mains as to whether or not the cage is opened in the intermediate $B_{10}C_2H_{12}^{2-}$ ion and its derivatives.

In the $PhCHB_{10}H_{10}CPh^-$ ion C(13) bridges in a way known previously for some nitrogen derivatives of boranes.[34] This result suggests that monocarbon carboranes may exist with either a bridging carbon atom or a skeletal type carbon atom. At least one of these two types of structures is known in the $B_{10}H_{12}CH^-$ ion.[35]

Acknowledgment. We thank the Office of Naval Research and the National Institutes of Health for support of this research and D. S. Kendall for helpful suggestions.

Registry No. $(Me_4N)^+(PhCHB_{10}H_{10}CPh)^-$, 39322-84-4.

Supplementary Marterial Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-2257.

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[34] W. N. Lipscomb and R. Lewin, *Advan. Chem. Ser.*, No. 42, 312 (1964).

[35] D. Hyatt, F. R. Scholer, L. J. Todd, and J. L. Warner, *Inorg. Chem.*, 6, 2229 (1967).

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Crystal and Molecular Structure of Triphenylmethylphosphonium 1,1,1-Tricarbonyl-4,6-dicarba-1-mangana-*closo*-nonaborate(1−)[1]

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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) Å, $b = 11.285$ (4) Å, $c = 11.464$ (5) Å, $\alpha = 105.79$ (1)°, $\beta = 104.46$ (1)°, $\gamma = 98.04$ (1)°, $d_o = 1.25$ g/cm³, and $d_c = 1.29$ g/cm³ for $Z = 2$. X-Ray diffraction intensities were collected by stationary-crystal, stationary-counter technique using Mo Kα 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 Å) and three boron atoms (two at 2.35 Å and one at 2.23 Å) of the eight-atom carborane cage. The anion has almost exact mirror symmetry, and the manganese–carborane cage can be described as a tricapped trigonal prism with one boron and two carbon atoms as the capping atoms.

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] 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-dicarba-1-mangana-*closo*-nonaborate(1−).[4]

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 × 0.14 mm × 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 $\chi = 90°$ 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 ($\lambda(K\alpha_1)$ 0.709261 Å, $\lambda(K\alpha_2)$ 0.713543 Å, $\lambda(K\beta)$ 0.632253 Å), and a least-squares analysis yielded accurate cell dimensions and the crystal orientation matrix. The derived cell dimensions (and standard deviations) are $a = 11.216$ (5) Å, $b = 11.285$ (4) Å, $c = 11.464$ (5) Å, $\alpha = 105.79$ (1)°, $\beta = 104.46$ (1)°, and $\gamma = 98.04$ (1)°. The density measured by flotation in a mixture of n-hexane and carbon tetrachloride was 1.25 g/cm³ compared to 1.29 g/cm³ calculated for two formula units in a unit cell volume of 1318 Å³. 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 Mo Kα radiation (0.003 in. of 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 $\chi = 0$–$90°$, $\phi = 0$–$360°$ from $2\theta = 0°$ to $2\theta = 45°$ ($(\sin\theta)/\lambda = 0.5385$) 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 (±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 $\chi = 90°$ showed no significant variation, the values of μ and μR are 5.9 cm^{-1} and 0.11, and the transmission factors are estimated to vary by less than 5%; no absorption correction was made to the intensities. The intensities were corrected for Lorentz and polarization factors.

Atomic scattering factors of Cromer and Waber[5] for the nonhydrogen atoms and those of Stewart, Davidson, and Simpson[6] for spherical hydrogen atoms were used. Real and imaginary dispersion corrections of Cromer[7] were used for manganese and phosphorus.

The function minimized by least-squares was $\Sigma w(\Delta F)^2/\Sigma wF_o^2$. 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 described[8] with the ignorance factor $p = 0.04$. The programs used in this study are listed in the same paper.[8]

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[1] Work done under the auspices of the U. S. Atomic Energy Commission.

[2] M. F. Hawthorne and A. D. Pitts, *J. Amer. Chem. Soc.*, 89, 7115 (1967).

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

[4] Named according to Figure 14, *Inorg. Chem.*, 7, 1945 (1968).

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

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

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

[8] F. J. Hollander, D. H. Templeton, and A. Zalkin, *Acta Crystallogr., Sect. B*, 29, 1289 (1973).

Table I. Coordinates and Thermal Parameters[a, b]

ATOM	X	Y	Z	B11	B22	B33	B12	B13	B23
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)					

[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 Å^2) is $T = \exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$ for the anisotropic atoms and $T = \exp[-B(\sin^2\theta)/\lambda^2]$ for the isotropic atoms.

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 nonhydrogen 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 ($R_1 = \Sigma|\Delta F|/\Sigma|F_o|$) to 0.12. The average thermal parameter for those atoms labeled "carbon" was 3.86 Å^2 compared to the average for the boron atoms of 6.43 Å^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 nonhydrogen 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 nonhydrogen 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 $R_2 = [\Sigma w(\Delta F)^2/\Sigma wF_o^2]^{1/2}$ 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 e/Å^3.[9] The final atomic parameters are given in Table I 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 II.

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

(9) See paragraph at end of paper regarding supplementary material.

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)
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)

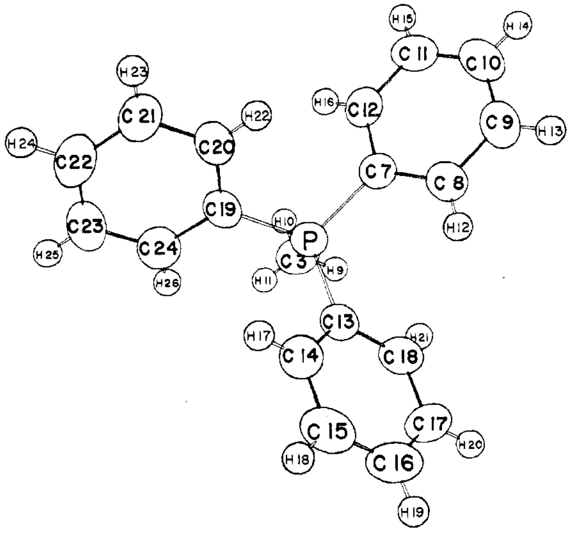

Figure 1. Conformation and labeling of the cation. Perspective view roughly down the pseudo-threefold axis. Thermal ellipsoids have been scaled to enclose 50% probability. Hydrogen atoms have been given an artificial isotropic thermal parameter of 2.0 Å^2.

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) *vs.* 1.794 (3) Å), a difference that is barely significant. The hydrogens on the methyl group are staggered with respect to the carbons on the phosphorus as expected.

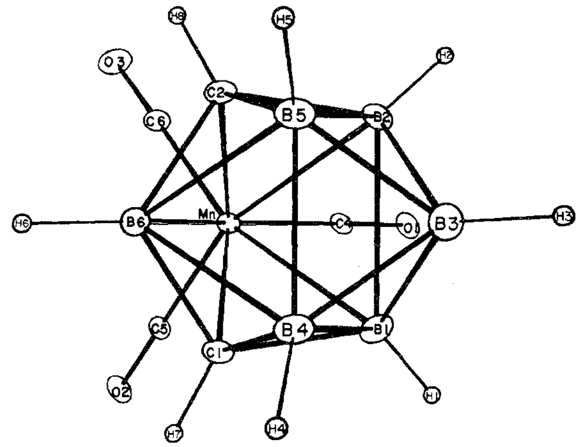

Figure 2. Conformation and labeling of the anion. Perspective view parallel to the noncrystallographic mirror plane.

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 an X-ray study of a crystal with significant thermal motion (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 118.4-119°; average for all other angles 120.2°, range 119.8-120.6°).

The results from this study are consistent with the results of Fritchie[10] on another TPMP salt. The average 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 noncrystallographic mirror plane running through Mn, B(3), and B(6) (Figures 2 and 3). 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

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

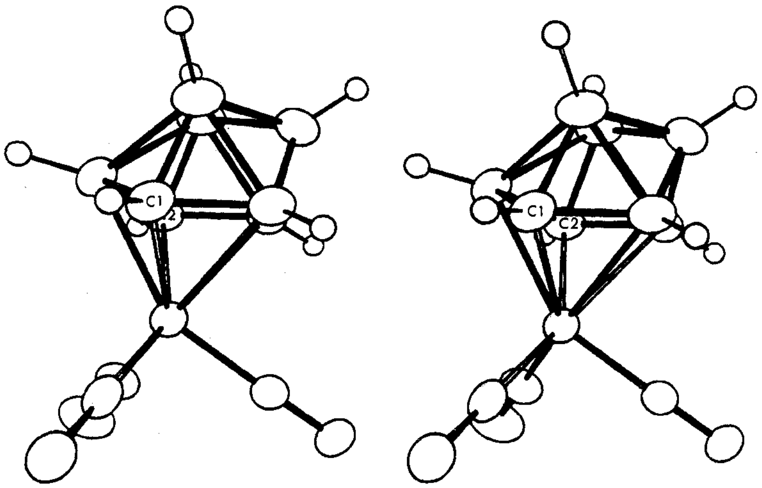

Figure 3. Stereoscopic view of the anion. The view direction is approximately perpendicular to the noncrystallographic mirror plane. Temperature ellipsoids have been scaled to enclose 20% probability. Hydrogens have been given artificial thermal parameters of 2.0 Å^2.

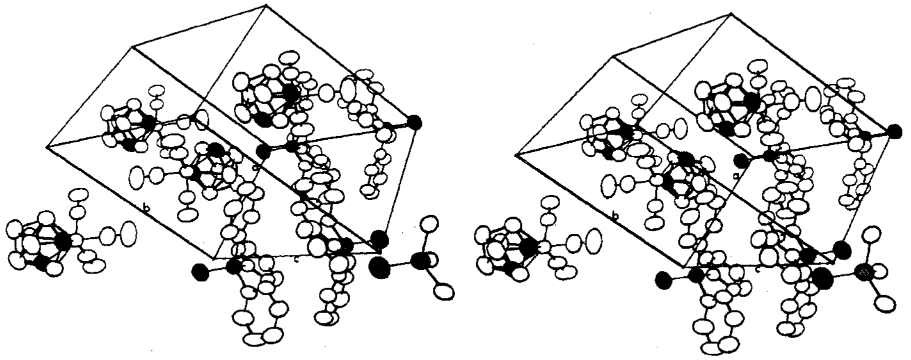

Figure 4. Stereoscopic view of the contents of the unit cell. The methyl carbons and the carbons in the anion are solid black. The phosphorus atoms have been stippled. Labeled axes are positive from the origin. Hydrogen atoms and the cations in the *b* direction have been omitted for clarity, as have the phenyl groups of the foremost cation.

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 $B_7H_7C_2(CH_3)_2$ molecule[11] in 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 molecule[11] 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 and 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 carborane.[12] The average B-C distance, 1.59 Å, is close to the average 1.60 Å found by Koetzle, Scarbrough, and Lipscomb.[11] In the anion $Co(B_7C_2H_9)_2^-$, 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]

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 intermolecular contacts are as follows: O(1)-C(3) (methyl carbon), 3.45 Å; O(2)-C(12), 3.24 Å; 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.

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Registry No. $[(C_6H_5)_3PCH_3]^+[(B_6C_2H_8)Mn(CO)_3]^-$, 41267-49-6.

Supplementary Material Available. A listing of observed structure factors, standard deviations, and final differences for $[(C_6H_5)_3PCH_3]^+[(B_6C_2H_8)Mn(CO)_3]^-$ will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from

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

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

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

the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-2262.

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Crystal and Molecular Structure of Dicarbacyclopentaboranyliron Tricarbonyl

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The crystal and molecular structure of $B_3C_2H_7Fe(CO)_3$ has been determined by low-temperature, single-crystal X-ray techniques. The crystals are monoclinic, space group $P2_1/m$, with $a = 6.327$ (3) Å, $b = 10.279$ (6) Å, $c = 6.607$ (3) Å, and $\beta = 99.64$ (4)°. The calculated density is 1.60 g/cm^3 for $Z = 2$. The structure was refined using full-matrix least-squares techniques using 1012 observed relfections to a conventional R value of 0.024. The dicarbacyclopentaboranyl(2−) ring is planar and the molecule possesses a mirror plane.

Introduction

The metallocarborane $B_3C_2H_7Fe(CO)_3$, a pale yellow liquid, was originally prepared[2] in the gas-phase thermal reaction of dicarba-*nido*-hexaborane(8), $B_4C_2H_8$, with iron pentacarbonyl, and was later obtained[3] in the reaction of dicarba-*nido*-pentaborane(7), $B_3C_2H_7$, with iron pentacarbonyl under ultraviolet light. From nmr and infrared data and bonding considerations, this species was assigned[2] a novel structure containing a planar B_3C_2 ring symmetrically π bonded to the iron atom, with two B-H-B bridges directed away from the metal. This structure, which may be regarded as an analog of the isoelectric metallocene cation $(\pi\text{-}C_5H_5)Fe(CO)_3{}^+$, has been confirmed in a single-crystal X-ray diffraction study which we now report.

Experimental Section

A sample[2] of $B_3C_2H_7Fe(CO)_3$ was transferred into a Pyrex capillary (0.55-mm diameter) using standard high-vacuum techniques. A crystal was then grown from the liquid (estimated melting point was +15 to 0°) in a nitrogen vapor cold stream,[4] mounted directly on a Picker FACS 1 diffractometer.

The crystal thus obtained was about 1 mm long and 0.55 mm in diameter and grew with the $\langle\bar{3}04\rangle$ reciprocal lattice vector coincident with the goniostat ϕ axis. A standard orientation procedure[5] determined a monoclinic unit cell with systematic extinctions only in the $\langle 0k0\rangle$ zone for odd reflections. Possible space groups are thus $P2_1/m$ (C_{2h}^2) and $P2_1$ (C_2^2).

Statistical tests for space group distinction proved ambiguous, so both space groups were used concurrently, and ultimately each produced the same R factor. The space group $P2_1/m$ was judged to provide a better model, using the magnitudes of the uncertainties of the bonded distances and angles as the criterion.

Alignment and data collection were accomplished using a Picker FACS I diffractometer, equipped with a highly oriented graphite monochromator ($\langle 002\rangle$ reflection) at a 2° takeoff angle and Mo Kα radiation.

The cell constants were determined by a least-squares fit of 12 centered reflections to be[6] $a = 6.327$ (3) Å, $b = 10.279$ (6) Å, $c = 6.607$ (3) Å, and $\beta = 99.64$ (4)°, at about −160°.

Owing to the low melting point and air sensitivity of this material, no attempt was made to measure the density of the crystal; however, the calculated density of 1.609 g/cm^3 for $Z = 2$ is a reasonable value for compounds of this type.

The intensity data were collected at a temperature estimated to be −160° using a continuous θ–2θ scan over a range of $2\theta = 2.5°$ plus dispersion correction at 2°/min. Ten-second background counts were taken at the limits of each scan. Reflections with a count rate of greater than 10,000 cps were retaken with an aluminum filter. The filter factor, q, was 10.79 and the σ of the filter was 0.4.

Counting statistics ($\sigma(x) = x^{1/2}$) were assumed valid. By standard propagation of errors

$$\sigma(I) = (Lp)q[p^2C^2 + N + k^2(B_1 + B_2)]^{1/2}$$

where p is a correction term to allow for nonrandom counting errors, $C = N - k(B_1 + B_2)$, k is a factor to scale each of the background counts to half the scan time, B_1 and B_2 are background counts, N is the total scan count, and q is the filter factor ($q = 1$, for unfiltered data).

There were 3222 reflections collected of which 392 were standards. At 98% probability of being significant ($I \geqslant 2.33\sigma(I)$), 1012 of the 1309 unique intensities were considered observed. The intensities of three reflections were monitored after each interval of 25 data collected. The average standard deviation of each was less than 5% with no significant trends.

Lorentz and polarization corrections were applied in the usual way. The linear absorption coefficient is 72 cm^{-1}, indicating absorption correction factors varying from 11 to 14, assuming a cylindrical sample approximation.[7] However no correction was made on the data because of the uncertainty about the thickness of the wall of the glass capillary and its absorption.

The form factors used were those of Cromer and Mann[8] for the neutral iron, oxygen, carbon, boron, and hydrogen atoms with appropriate[9] anomalous dispersion corrections for iron.

Solution and Refinement of Structure

Analysis of a standard Patterson map showed a unique peak in the Harker plane at $y = 0.25$ corresponding to the iron atom. The corresponding peak at $2x$, $2y$, $2z$ placed the iron atoms on the mirror plane in special position 2e at 0.39, 0.25, 0.35. Least-squares refinement[10] based on iron alone produced a value of the conventional R index of 0.355 where $R = \Sigma(|F_o| - |F_c{}^*|)/\Sigma|F_o|$. A difference Fourier map phased on the iron position showed seven peaks corresponding to the remaining heavy atoms in the molecule. Least-squares refinement of these positions led to a value of $R = 0.053$. A second difference synthesis based on all of the heavy atoms produced four unique peaks which were reasonably assigned as the hydrogen atoms. Refining all parameters, assuming isothermal motion of all atoms except hydrogen, which were fixed at $B = 2.0$ (the average isothermal

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(1) (a) Indiana University. (b) University of Virginia.

(2) R. N. Grimes, *J. Amer. Chem. Soc.*, 93, 261 (1971).

(3) D. A. Franz, V. R. Miller, and R. N. Grimes, *J. Amer. Chem. Soc.*, 94, 412 (1972).

(4) J. C. Huffman, J. N. Mueller, and W. E. Streib, Abstracts, American Crystallographic Society Meeting, Storrs, Conn., June 1973, No. H-6.

(5) J. C. Huffman, submitted for publication in *J. Appl. Chem.*

(6) The numbers in parentheses are the least-squares standard error of the least significant digit.

(7) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1965.

(8) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 24, 321 (1968).

(9) See ref 7, p 215. $\Delta f' = 0.350$ and $\Delta f'' = 0.90$.

(10) See paragraph at end of paper regarding supplementary material.