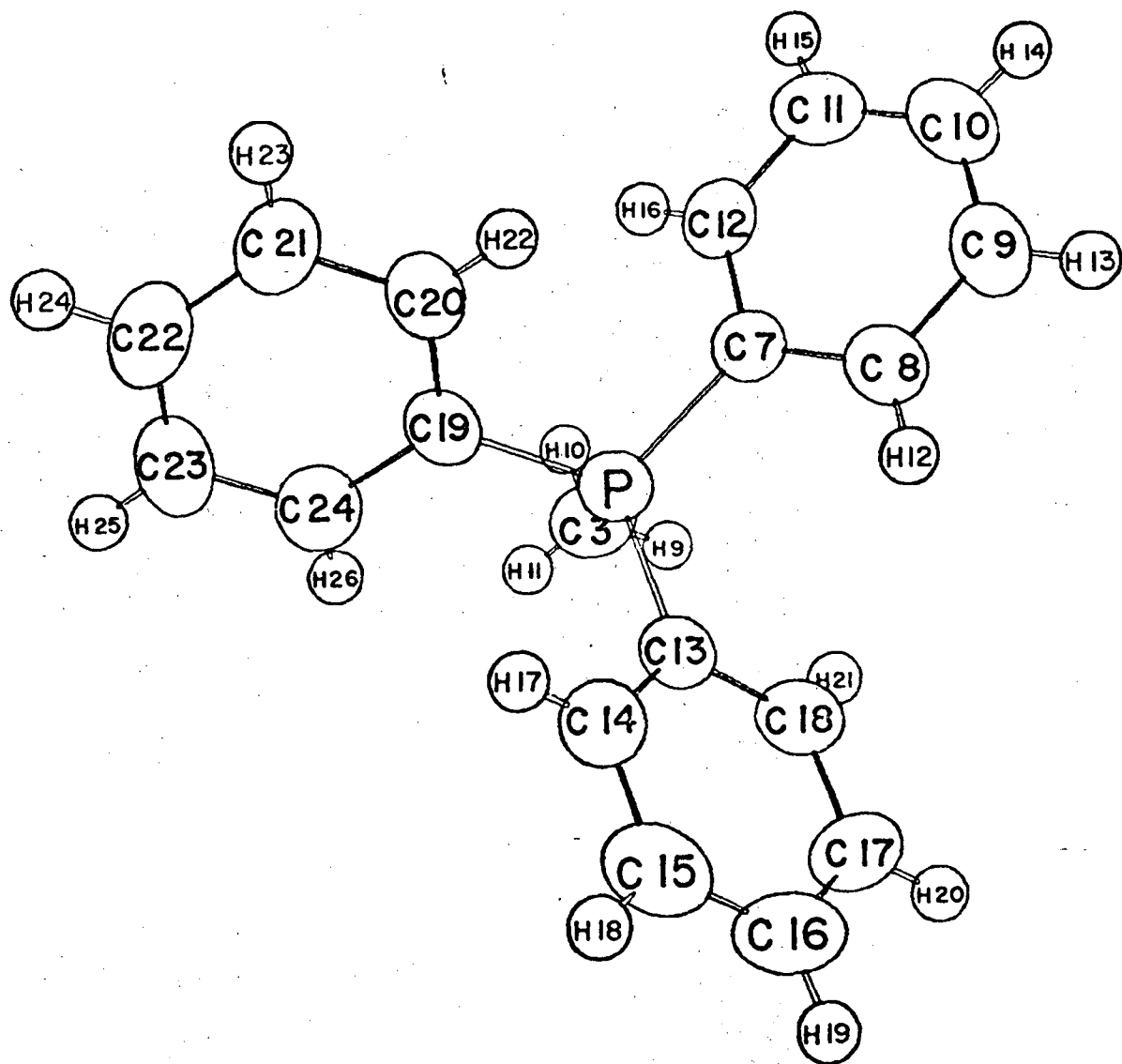
Perspective view parallel to the non-crystallographic mirror plane.

Figure 3. Stereoscopic view of the anion. The view

direction is approximately perpendicular to the non-crystallographic mirror plane. Temperature ellipsoids have been scaled to enclose 20% probability. Hydrogens have been given artificial thermal parameters of 2.0 \AA^2 .

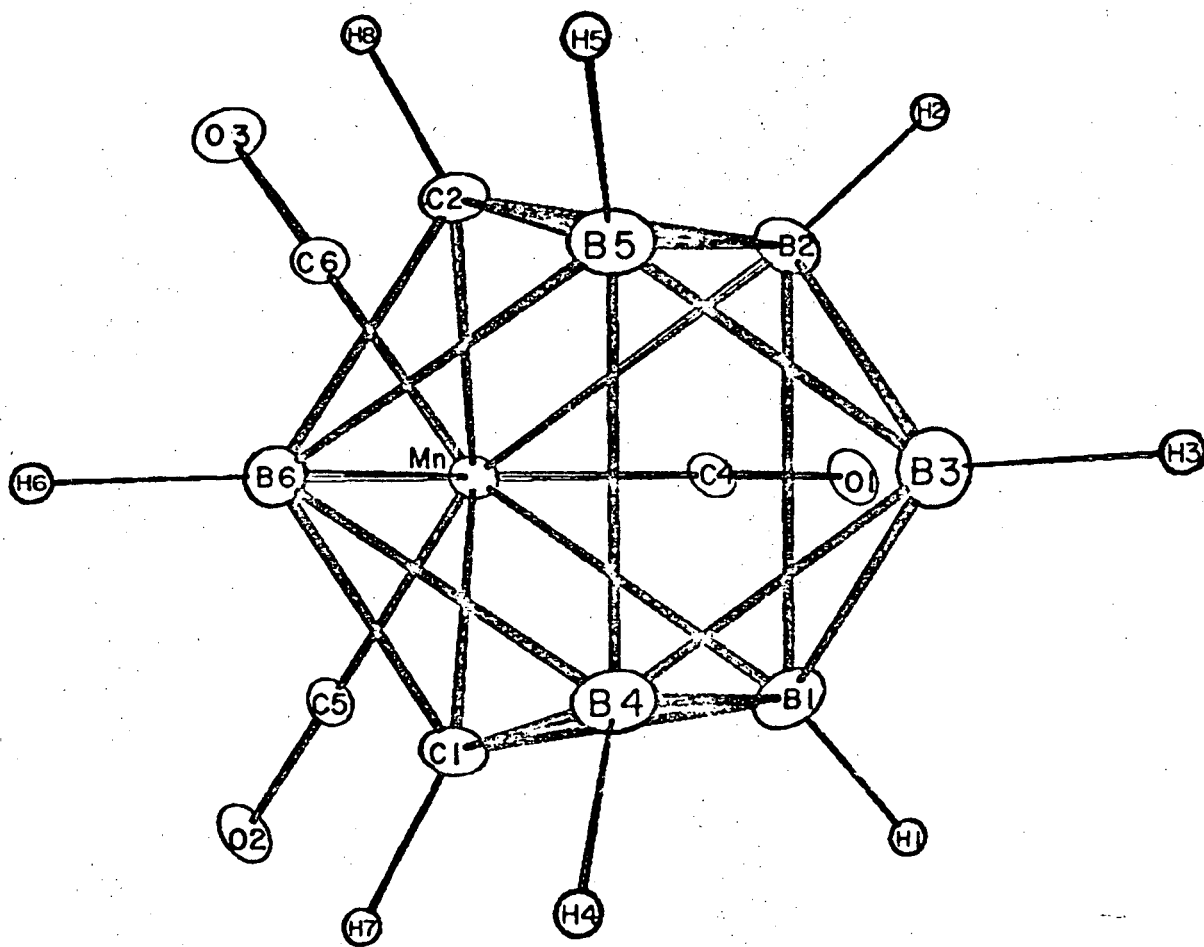
Figure 4. Stereoscopic view of the contents of the unit cell.

The methyl carbons and the carbons in the anion are solid black. The phosphorus atoms have been stippled. Labeled axes are positive from the origin. Hydrogen atoms and the cations in the b direction have been omitted for clarity, as have the phenyl groups of the foremost cation.



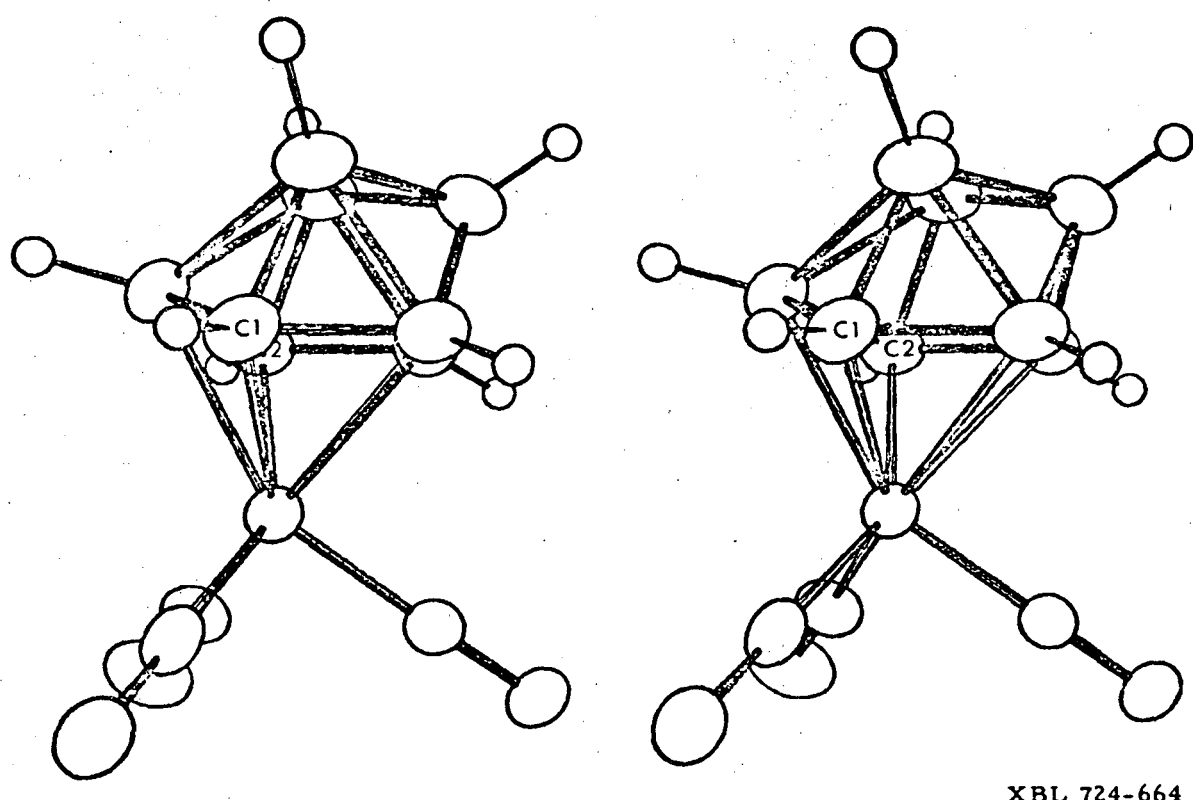
XBL 724-666

Figure 1.



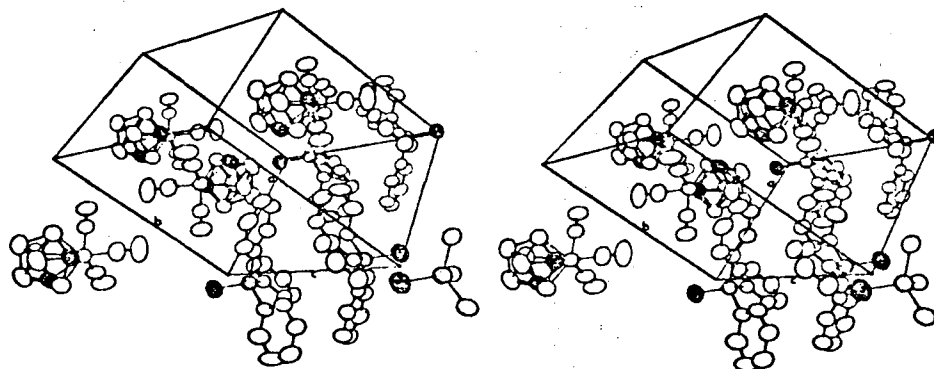
XBL 724-661

Figure 2.



XBL 724-664

Figure 3.



XBL 724-723

Figure 4.

APPENDIX

Observed Structure Factors, Standard Deviations and
Final Differences for $((C_6H_5)_3PCH_3)^+$ $((B_6C_2H_8)Mn(CO)_3)^-$.

All values multiplied by 10.0. An asterisk indicates
that the reflection was given zero weight in least squares.

OBSERVED STRUCTURE FACTORS, STANDARD DEVIATIONS, AND DIFFERENCES (210.03 FOR 242200-HM (C01) (C415)P-03) FIG. 0.01 - 5280
SC - ESTIMATED STANDARD DEVIATION OF FOM. DEL - /FOM/-/FCAL/. * INDICATES ZERO WEIGHTED DATA.

Table with 16 columns: H FOM SG DEL, H FOM SG DEL, H FOM SG DEL, H FOM SG DEL, H FOM SG DEL, H FOM SG DEL, H FOM SG DEL, H FOM SG DEL, H FOM SG DEL, H FOM SG DEL, H FOM SG DEL, H FOM SG DEL, H FOM SG DEL, H FOM SG DEL, H FOM SG DEL, H FOM SG DEL. The table contains a dense grid of numerical data points representing structure factors and differences.

UNOBSERVED STRUCTURE FACTORS FOR OAC280-MN-1(CO)3 (CONTINUED)
PAGE 2

Table with multiple columns of numerical data representing structure factors. The columns are organized into groups, each with a header like 'H F0B SG DEL'. The data consists of rows of numbers, some with signs, representing the observed structure factors for various reflections.

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720