

an angle of *ca.* 60° to that expected for disordered μ_2 -hydrido bridges. (See Figure 4.)

We should add that the systematic error between X-ray determined H...X distances and true internuclear distances will act in such a way that the true (*internuclear*) separation for H(FAC)-B(8) will be greater than 1.331 (22) Å, and perhaps as great as ~1.43 Å. Other H(FAC)-B and H(FAC)-C distances will not be so drastically affected.

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ing services were provided by the Computer Center of the University of Illinois at Chicago Circle on an IBM 370/158 computer; their assistance is gratefully acknowledged.

Supplementary Material 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, 24× 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 Street, N.W., Washington, D. C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-6310.

A New Type of Metalloborane. Structural and Spectroscopic Characterization of Tricarbonylmanganese Tridecahydrooctaborate, $(\text{CO})_3\text{MnB}_8\text{H}_{13}$

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Abstract: The title compound is the first structurally characterized example of a new type of metalloborane. It contains a tridentate B_8 ligand bound to manganese by two M-H-B bridge hydrogen bonds from borons bordering the open face of the borane cage and one M-H-B bond from an adjacent boron in the base of the borane cage. Crystals of the complex form in the orthorhombic space group *Pmcn* with unit cell parameters $a = 11.549$ (2) Å, $b = 5.506$ (1) Å, $c = 19.260$ (3) Å, $V = 1224.7$ (3) Å³, and $Z = 4$; $d_{\text{calcd}} = 1.294$ and $d_{\text{measd}} = 1.289$ (6) g/cm³. The X-ray crystal structure was solved by conventional heavy atom techniques and refined to $R_1 = 0.033$ and $R_2 = 0.041$ for 928 independent nonzero reflections on a Syntex P1 autodiffractometer. The molecule has crystallographic site symmetry C_s-m . The bond angles about the manganese indicate nearly perfect octahedral coordination.

The reaction of $\text{Mn}(\text{CO})_5\text{Br}$ with KB_9H_{14} in ethereal solvents has produced several metalloboranes in which the $\text{Mn}(\text{CO})_3$ moiety replaces the 6 (or 9) B-H unit in a decaborane-like framework; bonding to the rest of the cage is *via* a σ bond and two bridging hydrogen bonds.¹⁻³ Examples of these metalloboranes include 6-(CO)₃-6- $\text{MnB}_9\text{H}_{12}\text{L}$ (L = 2- OC_4H_8 , 5- OC_4H_8 , 2- $\text{O}(\text{C}_2\text{H}_5)_2$, and 8- $\text{O}(\text{CH}_2)_4\text{N}(\text{C}_2\text{H}_5)_3$) and salts of 6-(CO)₃-6- $\text{MnB}_9\text{H}_{13}^-$. An additional compound, $(\text{CO})_3\text{MnB}_8\text{H}_{13}$, is produced in small yields. It appears to be an elision product, in which the $(\text{CO})_3\text{Mn}$ moiety is bonded to the borane cage in a novel and unprecedented manner. We report here the synthesis, characterization, structure, and bonding of this compound.

Experimental Section

Reagents and Solvents. Potassium tetradecehydroonaborate(-1), KB_9H_{14} , was made by a modification¹ of the method of Benjamin, Stafiej, and Takacs.⁴ Manganese pentacarbonyl bromide

(1) (a) J. W. Lott and D. F. Gaines, *Inorg. Chem.*, in press; (b) J. W. Lott, Ph.D. Thesis, University of Wisconsin, Madison, Wisc., 1973.

(2) J. W. Lott, D. F. Gaines, H. Shenhav, and R. Schaeffer, *J. Amer. Chem. Soc.*, **95**, 3042 (1973).

(3) (a) D. F. Gaines, J. W. Lott, and J. C. Calabrese, *J. Chem. Soc., Chem. Commun.*, 295 (1973); (b) D. F. Gaines, J. W. Lott, and J. C. Calabrese, *Inorg. Chem.*, in press.

was prepared from the parent metal pentacarbonyl dimer, $\text{Mn}_2(\text{CO})_{10}$, and bromine. All other reagents and solvents were reagent grade and were used as received.

Compound Preparation. $(\text{CO})_3\text{MnB}_8\text{H}_{13}$ was prepared according to the method of Lott and Gaines.¹ In a typical reaction a solution of 0.9308 g of KB_9H_{14} (6.2 mmol) and 1.4357 g of $\text{Mn}(\text{CO})_5\text{Br}$ (5.2 mmol) in diethyl ether was refluxed for 3-6 hr. The reaction mixture was then stripped of solvent by evaporation under vacuum. The remaining oily red material was dissolved in a minimum of dichloromethane and placed on a Florisil-packed liquid chromatography column. Elution with heptane gave a bright yellow band, containing the $(\text{CO})_3\text{MnB}_8\text{H}_{13}$. If these yellow solutions were allowed to stand for several hours, definite signs of decomposition were observed. To minimize this decomposition the solution was quickly evaporated under vacuum immediately after its removal from the chromatography column. The solid material was then transferred to the bottom of a long (35-40 cm) Pyrex glass tube having a reasonably wide cross section (25-28 mm diameter) and equipped with a vacuum stopcock. The tube was then enclosed in two halves of a copper tubing heat sink and an outer glass tube for insulation. This assemblage was clamped vertically so that the bottom of the sample tube and several centimeters of the copper jacket were submerged in an oil bath. The tube was then evacuated continuously while the temperature was slowly raised to 45-52° overnight. The desired product was then separated from impurities (generally $\text{Mn}_2(\text{CO})_{10}$ and $\text{Mn}_2(\text{CO})_5\text{Br}_2$) by cutting the tube into sections and checking the golden yellow crystals which had grown on the walls of each section by infrared spectroscopy. Very pure $(\text{CO})_3\text{MnB}_8\text{H}_{13}$ was obtained in this manner. The yield from a

(4) L. E. Benjamin, S. F. Stafiej, and E. A. Takacs, *J. Amer. Chem. Soc.*, **85**, 2674 (1963).

typical reaction was 0.095 g (0.4 mmol), 4%. The compound melts at 66–67° without decomposition. As previously described,¹ 6-(CO)₃-6MnB₉H₁₂-2-O(C₂H₅)₂ and K⁺6-(CO)₃-6-MnB₉H₁₃⁻ are also produced.

Spectroscopic Characterization. Infrared Spectrum. The KBr mull spectrum of (CO)₃MnB₉H₁₃ was recorded on a Perkin-Elmer Model 700 infrared spectrophotometer at an 8-min scan speed. The spectrum contains three B–H stretching frequencies at 2645 (s, sh), 2615 (s), and 2580 (s) cm⁻¹ and two C–O stretching frequencies at 2090 (vs) and 1955 (vs, b) cm⁻¹. Other absorptions are at 1440 (m), 1095 (w), 1065 (w), 1045 (w), 1020 (vw), 990 (m), 950 (w, sh), 935 (m), 880 (m), 780 (m), 735 (m), 695 (m, sh), and 680 (s) cm⁻¹. All frequencies are ±10 cm⁻¹.

Raman Spectrum. The laser Raman spectrum was recorded on a Spex Ramalog 1401 Raman spectrometer, using a 6471-Å excitation source, a Spectro-Physics Model 165-01 krypton laser. The spectrum of the solid crystalline product, measured in centimeters⁻¹ from the exciting radiation, contains B–H stretching frequencies at 2609 (w), 2605 (vw, sh), 2595 (w), 2585 (mw), 2573 (w), 2553 (w, sh), and 2542 (m) cm⁻¹ and C–O stretching frequencies at 2065 (mw), 1997 (w), 1971 (mw), 1966 (m), 1956 (ms), and 1939 (vw) cm⁻¹. Other peaks are at 1451 (vw, b), 1310 (vw, vb), 1075 (vw, b), 1064 (vw), 1051 (w), 1036 (vw), 984 (w, vb), 880 (w, sh), 868 (m), 840 (w), 819 (w, sh), 807 (mw, sh), 798 (mw), 768 (w), 757 (w), 687 (w, sh), 678 (w), 663 (vw, sh), 643 (w), 640 (w, sh), 614 (mw), 543 (w), 518 (m), 494 (m), 475 (s), 462 (m), 434 (mw), 376 (m), 242 (vs), 210 (w), 193 (m), 122 (vs), 111 (vs), 92 (vs), 85 (vs), and 69 (ms) cm⁻¹. All frequencies are ±10 cm⁻¹.

Ultraviolet Spectrum. This was recorded on a Cary 14 uv spectrophotometer, using solutions in CH₂Cl₂. Maxima and their extinction coefficients are at 5750 (ε 2.0), 3925 (ε 18.6), and 2650 Å (ε 52.7).

Mass Spectrum. The compound was volatile enough for a mass spectrum to be obtained (Figure 1) on an AEI MS902 mass spectrometer. The 70-eV mass spectrum of (CO)₃MnB₉H₁₃ follows the pattern established for metal carbonyl metalboranes.¹ Envelopes at parent, parent minus two carbon monoxides, and parent minus three carbon monoxides are evident. A peak match for the parent peak was used for molecular weight determination: calculated for (¹²C¹⁶O)₃⁵⁵Mn¹¹B₉H₁₃, 240.0990; found, 240.1001.

Nmr Spectra. These were obtained using a Varian XL-100 spectrometer equipped with standard Varian accessories and modifications.

The 32.1-MHz ¹¹B nmr spectrum of (CO)₃MnB₉H₁₃ (Figure 2) is assigned as follows: resonance assignment, chemical shift in parts per million referenced to BF₃·O(C₂H₅)₂ (coupling constant) [relative area]: B(4,7) or B(5,6), -7.5(160)[2]; B(5,6) or B(4,7), 0.3(160)[2]; B(1), 7.8(singlet)[1]; B(3,8), 52.0(140-further coupling from bridging H's of 60)[2]; B(2), 57.3(160)[1].

The 100-MHz ¹H nmr spectrum (¹¹B decoupled) (Figure 3) is assigned as follows: resonance assignment, chemical shift (τ) referenced to TMS (solvent) [relative area]: H(3–8), 6.3, 6.9, 9.1-(CD₂Cl₂)[2,2,2]; H(2), 9.3(CD₂Cl₂)[1]; H(10,12), 12.1(C₆D₆)[2]; H(11), 12.3(C₆D₆)[1]; H(9,13), 19.3(CD₂Cl₂)[2]; H(1), 21.2(CD₂Cl₂)[1].

Crystallographic Characterization. Crystal Preparation. Crystals of (CO)₃MnB₉H₁₃ were placed in one end of a Pyrex tube of approximately 10 mm o.d. and 20 cm in length. The tube was then sealed under vacuum. By establishing a small temperature gradient at ~50°, single crystals were grown by sublimation in 2 days. The crystal finally chosen was approximately orthorhombic (0.28 × 0.28 × 0.15 mm) with the following faces: ±[(10 $\bar{2}$), (001), (100), (102), (11 $\bar{1}$)], (010). The crystal was then glued to a glass fiber and sealed under argon in a Lindemann glass capillary.

X-Ray Measurements. Diffraction data were collected on a Syntex P1 autodiffractometer equipped with a graphite monochromated Mo K α source. After careful centering of the crystal using optical and X-ray tube alignment, 15 preliminary reflections were centered in 2 θ , χ , and ω . The orthorhombic lattice symmetry *D*_{2h}-2/m2/m2/m indicated in the Syntex auto-indexing procedure⁵ was verified by partial rotation photographs along each of the three reciprocal axes. Intensity data were collected by a variable θ -2 θ scan speed technique (2–24°/min) with each background count lasting 0.67 times the scan time. Two standard reflections, which were used to monitor the intensity for electronic and crystal stability every 50 reflections, indicated no significant variation (±1.5%), and no normalization was needed. The data were reduced⁶ in the usual

manner, with the standard deviation of each corrected intensity estimated from the formula $\sigma(I) = T_R[S + (B_1 + B_2)/B_R + qI]^{1/2}$, where T_R is the 2 θ scan rate in degrees per minute, S is the total integrated scan count, B_1 and B_2 are the background counts, B_R is the ratio of the background to scan count times, and q is assigned a value of 0.003. The integrated intensity, I , was taken as $[S - (B_1 + B_2)/B_R]T_R$. The intensities were corrected for Lorentz and polarization effects, and then converted to structure factor amplitudes $|F_o| = (I/Lp)^{1/2}$ with $\sigma(F) = \sigma(I)/(2F_oLp)$. The intensities were not corrected for absorption, since the variation of the calculated transmission coefficients for the block-like crystal ($\mu = 11.0$ cm⁻¹) ranged from 0.77 to 0.80. Effects of extinction were also ignored. Of the 1292 independent reflections measured ($2^\circ \leq 2\theta \leq 55^\circ$), 928 were observed ($I > 2\sigma(I)$) and were used throughout the structural analysis.

Crystal Data. (CO)₃MnB₉H₁₃ (mol wt 238.55) is orthorhombic: $a = 11.549(2)$, $b = 5.506(1)$, $c = 19.260(3)$ Å; $V = 1224.7(3)$ Å³; $Z = 4$; $d_{\text{calcd}} = 1.294$, $d_{\text{measd}} = 1.289(6)$ g/cm³ (determined by the flotation method using aqueous ZnCl₂ solutions); and $F(000) = 480$. Systematic absences of $\{hk0\}$ for $h + k$ odd and of $\{h0l\}$ for l odd define the probable space group as either *P2₁cn* [nonstandard setting of *Pna2₁* (*C*_{2v}⁹, No. 33)] or *Pmcn* [nonstandard setting of *Pnma* (*D*_{2h}¹⁶, No. 62)]. The structure was successfully refined in the latter centrosymmetric space group, containing an eightfold set of general positions: $\pm(x, y, z; 1/2 + x, 1/2 + y, 1/2 - z; x, 1/2 - y, 1/2 + z)$.

Structure Refinement. A Patterson synthesis revealed the position of the manganese atom on the mirror plane, assuming the centrosymmetric space group *Pmcn*. This space group was then utilized during the entire structural determination; its use was verified by the successful least-squares refinement of the crystal structure. The first Fourier synthesis phased on the coordinates of the Mn ($R_1^{7a} = 0.549$) yielded the structure directly.

After two cycles of full-matrix, isotropic least-squares refinement of all nonhydrogen atoms the R_1 and R_2^{7b} values were reduced to 0.089 and 0.118, respectively. A difference Fourier synthesis then revealed the positions of all the hydrogen atoms, and these positions were used in a third full-matrix least-squares isotropic cycle, varying all factors except the temperature factors for the hydrogens, which were kept constant at 6.0 Å², to give $R_1 = 0.074$ and $R_2 = 0.094$. Refinement was continued with anisotropic thermal motion for all nonhydrogen atoms and allowing the hydrogen isotropic temperature factors to vary. After three cycles of full-matrix least squares, refinement converged to a final $R_1 = 0.033$, $R_2 = 0.041$, and error-of-fit parameter^{7c} of 1.09. No attempt was made to refine the hydrogens anisotropically.

In all refinements, the scattering factors of Hanson, *et al.*,⁸ were utilized for the nonhydrogen atoms and those of Stewart, *et al.*,⁹ for the hydrogen atoms, along with real and imaginary anomalous dispersion corrections^{10,11} for the manganese atom. The function minimized in the refinements was $\sum w_i(|F_o| - |F_c|)^2$, with the weights w_i set equal to $1/\sigma(F_o)^2$.

Discussion

Spectroscopic Analysis. The structure of (CO)₃-MnB₉H₁₃ was difficult to determine in the absence of X-ray data since no previous metalboranes could be used as exact analogs. Only one other metal-B₉ system is known and it is proposed¹² to have a B₉-like cage

(6) All crystallographic programs used in structural determination and least-squares refinement were written by one of us (J. C. C.). The absorption correction program DEAR (J. F. Blount) uses the Gaussian integration method of Busing and Levy. Plots were made using ORTEP (C. K. Johnson).

(7) (a) $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$. (b) $R_2 = [\sum w_i |F_o| - |F_c|]^2 / \sum w_i |F_o|^2$. (c) The standard deviation of an observation of unit weight, defined as $[\sum w_i |F_o| - |F_c|]^2 / (m - n)^{1/2}$, where m is the number of observations and n the number of parameters fitted to the data set.

(8) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964).

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

(10) The values of the dispersion corrections to the atomic scattering factors for Mo K α radiation for Mn are $\Delta f' = 0.4$ and $\Delta f'' = 0.9$.¹¹

(11) Anomalous dispersion corrections were made using values from the "International Tables for X-ray Crystallography," Vol. III, K. Lonsdale, Ed., The Kynoch Press, Birmingham, England, 1962.

(12) A. R. Kane, L. J. Guggenberger, and E. L. Muettterties, *J. Amer. Chem. Soc.*, **92**, 2571 (1970).

(5) R. A. Sparks, *et al.*, "P1 Autodiffractometer Operations Manual," Syntex Analytical Instruments Division, Cupertino, Calif., 1970.

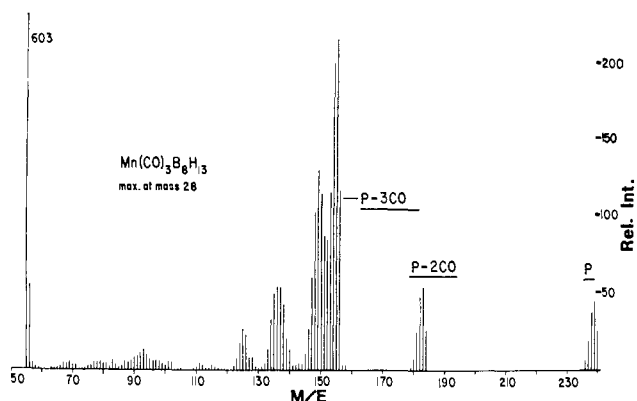


Figure 1. The 70-eV mass spectrum of $(\text{CO})_3\text{MnB}_8\text{H}_{13}$ with intensities relative to the CO^+ peak at m/e 28, weighted as 1000.

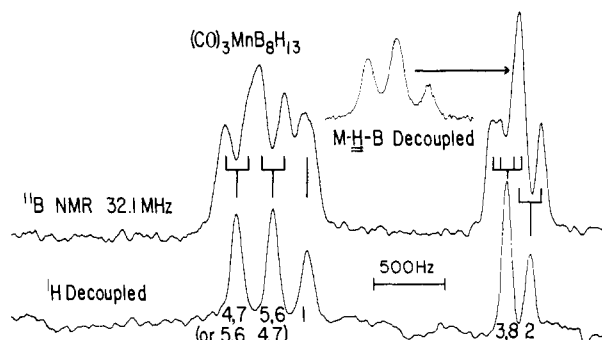


Figure 2. The 32.1-MHz ^{11}B nmr time averaged spectra of $(\text{CO})_3\text{MnB}_8\text{H}_{13}$. In the lower spectrum all ^1H interactions are decoupled using white noise modulation. The middle trace is normal while the upper trace shows the change in the high field group upon ^1H irradiation at the position corresponding to the M-H-B bridge hydrogens.

structure and four B-H-B bridge hydrogens. The molecular formula and the mass spectral fragmentation pattern (Figure 1) suggest that the $\text{Mn}(\text{CO})_3$ moiety is attached to the B_8H_{13} ligand. The 32.1-MHz ^{11}B nmr spectrum consists of two sets of peaks (Figure 2). The low field set consists of two overlapping doublets, each of intensity 2, followed by a singlet of intensity 1. The high field group contains two overlapping doublets with relative intensities of 2:1. Metal-hydrogen-boron bridge coupling was established by ^1H irradiation (white noise modulated) at a frequency corresponding to the M-H-B bridge hydrogen resonances and observing the effects on the split doublet at δ 51.7 (see Figure 2). It was apparent from the reproducible shoulders on the singlet at δ 7.8 that MHB-bridge hydrogen coupling was almost certainly in effect here as well. The ^{11}B nmr spectrum of $(\text{CO})_3\text{MnB}_8\text{H}_{13}$ could not be rationalized simply on the basis of an *i*- or *n*- B_9H_{15} spectrum as had the $\text{Mn}-\text{B}_9$ metal-laboranes on the basis of $\text{B}_{10}\text{H}_{14}$.

The ^{11}B decoupled ^1H nmr spectrum measured at 100 MHz registers two different types of MHB bridge hydrogen resonances with relative intensities of 2:1 at τ 19.3 and 21.2, respectively. In dichloromethane a single BHB bridge hydrogen resonance of relative intensity 3 is observed at τ 11.7. In benzene this BHB resonance is resolved into two peaks having relative intensities of 2:1 at τ 12.1 and 12.3. Terminal B-H resonances

present in dichloromethane- d_2 are at τ 6.3, 6.9, 9.1, and 9.3, but in benzene- d_6 the two lowest field peaks become a single larger peak at τ 6.7 (Figure 3). The exact nature of the solvent interaction which produces this phenomenon has not yet been determined. The ^1H nmr spectrum indicates two types of MHB bridge hydrogens in a 2:1 ratio and BHB-bridge hydrogens in the same ratio. From these data and the molecular formula, it is apparent that one boron has no terminal hydrogen. The nmr data thus suggest consideration of at least two possible structures having nominal C_s symmetry. A plausible but incorrect structure proposal is shown in Figure 4. Static bridge hydrogens are postulated between B(5) and B(6) and between B(9) and B(8), and a third bridge hydrogen was thought to be rapidly tautomerizing between the B(6), B(7) position and the B(7), B(8) position, without undergoing rapid exchange with any other terminal or bridging hydrogen positions. This type of exchange process has previously been proposed for $\text{B}_8\text{H}_{12}^{13}$ and its derivatives,¹⁴ and for $\text{B}_9\text{H}_{14}^-$.¹⁵ The spectral data could not distinguish between this structure and the alternate correct structure, which is actually most closely related to the atom arrangement in B_8H_{12} .

In order to determine the correct structure, an X-ray crystal structure determination was undertaken.

Description of the Structure. The positions and isotropic thermal parameters for all atoms in $(\text{CO})_3\text{Mn}-\text{B}_8\text{H}_{13}$ are given in Table I, and the anisotropic thermal

Table I. Atomic Coordinates (Fractional, $\times 10^4$) and Thermal Parameters (\AA^2)^a

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
Mn	2500.0 (—)	2226.1 (9)	1801.5 (3)	
C(1)	2500 (—)	295 (7)	2566 (2)	
O(1)	2500 (—)	-927 (6)	3042 (2)	
C(2) ^b	1368 (3)	4161 (5)	2146 (1)	
O(2)	656 (2)	5384 (4)	2354 (1)	
B(1) ^c	2500 (—)	2337 (7)	644 (2)	
B(2)	2500 (—)	3483 (8)	-211 (2)	
B(3)	1720 (3)	-41 (5)	927 (2)	
B(4)	1249 (3)	1966 (6)	172 (2)	
B(5)	1735 (4)	1381 (7)	-697 (2)	
H(1)	2500 (—)	3914 (67)	1077 (18)	3.0 (8)
H(2)	2500 (—)	5354 (82)	-352 (22)	4.7 (10)
H(3)	1456 (27)	-1858 (50)	796 (13)	3.7 (6)
H(4)	460 (24)	2828 (43)	227 (13)	3.1 (5)
H(5)	1241 (29)	1690 (57)	-1162 (16)	5.0 (7)
H(9)	1312 (25)	481 (51)	1451 (15)	4.2 (6)
H(10)	1166 (26)	326 (59)	-229 (17)	5.4 (8)
H(11)	2500 (—)	-314 (97)	-812 (24)	5.9 (12)

^a Standard deviations of the last significant figure given in parentheses. ^b C(3), O(3), B(6), B(7), B(8), H(6), H(7), H(8), H(12), and H(13) are related by mirror symmetry to C(2), O(2), B(5), B(4), B(3), H(5), H(4), H(3), H(10), and H(9), respectively. ^c The boron atoms are numbered according to the convention of *Inorg. Chem.*, **7**, 1945 (1968).

parameters for all nonhydrogen atoms are given in Table II. Interatomic distances are given in Table III, and intermolecular angles are given in Table IV. Distances and angles along with their estimated standard deviations were calculated from the full variance-

(13) V. T. Brice, H. D. Johnson, II, and S. G. Shore, *J. Chem. Soc., Chem. Commun.*, 1128 (1972).

(14) V. T. Brice and S. G. Shore, *Inorg. Chem.*, **12**, 309 (1973).

(15) P. C. Keller, *Inorg. Chem.*, **9**, 75 (1970).

Table II. Anisotropic Thermal Parameters^a ($\times 10^4$)

Atom	β_{11}^b	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mn	63.8 (5)	200.5 (20)	20.2 (2)	0 (—)	0 (—)	-3.3 (5)
C(1)	95 (4)	267 (14)	23 (1)	0 (—)	0 (—)	-14 (3)
O(1)	207 (5)	348 (12)	24 (1)	0 (—)	0 (—)	13 (3)
C(2)	81 (3)	275 (10)	28 (1)	-12 (4)	7 (1)	-8 (2)
O(2)	110 (2)	389 (9)	52 (1)	44 (4)	24 (1)	-23 (2)
B(1)	59 (3)	165 (12)	21 (1)	0 (—)	0 (—)	0 (3)
B(2)	85 (4)	244 (15)	23 (1)	0 (—)	0 (—)	9 (4)
B(3)	60 (2)	215 (10)	22 (1)	-10 (4)	1 (1)	3 (2)
B(4)	63 (2)	283 (11)	27 (1)	-6 (5)	-5 (1)	0 (3)
B(5)	105 (4)	355 (12)	22 (1)	-18 (6)	-8 (2)	10 (3)

^a Standard deviations of the last significant figure given in parentheses. ^b The form of the anisotropic thermal factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

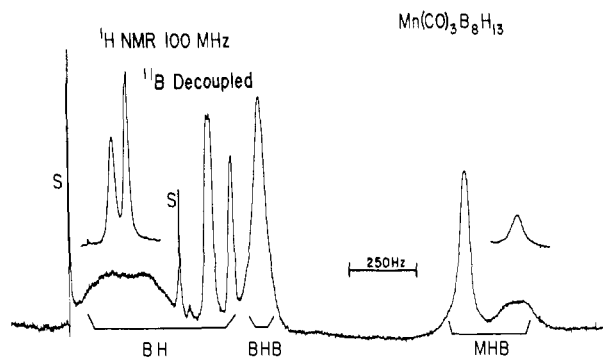


Figure 3. The 100-MHz ¹H nmr spectrum of $(\text{CO})_3\text{MnB}_8\text{H}_{13}$ in CD_2Cl_2 using Fourier transform techniques with all ¹¹B interactions decoupled.

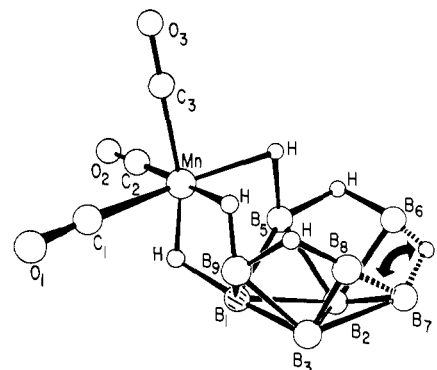


Figure 4. A possible structure for $(\text{CO})_3\text{MnB}_8\text{H}_{13}$. A terminal hydrogen has been omitted on each boron atom except B₁, which has no terminal hydrogen. The bridging hydrogen between B₆ and B₇ was postulated as tautomerizing with the mirror plane related position between B₇ and B₃.

Table III. Interatomic Distances for $(\text{CO})_3\text{MnB}_8\text{H}_{13}$ (in Å)^a

Mn-C(1)	1.816 (4)	B(2)-B(5)	1.732 (6)
Mn-C(2)	1.813 (3)	B(2)-H(2)	1.065 (44)
Mn-B(1)	2.231 (4)	B(3)-B(4)	1.905 (4)
Mn-B(3)	2.282 (3)	B(3)-B(8)	1.801 (6)
Mn-H(1)	1.676 (35)	B(3)-H(3)	1.076 (28)
Mn-H(9)	1.807 (28)	B(3)-H(9)	1.151 (28)
C(1)-O(1)	1.137 (5)	B(4)-B(5)	1.795 (5)
C(2)-O(2)	1.136 (3)	B(4)-H(4)	1.033 (27)
B(1)-B(2)	1.676 (6)	B(4)-H(10)	1.193 (33)
B(1)-B(3)	1.680 (4)	B(5)-B(6)	1.767 (9)
B(1)-B(4)	1.718 (4)	B(5)-H(5)	1.075 (32)
B(1)-H(1)	1.205 (36)	B(5)-H(10)	1.257 (31)
B(2)-B(4)	1.824 (4)	B(5)-H(11)	1.304 (38)

^a Standard deviations of the last significant figure given in parentheses.

covariance matrix obtained from the last refinement cycle.

The molecular structure of $(\text{CO})_3\text{MnB}_8\text{H}_{13}$ is shown in Figure 5. A bottom view is shown in Figure 6, and a stereoscopic view is shown in Figure 7. Figure 6 shows that the molecule is crystallographically constrained to C_s -*m* symmetry, with C(1), O(1), Mn, B(1), B(2), H(1), H(2), and H(11) on the mirror plane. The molecule consists of a $\text{Mn}(\text{CO})_3$ fragment bonded to the tridentate B_8H_{13} ligand by two $\text{M}-\text{H}-\text{B}$ bridge hydrogen bonds from borons, B(3) and B(8), bordering the open face of the borane cage and one $\text{M}-\text{H}-\text{B}$ bond from an adjacent boron, B(1), in the base of the borane cage. The manganese is octahedrally coordinated (see Table IV) and approximately centered over the B(1)-B(3)-B(8) triangle. The B_8H_{13} cage differs from

that of B_8H_{12} ¹⁶ in that the former contains no bridging hydrogen between B(3) and B(8). Instead there are three $\text{Mn}-\text{H}-\text{B}$ bridge hydrogens, H(1), H(9), and H(13), and B(1) no longer has a terminal hydrogen attached to it.

The closest approaches between molecules in the unit cell are 2.5, 2.8, and 2.9 Å for the $\text{H}\cdots\text{H}$ contacts and 3.12, 3.15, and 3.25 Å for the $\text{O}\cdots\text{H}$ contacts. These distances are somewhat longer than normal van der Waals distances (*e.g.*, 2.4 Å for $\text{H}\cdots\text{H}$ and 2.60 Å for $\text{O}\cdots\text{H}$ intermolecular contacts)¹⁷ and indicate that the solid state structure of $(\text{CO})_3\text{MnB}_8\text{H}_{13}$ is not appreciably affected by crystal-packing forces.

Bonding. The most salient and heretofore unknown stereochemical feature observed in this study is the hydrogen bridge bond from the metal to a basal boron of a large polyhedral fragment. In previous structural studies of complexes containing $\text{Mn}-\text{H}-\text{B}$ bonds¹⁻³ these bonds were between the metal and boron atoms on the open face of the nido or arachno borane cage. Representative significant changes in bond lengths and angles in related compounds are listed in Table V.

The electron bookkeeping for $(\text{CO})_3\text{MnB}_8\text{H}_{13}$ can be approached from two different viewpoints, namely the

(16) R. E. Envione, F. P. Boer, and W. N. Lipscomb, *Inorg. Chem.*, **3**, 1659 (1964).

(17) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260.

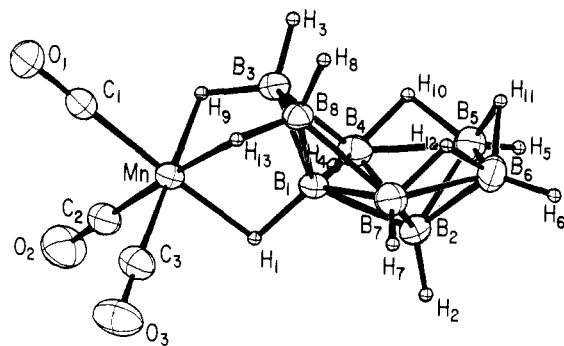


Figure 5. The structure of $(\text{CO})_3\text{MnB}_8\text{H}_{13}$. In this ORTEP diagram, 30% probability contours were plotted for atomic vibration ellipsoids. An isotropic temperature factor of 0.7 was assigned to all hydrogens.

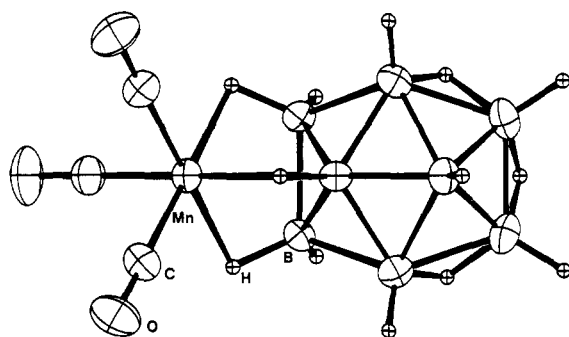


Figure 6. A bottom view of the structure of $(\text{CO})_3\text{MnB}_8\text{H}_{13}$, showing the C_s symmetry of the molecule.

effective atomic number (EAN) rule, with attention centering on the manganese, or Wade's rules,¹⁸ with attention centering on the borane cage. The compound can be formally considered as a $(\text{CO})_3\text{Mn}^0$ moiety with a $\text{B}_8\text{H}_{13}^0$ ligand or a $(\text{CO})_3\text{Mn}^1$ moiety with a $\text{B}_8\text{H}_{13}^-$ ligand. Considering the former assignment, the EAN rule requires that Mn acquire 11 electrons in addition to the seven it already has. Six are contributed from the three carbonyls and five from the three hydrogen bridges. Drawing a parallel between $(\text{CO})_3\text{MnB}_8\text{H}_{13}$ and $\text{Mn}(\text{CO})_5\text{Br}$, the $\text{Mn}(\text{CO})_3$ moiety needs two more Lewis base coordinate bonds and one covalent bond. The $\text{B}(3)\text{-H}(9)$ and $\text{B}(8)\text{-H}(13)$ localized molecular orbitals can formally replace carbonyls as Lewis bases, and the $\text{B}(1)\text{-H}(1)$ localized molecular orbital can formally replace bromine in a covalent bond. Using Wade's rules, B_8H_{12} has ten pairs of electrons in cage molecular orbitals, $\text{B}_8\text{H}_{13}^-$ has 11 pairs, and $(\text{CO})_3\text{MnB}_8\text{H}_{13}$ has 11 pairs. Thus, B_8H_{12} is predicted to be nido, since it has two more pairs of electrons than it has vertices in the cage, $\text{B}_8\text{H}_{13}^-$ is predicted to be arachno, since it has three more pairs than vertices, and $(\text{CO})_3\text{MnB}_8\text{H}_{13}$ is nido if the Mn is considered part of the cage and arachno if Mn is not considered part of the cage. However, if Mn is considered part of the cage, $\text{B}(1)$ violates the assumption¹⁸ that each atom at a vertex contributes only three orbitals to the cage molecular orbitals. So if the cage has

(18) (a) K. Wade, *Chem. Commun.*, 792 (1971); (g) K. Wade, *Inorg. Nucl. Chem. Lett.*, **8**, 559 (1972); (c) D. M. P. Mingos, *Nature Phys. Sci.*, **236**, 99 (1972).

Table IV. Intramolecular Angles for $(\text{CO})_3\text{MnB}_8\text{H}_{13}$ (in deg)^a

$\text{C}(1)\text{-Mn-C}(2)$	92.7 (1)	$\text{Mn-B}(3)\text{-B}(1)$	66.5 (2)
$\text{C}(1)\text{-Mn-B}(1)$	145.7 (2)	$\text{Mn-B}(3)\text{-B}(4)$	111.0 (2)
$\text{C}(1)\text{-Mn-B}(3)$	106.2 (1)	$\text{Mn-B}(3)\text{-B}(8)$	66.8 (1)
$\text{C}(1)\text{-Mn-H}(1)$	177.8 (13)	$\text{Mn-B}(3)\text{-H}(3)$	142.5 (14)
$\text{C}(1)\text{-Mn-H}(9)$	89.5 (9)	$\text{Mn-B}(3)\text{-H}(9)$	51.5 (14)
$\text{C}(2)\text{-Mn-C}(3)$	92.3 (2)	$\text{B}(1)\text{-B}(3)\text{-B}(4)$	56.9 (2)
$\text{C}(2)\text{-Mn-B}(1)$	110.5 (1)	$\text{B}(1)\text{-B}(3)\text{-B}(8)$	57.6 (1)
$\text{C}(2)\text{-Mn-B}(3)$	107.9 (1)	$\text{B}(1)\text{-B}(3)\text{-H}(3)$	143.3 (15)
$\text{C}(2)\text{-Mn-B}(8)$	151.2 (1)	$\text{B}(1)\text{-B}(3)\text{-H}(9)$	108.1 (14)
$\text{C}(2)\text{-Mn-H}(1)$	88.8 (9)	$\text{B}(4)\text{-B}(3)\text{-B}(8)$	106.6 (1)
$\text{C}(2)\text{-Mn-H}(9)$	84.4 (9)	$\text{B}(4)\text{-B}(3)\text{-H}(3)$	106.3 (14)
$\text{C}(2)\text{-Mn-H}(13)$	176.1 (9)	$\text{B}(4)\text{-B}(3)\text{-H}(9)$	114.0 (14)
$\text{B}(1)\text{-Mn-B}(3)$	43.7 (1)	$\text{B}(8)\text{-B}(3)\text{-H}(3)$	106.5 (17)
$\text{B}(1)\text{-Mn-H}(1)$	32.1 (13)	$\text{B}(8)\text{-B}(3)\text{-H}(9)$	114.2 (14)
$\text{B}(1)\text{-Mn-H}(9)$	68.9 (9)	$\text{H}(3)\text{-B}(3)\text{-H}(9)$	108.7 (20)
$\text{B}(3)\text{-Mn-B}(8)$	46.5 (2)		
$\text{B}(3)\text{-Mn-H}(1)$	71.9 (12)	$\text{B}(1)\text{-B}(4)\text{-B}(2)$	59.6 (2)
$\text{B}(3)\text{-Mn-H}(9)$	29.9 (9)	$\text{B}(1)\text{-B}(4)\text{-B}(3)$	55.0 (2)
$\text{B}(3)\text{-Mn-H}(13)$	74.5 (9)	$\text{B}(1)\text{-B}(4)\text{-B}(5)$	104.6 (3)
$\text{H}(1)\text{-Mn-H}(9)$	89.1 (12)	$\text{B}(1)\text{-B}(4)\text{-H}(4)$	129.3 (15)
$\text{H}(9)\text{-Mn-H}(13)$	98.9 (18)	$\text{B}(1)\text{-B}(4)\text{-H}(10)$	120.0 (15)
		$\text{B}(2)\text{-B}(4)\text{-B}(3)$	110.4 (2)
$\text{Mn-C}(1)\text{-O}(1)$	179.5 (4)	$\text{B}(2)\text{-B}(4)\text{-B}(5)$	57.2 (2)
$\text{Mn-C}(2)\text{-O}(2)$	179.1 (3)	$\text{B}(2)\text{-B}(4)\text{-H}(4)$	122.0 (14)
		$\text{B}(2)\text{-B}(4)\text{-H}(10)$	98.5 (15)
$\text{Mn-B}(1)\text{-B}(2)$	160.6 (3)	$\text{B}(3)\text{-B}(4)\text{-B}(5)$	121.2 (2)
$\text{Mn-B}(1)\text{-B}(3)$	69.8 (2)	$\text{B}(3)\text{-B}(4)\text{-H}(4)$	116.1 (15)
$\text{Mn-B}(1)\text{-B}(4)$	121.7 (2)	$\text{B}(3)\text{-B}(4)\text{-H}(10)$	94.5 (15)
$\text{Mn-B}(1)\text{-H}(1)$	47.7 (17)	$\text{B}(5)\text{-B}(4)\text{-H}(4)$	117.0 (15)
$\text{B}(2)\text{-B}(1)\text{-B}(3)$	125.6 (2)	$\text{B}(5)\text{-B}(4)\text{-H}(10)$	44.3 (15)
$\text{B}(2)\text{-B}(1)\text{-B}(4)$	63.2 (2)	$\text{H}(4)\text{-B}(4)\text{-H}(10)$	110.1 (20)
$\text{B}(2)\text{-B}(1)\text{-H}(1)$	112.9 (17)		
$\text{B}(3)\text{-B}(1)\text{-B}(4)$	68.2 (2)	$\text{B}(2)\text{-B}(5)\text{-B}(4)$	62.3 (2)
$\text{B}(3)\text{-B}(1)\text{-B}(7)$	122.0 (3)	$\text{B}(2)\text{-B}(5)\text{-B}(6)$	59.3 (2)
$\text{B}(3)\text{-B}(1)\text{-B}(8)$	64.8 (3)	$\text{B}(2)\text{-B}(5)\text{-H}(5)$	128.0 (17)
$\text{B}(3)\text{-B}(1)\text{-H}(1)$	109.7 (14)	$\text{B}(2)\text{-B}(5)\text{-H}(10)$	100.8 (15)
$\text{B}(4)\text{-B}(1)\text{-B}(7)$	114.4 (3)	$\text{B}(2)\text{-B}(5)\text{-H}(11)$	103.0 (17)
$\text{B}(4)\text{-B}(1)\text{-H}(1)$	116.9 (6)	$\text{B}(4)\text{-B}(5)\text{-B}(6)$	108.2 (2)
		$\text{B}(4)\text{-B}(5)\text{-H}(5)$	125.6 (17)
$\text{B}(1)\text{-B}(2)\text{-B}(4)$	57.2 (2)	$\text{B}(4)\text{-B}(5)\text{-H}(10)$	41.5 (15)
$\text{B}(1)\text{-B}(2)\text{-B}(5)$	105.4 (3)	$\text{B}(4)\text{-B}(5)\text{-H}(11)$	119.9 (21)
$\text{B}(1)\text{-B}(2)\text{-H}(2)$	125.8 (24)	$\text{B}(6)\text{-B}(5)\text{-H}(5)$	122.1 (17)
$\text{B}(4)\text{-B}(2)\text{-B}(5)$	60.6 (2)	$\text{B}(6)\text{-B}(5)\text{-H}(10)$	121.5 (14)
$\text{B}(4)\text{-B}(2)\text{-B}(6)$	108.4 (3)	$\text{B}(6)\text{-B}(5)\text{-H}(11)$	47.3 (16)
$\text{B}(4)\text{-B}(2)\text{-B}(7)$	104.7 (3)	$\text{H}(5)\text{-B}(5)\text{-H}(10)$	113.1 (23)
$\text{B}(4)\text{-B}(2)\text{-H}(2)$	123.1 (8)	$\text{H}(5)\text{-B}(5)\text{-H}(11)$	109.4 (26)
$\text{B}(5)\text{-B}(2)\text{-B}(6)$	61.4 (3)	$\text{H}(10)\text{-B}(5)\text{-H}(11)$	98.3 (24)
$\text{B}(5)\text{-B}(2)\text{-H}(2)$	120.6 (19)		
		$\text{Mn-H}(1)\text{-B}(1)$	100.2 (23)
		$\text{Mn-H}(9)\text{-B}(3)$	98.6 (18)
		$\text{B}(4)\text{-H}(10)\text{-B}(5)$	94.2 (22)
		$\text{B}(5)\text{-H}(11)\text{-B}(6)$	85.3 (32)

^a Standard deviations of the last significant figure given in parentheses.

only eight vertices, then the $\text{Mn}(\text{CO})_3$ moiety contributes one electron to the cage,¹⁸ six BH moieties contribute 12 electrons, two BH_2 moieties contribute six, and three BHB bridge hydrogens contribute three electrons, for a total of 11 electron pairs, which correspond to an arachno structure. The $\text{Mn}(\text{CO})_3$ moiety in this compound is not considered part of the cage but rather as a face bridging group. By convention¹⁸ bridging hydrogen atoms in boranes and bridging carbonyl groups in transition metal cluster complexes are not considered to be cage vertices. An example of a metal carbonyl group considered as a face bridging group is preceded by $\text{Os}_6(\text{CO})_{18}$,¹⁹ in which two $\text{Os}(\text{CO})_3$ fragments, each contributing two electrons, bridge a

(19) R. Mason, K. M. Thomas, and D. M. P. Mingos, *J. Amer. Chem. Soc.*, **95**, 3802 (1973).

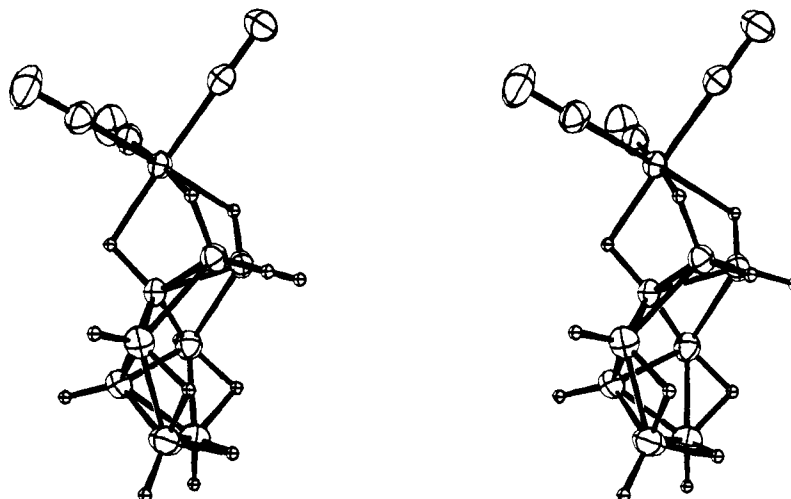


Figure 7. A stereoscopic view of the structure of $(\text{CO})_3\text{MnB}_9\text{H}_{13}$.

Table V. Comparison of Bond Lengths (in Å) and Angles (in deg)

Bond in $(\text{CO})_3\text{MnB}_9\text{H}_{13}$	Distance	Distance	In compared molecule	Deviation origin ^a
Mn-H(1)	1.68 (4)	$\left\{ \begin{array}{l} 1.60 (2)^b \\ 1.5-1.8^c \\ 1.14 (3)^d \\ 1.3-1.8^e \end{array} \right.$	Mn(CO) ₃ H	(1)
Mn-H(9)	1.81 (3)		HMn ₃ (CO) ₁₀ (BH ₃) ₂	(1)
B(1)-H(1)	1.21 (4)		B ₅ H ₁₂	(1)
B(3)-B(8)	1.801 (6)		1.674 (4) ^d	HMn ₃ (CO) ₁₀ (BH ₃) ₂ B ₅ H ₁₂
Angle in $(\text{CO})_3\text{MnB}_9\text{H}_{13}$	Value	Value	In compared molecule	Deviation origin
B(3)-Mn-B(8)	46.5 (2)	$\left\{ \begin{array}{l} 80.2 (2)^e \\ 81.4 (2)^f \end{array} \right.$	(CO) ₃ MnB ₉ H ₁₂ (5-OC ₄ H ₉)	(3)
B(3)-B(1)-B(8)	64.8 (3)		$\left\{ \begin{array}{l} 106.3 (3)^e \\ 108.2 (5)^f \end{array} \right.$	(CO) ₃ MnB ₉ H ₁₂ (8-O(CH ₂) ₄ N(C ₂ H ₅) ₃) (CO) ₃ MnB ₉ H ₁₂ (5-OC ₄ H ₉)
B(2)-B(1)-B(8)	125.6 (2)	113.38 (8) ^d	(CO) ₃ MnB ₉ H ₁₂ (8-O(CH ₂) ₄ N(C ₂ H ₅) ₃)	(3)
B(3)-B(1)-B(7)	122.0 (3)	108.47 (3) ^d	B ₅ H ₁₂	(2)
B(3)-B(1)-H(1)	110 (1)	123.5 (3) ^d	B ₅ H ₁₂	(1)
B(4)-B(1)-B(7)	114.4 (3)	104.84 (?) ^d	B ₅ H ₁₂	(2)
B(4)-B(3)-H(3)	106 (1)	118.4 (8) ^d	B ₅ H ₁₂	(2)
B(8)-B(3)-H(3)	106 (2)	131.9 (6) ^d	B ₅ H ₁₂	(2)

^a Nearly all deviations can be attributed to one of three causes: (1) a terminal hydrogen becoming a bridging hydrogen, (2) steric expansion due to coordination of Mn(CO)₃ and lack of B(3)-H-B(8) bridge hydrogen, or (3) direct B(3)-B(8) bonding. ^b S. J. LaPlaca, W. C. Hamilton, J. A. Ibers, and A. Davison, *Inorg. Chem.*, **8**, 1928 (1969). ^c H. D. Kaesz, W. Fellman, G. R. Wilkes, and L. F. Dahl, *J. Amer. Chem. Soc.*, **87**, 2753 (1965); G. R. Wilkes, Ph.D. Thesis, University of Wisconsin, Madison, 1965. ^d Reference 16. Our numbering convention is different from the one used in their paper. ^e Reference 1. B(3) and B(8) in $(\text{CO})_3\text{MnB}_9\text{H}_{13}$ correspond to B(5) and B(7), respectively, in this molecule. ^f Reference 3. B(3) and B(8) in $(\text{CO})_3\text{MnB}_9\text{H}_{13}$ correspond to B(5) and B(7), respectively, in this molecule.

tetrahedral cage of four osmium atoms. In $(\text{CO})_3\text{-MnB}_9\text{H}_{13}^-$ and related compounds,¹⁻³ however, the manganese is considered part of the cage framework in a decaborane-like structure (nido), where the cage has 12 pairs of electrons.

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Supplementary Material Available. Tables of observed and calculated structure factor amplitudes and mass spectral data 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, 24 × 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 and \$2.00 for microfiche referring to code number JACS-74-6318.