Contribution from the Department of Chemistry,
University of Wisconsin, Madison, Wisconsin 53706

# Low-Temperature Crystal and Molecular Structure of Tricarbonyl[octahydrotriborato(1−)]manganese, $(CO)_3MnB_3H_8$

STEVEN J. HILDEBRANDT, DONALD F. GAINES,* and JOSEPH C. CALABRESE

*Received May 5, 1977*

The low-temperature and solid-state structure of tricarbonyl[octahydrotriborato(1−)]manganese, $(CO)_3MnB_3H_8$, consists of a tridentate $B_3H_8^-$ ligand bound to the manganese atom through three Mn–H–B bridge hydrogen bonds, one bridge bond to each boron atom. The molecule has approximate $C_s$ symmetry with the octahedral coordination sphere of the manganese atom completed by three carbonyl ligands and three hydrogens bridging to the borane. The carbonyls have a *fac* orientation, as do the manganese–hydrogen–boron hydrogen bridges. Each boron atom has a single terminal hydrogen atom bound to it. The other two hydrogens present in the molecule bridge between boron atoms. Within experimental error ($\pm 2\sigma$), the three boron atoms form an equilateral triangle. Crystals of $(CO)_3MnB_3H_8$ form in the monoclinic space group $P2_1/c$ with unit cell parameters (at −95 °C) $a = 16.069$ (9) Å, $b = 5.901$ (3) Å, $c = 11.722$ (6) Å, $\beta = 95.10$ (4)°, $V = 1107$ (1) Å$^3$, and $Z = 4$. The x-ray structure was solved by the heavy-atom method and refined to $R_1 = 0.047$ and $R_2 = 0.058$ for 1333 independent $\theta$–$2\theta$ observed reflections. This is the first reported complex in which the octahydrotriborate ligand functions in a tridentate manner.

## Introduction

Tricarbonyl[octahydrotriborato(1−)]manganese, $(CO)_3MnB_3H_8$, is a yellow-orange liquid that behaves as a fluxional molecule on the NMR time scale. The $^1H$ NMR spectrum exhibits only two signals: (1) a low-field resonance of area 5 corresponding to those hydrogens only bonded to boron and (2) a high-field resonance of area 3 corresponding to hydrogens bridging between manganese and boron atoms. The $^{11}B$ NMR spectrum consists of a single resonance down to −80 °C, indicating equality of the three boron environments. The ill-defined fine structure associated with this resonance has been examined by line-narrowing and selective decoupling techniques. The experiments suggest that the three Mn–H–B hydrogen atoms are static, whereas the B–H and B–H–B hydrogen atoms are exchanging with each other around the periphery of the $B_3$ ring. This exchange would render the boron atoms equivalent, as observed.[1] In order to confirm this NMR analysis, a low-temperature single-crystal x-ray structural determination was undertaken to elucidate the static configuration of the $(CO)_3MnB_3H_8$ molecule and verify the novel tridentate functionality of the $B_3H_8^-$ ligand.

## Experimental Section

**Preparation of $(CO)_3MnB_3H_8$.** Standard high-vacuum techniques were employed in the synthesis of this compound.[2] The $(CO)_3MnB_3H_8$ was prepared from $(CO)_4MnB_3H_8$ by passage of the latter complex through a hot tube at 180 °C in a dynamic vacuum system.[3] The evolved carbon monoxide was continuously removed from the system so as to prevent recombination according to the reaction

$$(CO)_4MnB_3H_8 \underset{+CO}{\overset{\substack{\Delta \\ -CO}}{\rightleftarrows}} (CO)_3MnB_3H_8$$

The purification of the $(CO)_3MnB_3H_8$ was achieved on the vacuum line by distillation through a U-trap at −15 °C and condensation in a −45 °C U-trap.

**Single-Crystal X-Ray Data.** The air sensitivity of $(CO)_3MnB_3H_8$ necessitated the loading and sealing of Pyrex x-ray capillaries on the vacuum line. Capillaries containing the neat liquid (mp −7 °C) or methylene chloride solutions of $(CO)_3MnB_3H_8$ yielded thin multiple crystals unsatisfactory for x-ray analysis. However, it was found that solutions of $(CO)_3MnB_3H_8$ in toluene afforded suitably thicker crystals due to cocrystallization of the toluene with the $(CO)_3MnB_3H_8$. A capillary containing the $(CO)_3MnB_3H_8$/toluene mixture (~30/70 by volume) was mounted on a Syntex $P\bar{1}$ four-circle computer-controlled diffractometer equipped with LT-1 low-temperature accessories. A crystal of approximate dimensions 0.085 × 0.50 × 1.05 mm was grown at −48 ± 2 °C. The crystal was then cooled to −95 ± 8 °C and 15 diffraction maxima were automatically centered in $2\theta$, $\chi$, and $\omega$. Graphite-monochromated Mo K$\alpha$ ($\lambda$ 0.7107 Å) radiation was used throughout the alignment and data collection procedures. The Syntex routines indicated a monoclinic lattice with dimensions $a = 16.069$ (9) Å, $b = 5.901$ (3) Å, $c = 11.722$ (6) Å, $\beta = 95.10$ (4)°, and unit cell volume of 1107 (1) Å$^3$. Systematic absences for $0k0$ with $k$ = odd and $h0l$ with $l$ = odd uniquely defined the space group as $P2_1/c$ ($C_{2h}^5 \equiv$ No. 14).[4] The monoclinic symmetry and associated lattice constants were verified by partial rotation photographic projections along each of the three reciprocal axes. The calculated density is 1.353 g/cm$^3$ assuming four molecules of $(CO)_3MnB_3H_8$ and two molecules of toluene per unit cell (vide infra).

Intensity data were collected using the $\theta$–$2\theta$ scan technique with variable scan speeds (from 2 to 24°/min) with each background count lasting two-thirds of the time used for the scan count. The intensities of two standard reflections ($11\bar{3}$ and 412) were monitored every 50 reflections and were constant throughout the data collection procedure. All data were collected with the crystal temperature held at −95 ± 8 °C. A total of 2394 reflections were collected over the range $3.0 \leq 2\theta < 50.0°$. The data were reduced in the usual manner, with the standard deviation of each corrected intensity estimated from the formula $\sigma(I) = T_R[S + (B_1 + B_2)/B_R^2 + q(I)^2]^{1/2}$, where $T_R$ is the $2\theta$ 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 set equal to 0.003. The merged data yielded 1666 independent reflections, of which 1333 were observed [$I > 2.0\sigma(I)$] and were used in the solution and refinement of the structure. The intensities were not corrected for absorption.

**Solution and Refinement of the Structure.**[5] The solution of the structure was accomplished using the standard heavy-atom method. The solution revealed the location of one molecule of $(CO)_3MnB_3H_8$ and $^1/_2$ molecule of toluene (on the inversion center) per asymmetric unit. Initial Fourier and least-squares refinements also yielded positions for all hydrogen atoms in the $(CO)_3MnB_3H_8$ molecule. Isotropic refinement with the toluene molecule constrained to a rigid group, converged with $R_1 = 0.088$ and $R_2 = 0.112$.[6] The final refinement series included anisotropic temperature factors for Mn, B, and carbonyl atoms and fixed atom positions for all toluene hydrogen atoms ($\beta_{iso} = 8.0$ Å$^2$), with toluene methyl hydrogens disordered as six half-weighted hydrogens, converged to a final $R_1 = 0.047$ and $R_2 = 0.058$. The final difference map indicated a weak peak of 0.16 e at the site between B(1) and B(3) appropriate for a bridging hydrogen atom, suggesting a possible small amount of threefold disorder in the $B_3H_8^-$ ligand. However, attempts to refine a disorder of this type were unsuccessful. Also indicated on the final difference map were additional peaks near the toluene disorder suggesting a strong libration of the toluene molecule. The final data to parameter ratio was 9.8 and the standard deviation in an observation of unit weight was 1.58.[6] The scattering factors of Hanson et al.[7] were used for the nonhydrogen atoms and those of Stewart et al.[8] for the hydrogen atoms. All least-squares refinements were based on the minimization of $\sum w_i(|F_o| - |F_c|)^2$, with the weights $w_i$ set equal to $1/\sigma_{F_o}{}^2$. The estimated standard deviations given in the tables were calculated from the full variance–covariance matrix obtained from the last least-squares refinement cycle.

0020-1669/78/1317-0790$01.00/0

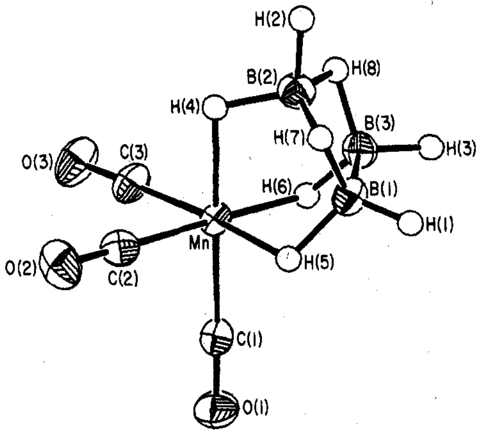

**Figure 1.** The static molecular structure of $(CO)_3MnB_3H_8$ showing the numbering system used in this study. In this ORTEP diagram 30% probability contours were plotted for the atomic vibration ellipsoids. The hydrogen atoms are represented by spheres of 0.15 Å radius.

The atomic coordinates and isotropic thermal parameters of the hydrogen atoms are listed in Table I, and the anisotropic temperature factors for the nonhydrogen atoms are listed in Table II. Interatomic distances and intramolecular angles are listed in Tables III and IV, respectively. Table V lists the atomic coordinates and the isotropic thermal parameters for the atoms in the toluene molecule.

**Table I.** Final Atom Positional Parameters (×10$^4$) and Thermal Parameters (A$^2$) for $(CO)_3MnB_3H_8$[a]

| Atom | $x$ | $y$ | $z$ | $B$, A$^2$ |
|---|---|---|---|---|
| Mn | 3294.2 (5) | 440.8 (12) | 1150.2 (5) | |
| O(1) | 4577 (3) | 2551 (8) | −160 (3) | |
| O(2) | 4546 (3) | −2270 (8) | 2540 (3) | |
| O(3) | 3105 (3) | −3248 (7) | −544 (3) | |
| C(1) | 4086 (3) | 1753 (8) | 348 (4) | |
| C(2) | 4069 (3) | −1218 (10) | 2009 (4) | |
| C(3) | 3163 (4) | −1811 (9) | 103 (4) | |
| B(1) | 2777 (4) | 3061 (11) | 2320 (5) | |
| B(2) | 2113 (4) | 743 (11) | 2137 (5) | |
| B(3) | 2134 (4) | 2682 (12) | 1053 (5) | |
| H(1) | 2786 (58) | 4650 (161) | 2590 (88) | 11.3 (29) |
| H(2) | 1619 (36) | 59 (95) | 2643 (52) | 4.9 (13) |
| H(3) | 1762 (36) | 4127 (96) | 735 (49) | 4.8 (13) |
| H(4) | 2511 (31) | −802 (86) | 1790 (42) | 3.5 (11) |
| H(5) | 3506 (27) | 2457 (83) | 2232 (34) | 2.6 (9) |
| H(6) | 2602 (28) | 2035 (77) | 420 (37) | 2.7 (10) |
| H(7) | 2564 (36) | 1817 (110) | 3073 (52) | 5.9 (15) |
| H(8) | 1626 (40) | 1294 (119) | 1224 (54) | 6.1 (15) |

[a] Standard deviations of the last significant figure are given in parentheses in this and in all following tables.

## Description of the Structure.

The static molecular structure of $(CO)_3MnB_3H_8$ and the numbering system used in this investigation are shown in Figures 1 and 2. It can be seen that the molecule possesses $C_s$ symmetry and, with the exception of H(7) and H(8), $C_{3v}$ symmetry. The disorder of the toluene is shown in Figure 3. The octahydrotriborate moiety functions as a tridentate ligand, bound to the manganese atom via three single hydrogen bridges to each boron atom. The tridentate behavior of the $B_3H_8^-$ unit is unique to the $(CO)_3MnB_3H_8$ complex. Previously only bidentate $B_3H_8^-$ behavior[9] has been observed.[10] $(CO)_3MnB_8H_{13}$[11c] is the only other metalloborane known to bond a single metal atom to a borane framework through three doubly bridging hydrogen atoms to three different boron atoms.

Table VI compares the bond lengths and bond angles of representative bidentate $B_3H_8^-$ metal complexes and of free $B_3H_8^-$ with those distances and angles found for the tridentate $B_3H_8^-$ encountered in the $(CO)_3MnB_3H_8$ molecule. The major structural change in going from bidentate to tridentate octahydrotriborate ligand is, of course, the equivalence of the three Mn–B distances and the corresponding decrease in the dihedral angle between the planes B(1)B(2)B(3) and B(1)-

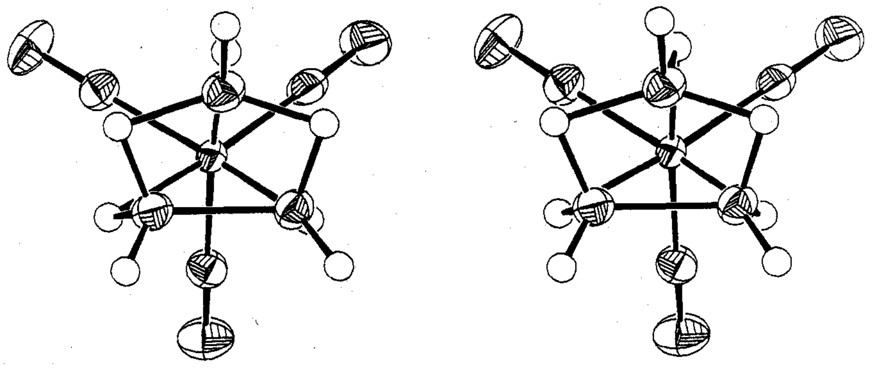

**Figure 2.** A stereoscopic view of $(CO)_3MnB_3H_8$.

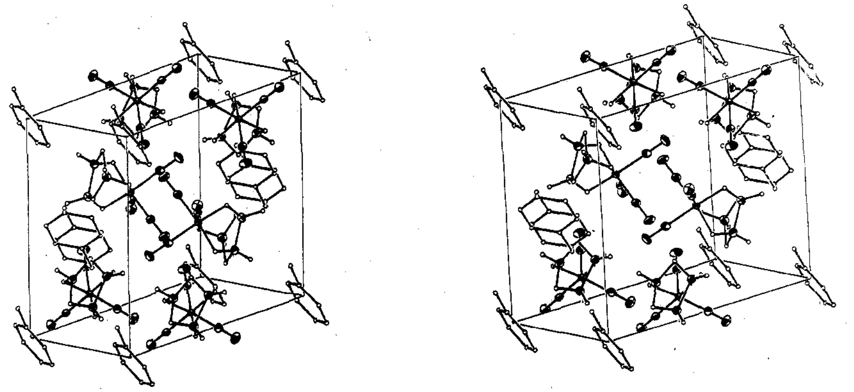

**Figure 3.** A stereoscopic projection of the monoclinic unit cell. The atomic vibration ellipsoids are contoured at the 20% probability level. The hydrogen atoms of the $(CO)_3MnB_3H_8$ molecule and the toluene carbon atoms are represented by spheres of 0.10 Å radius. The nature of the disorder is shown by the toluene molecules in the faces of the unit cell. For reasons of clarity, only one toluene molecule orientation is shown at the vertices of the unit cell, and all toluene hydrogen atoms have been omitted.

**Table II.** Anisotropic Thermal Parameters[a] (×$10^4$) for $(CO)_3MnB_3H_8$

| Atom | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|
| Mn | 31.3 (3) | 171.9 (22) | 34.1 (5) | −3.3 (8) | −1.7 (3) | 5.4 (10) |
| O(1) | 53 (2) | 342 (14) | 97 (4) | −16 (5) | 27 (2) | 28 (6) |
| O(2) | 51 (2) | 456 (17) | 87 (4) | 48 (5) | −6 (2) | 69 (7) |
| O(3) | 85 (9) | 262 (14) | 68 (3) | −19 (5) | 12 (2) | −37 (6) |
| C(1) | 38 (2) | 206 (17) | 63 (4) | 6 (5) | 4 (3) | −6 (6) |
| C(2) | 38 (2) | 287 (17) | 54 (4) | −6 (5) | 6 (2) | 10 (7) |
| C(3) | 52 (3) | 213 (18) | 48 (4) | −8 (5) | 3 (2) | 17 (7) |
| B(1) | 45 (3) | 213 (20) | 57 (5) | −1 (6) | 6 (3) | 3 (7) |
| B(2) | 35 (3) | 287 (23) | 65 (5) | 1 (6) | 9 (3) | 19 (9) |
| B(3) | 33 (3) | 252 (19) | 64 (5) | 8 (6) | −0 (3) | 19 (8) |

[a] Anisotropic temperature factors are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

**Table III.** Interatomic Distances (Å) for $(CO)_3MnB_3H_8$

| | | | |
|---|---|---|---|
| Mn-C(1) | 1.820 (6) | B(1)-B(2) | 1.737 (9) |
| Mn-C(2) | 1.817 (6) | B(1)-B(3) | 1.748 (9) |
| Mn-C(3) | 1.808 (5) | B(1)-H(1) | 0.989 (95) |
| Mn-B(1) | 2.273 (7) | B(1)-H(5) | 1.237 (43) |
| Mn-B(2) | 2.316 (7) | B(1)-H(7) | 1.221 (62) |
| Mn-B(3) | 2.281 (7) | B(2)-B(3) | 1.713 (9) |
| Mn-H(4) | 1.689 (50) | B(2)-H(2) | 1.109 (61) |
| Mn-H(5) | 1.750 (44) | B(2)-H(4) | 1.205 (51) |
| Mn-H(6) | 1.639 (44) | B(2)-H(7) | 1.411 (59) |
| C(1)-O(1) | 1.133 (6) | B(2)-H(8) | 1.310 (63) |
| C(2)-O(2) | 1.129 (6) | B(3)-H(3) | 1.088 (57) |
| C(3)-O(3) | 1.136 (6) | B(3)-H(6) | 1.166 (46) |
| | | B(3)-H(8) | 1.186 (67) |

MB(3), from a range of 115–120° in bidentate complexes to 78.3° in $(CO)_3MnB_3H_8$.

An additional change is the equivalence of the B–B distances within the $B_3H_8^-$ ligand resulting in a nearly equilateral triangle of boron atoms with all BBB angles close to the ideal 60°. In the bidentate complexes the hydrogen bridged B–B distances are significantly longer than the nonbridged B–B distance. The result is a ring of boron atoms in $(CO)_3MnB_3H_8$ that more closely resembles free $B_3H_8^-$[14] than bidentate metal $B_3H_8^-$ complexes.

The octahedral coordination about the manganese atom is shown by inspection of Figure 1 and the appropriate angles in Table IV. The six coordination sites are occupied by three *fac* terminal carbonyl ligands and three *fac* hydrogen atoms. All Mn–H, Mn–B, Mn–C, and C–O bond distances fall in the normally observed ranges for octahedral organometallic[12] and metalloborane[11] manganese complexes. Within the $(CO)_3MnB_3H_8$ molecule all Mn–C bond distances and all C–O bond distances are statistically equivalent. The same equivalence is not observed in the $(CO)_4CrB_3H_8^-$ complex,[9a] in which the axial Cr–C distances are longer than the equatorial Cr–C distances. On the basis of molecular orbital calculations, Guggenberger concluded that an increased back-donation of π-electron density from the chromium atom to the equatorial carbonyl ligands (as compared to the axial carbonyl ligands) was responsible for the observed Cr–C bond length differences in the $(CO)_4CrB_3H_8^-$ molecule.[9a] The equality of the Mn–C and the C–O bond lengths in $(CO)_3MnB_3H_8$ therefore infers that each carbon monoxide ligand in this molecule is bonded to the manganese atom in an identical fashion.

The tetrahedral coordination about each of the boron atoms is preserved in going from the bidentate to the tridentate $B_3H_8^-$ complex. All B–$H_{terminal}$ and B–$H_{bridge}$ distances and angles for B(1) and B(3) in $(CO)_3MnB_3H_8$ are essentially unchanged from the analogous distances and angles in the bidentate complexes. Examination of Table VII, which lists the deviations of several atoms from their idealized plane positions, indicates that the M–H–B and B–H–B bridge hydrogen atoms are further from the B(1)MB(3) and B(1)B(2)B(3) planes in the $(CO)_3MnB_3H_8$ molecule than in the $Be(B_3H_8)_2$[13] molecule. If the boron atoms are to remain as nearly tetrahedral as possible, these changes may be viewed as a necessary geometrical consequence resulting from the folding of the $B_3H_8^-$ group along the B(1)–B(3) bond in its conversion from bidentate to tridentate ligation.

**Table IV.** Intramolecular Bond Angles (deg) for $(CO)_3MnB_3H_8$

| | |
|---|---|
| C(1)-Mn-C(2) | 92.3 (2) |
| C(1)-Mn-C(3) | 90.4 (2) |
| C(1)-Mn-B(1) | 109.4 (2) |
| C(1)-Mn-B(2) | 150.1 (2) |
| C(1)-Mn-B(3) | 109.5 (2) |
| C(1)-Mn-H(4) | 175.2 (16) |
| C(1)-Mn-H(5) | 89.2 (14) |
| C(1)-Mn-H(6) | 87.7 (16) |
| C(2)-Mn-C(3) | 90.7 (2) |
| C(2)-Mn-B(1) | 107.6 (2) |
| C(2)-Mn-B(2) | 108.5 (2) |
| C(2)-Mn-B(3) | 149.0 (2) |
| C(2)-Mn-H(4) | 91.2 (16) |
| C(2)-Mn-H(5) | 83.4 (15) |
| C(2)-Mn-H(6) | 177.3 (16) |
| C(3)-Mn-B(1) | 152.0 (3) |
| C(3)-Mn-B(2) | 110.2 (2) |
| C(3)-Mn-B(3) | 110.3 (2) |
| C(3)-Mn-H(4) | 86.3 (17) |
| C(3)-Mn-H(5) | 174.1 (15) |
| C(3)-Mn-H(6) | 92.0 (16) |
| B(1)-Mn-B(2) | 44.5 (2) |
| B(1)-Mn-B(3) | 45.1 (2) |
| B(1)-Mn-H(4) | 72.6 (18) |
| B(1)-Mn-H(5) | 32.7 (14) |
| B(1)-Mn-H(6) | 69.9 (16) |
| B(2)-Mn-B(3) | 43.7 (2) |
| B(2)-Mn-H(4) | 30.1 (17) |
| B(2)-Mn-H(5) | 72.6 (14) |
| B(2)-Mn-H(6) | 70.6 (16) |
| B(3)-Mn-H(4) | 68.6 (17) |
| B(3)-Mn-H(5) | 75.4 (15) |
| B(3)-Mn-H(6) | 29.2 (16) |
| H(4)-Mn-H(5) | 94.5 (22) |
| H(4)-Mn-H(6) | 89.0 (23) |
| H(5)-Mn-H(6) | 93.9 (22) |
| Mn-C(1)-O(1) | 179.2 (5) |
| Mn-C(2)-O(2) | 179.3 (5) |
| Mn-C(3)-O(3) | 177.9 (5) |
| Mn-B(1)-B(2) | 69.1 (3) |
| Mn-B(1)-B(3) | 67.7 (3) |
| Mn-B(1)-H(1) | 147.4 (58) |
| Mn-B(1)-H(5) | 49.7 (21) |
| Mn-B(1)-H(7) | 99.7 (29) |
| B(2)-B(1)-B(3) | 58.9 (4) |
| B(2)-B(1)-H(1) | 141.0 (56) |
| B(2)-B(1)-H(5) | 109.8 (23) |
| B(2)-B(1)-H(7) | 53.6 (28) |
| B(3)-B(1)-H(1) | 112.5 (56) |
| B(3)-B(1)-H(5) | 112.7 (20) |
| B(3)-B(1)-H(7) | 110.8 (28) |
| H(1)-B(1)-H(5) | 108.2 (58) |
| H(1)-B(1)-H(7) | 109.6 (67) |
| H(5)-B(1)-H(7) | 102.5 (34) |
| Mn-B(2)-B(1) | 66.4 (3) |
| Mn-B(2)-B(3) | 67.0 (3) |
| Mn-B(2)-H(2) | 153.8 (30) |
| Mn-B(2)-H(4) | 44.8 (24) |
| Mn-B(2)-H(7) | 92.1 (24) |
| Mn-B(2)-H(8) | 93.9 (28) |
| B(1)-B(2)-B(3) | 60.9 (4) |
| B(1)-B(2)-H(2) | 133.1 (30) |
| B(1)-B(2)-H(4) | 107.4 (24) |
| B(1)-B(2)-H(7) | 44.1 (26) |
| B(1)-B(2)-H(8) | 102.8 (31) |
| B(3)-B(2)-H(2) | 134.6 (30) |
| B(3)-B(2)-H(4) | 102.1 (24) |
| B(3)-B(2)-H(7) | 103.6 (27) |
| B(3)-B(2)-H(8) | 43.7 (30) |
| H(2)-B(2)-H(4) | 109.4 (37) |
| H(2)-B(2)-H(7) | 95.2 (38) |
| H(2)-B(2)-H(8) | 97.0 (41) |
| H(4)-B(2)-H(7) | 110.6 (35) |
| H(4)-B(2)-H(8) | 102.0 (37) |
| H(7)-B(2)-H(8) | 138.8 (41) |
| Mn-B(3)-B(1) | 67.2 (3) |
| Mn-B(3)-B(2) | 69.2 (3) |
| Mn-B(3)-H(3) | 153.3 (31) |
| Mn-B(3)-H(6) | 43.2 (21) |
| Mn-B(3)-H(8) | 99.4 (32) |
| B(1)-B(3)-B(2) | 60.2 (4) |
| B(1)-B(3)-H(3) | 117.2 (29) |
| B(1)-B(3)-H(6) | 102.5 (21) |
| B(1)-B(3)-H(8) | 108.0 (31) |
| B(2)-B(3)-H(3) | 137.0 (31) |
| B(2)-B(3)-H(6) | 108.0 (22) |
| B(2)-B(3)-H(8) | 49.8 (31) |
| H(3)-B(3)-H(6) | 113.9 (37) |
| H(3)-B(3)-H(8) | 103.5 (42) |
| H(6)-B(3)-H(8) | 111.9 (39) |
| Mn-H(4)-B(2) | 105.1 (33) |
| Mn-H(5)-B(1) | 97.6 (26) |
| Mn-H(6)-B(3) | 107.6 (30) |
| B(1)-H(7)-B(2) | 82.3 (35) |
| B(2)-H(8)-B(3) | 86.5 (42) |

It is interesting to note that the internuclear distances and angles around B(2) do not change significantly upon transformation from bidentate to tridentate $B_3H_8^-$ ligand functionality. For example, H(4) is a terminal hydrogen in bidentate $B_3H_8^-$ complexes and a M–H–B bridge hydrogen in the tridentate $B_3H_8^-$ complex. The H(2)–B(2)–H(4) angles, however, are effectively identical in the two types of complexes. Molecular orbital calculations for uncomplexed $B_3H_8^-$[15] and

Table V. Final Atomic Positional Parameters (×10⁴) and Thermal Parameters (Å²) for the Toluene Molecule

| Atom | *x* | *y* | *z* | *B*, Å² |
|---|---|---|---|---|
| C(4) | 9757 | 5011 | 5545 | 5.3 (3) |
| C(5) | 9749 | 3178 | 4800 | 5.1 (5) |
| C(6) | 10223 | 3239 | 3865 | 7.2 (4) |
| C(7) | 10705 | 5134 | 3675 | 6.6 (4) |
| C(8) | 10714 | 6967 | 4420 | 5.6 (3) |
| C(9) | 10240 | 6906 | 5355 | 6.8 (7) |
| C(10) | 9239 | 4945 | 6568 | 12.4 (10) |
| H(9) | 9418 | 1884 | 4930 | 8.0 |
| H(10) | 10216 | 1986 | 3355 | 8.0 |
| H(11) | 11029 | 5175 | 3035 | 8.0 |
| H(12) | 11044 | 8262 | 4289 | 8.0 |
| H(13) | 10246 | 8160 | 5864 | 8.0 |
| H(14) | 9563 | 4317 | 7208 | 8.0 |
| H(15) | 9074 | 6442 | 6746 | 8.0 |
| H(16) | 8757 | 4038 | 6388 | 8.0 |
| H(17) | 8699 | 5548 | 6353 | 8.0 |
| H(18) | 9188 | 3424 | 6815 | 8.0 |
| H(19) | 9505 | 5828 | 7173 | 8.0 |

for $(CO)_4CrB_3H_8^-$ [9a] indicate that the unique boron atom, B(2), is more positively charged than B(1) and B(3). This is supported by the observation that the relatively positively charged B–H–B bridge hydrogen atoms are closer to B(1) and B(3) than to B(2) in all known $B_3H_8^-$ species. This same trend is also observed in $(CO)_3MnB_3H_8$ although the four B–H–B bridged hydrogen–boron distances are statistically equivalent within the error limits of this study.

The electron bookkeeping for $(CO)_3MnB_3H_8$ can be systematized according to three different methods. Using the effective atomic number (EAN) rule,[16] the center of attention is on the manganese atom. By this method the compound can formally be viewed as consisting of $Mn^0$ with a neutral $B_3H_8^0$ ligand or as $Mn^+$ with a $B_3H_8^-$ ligand. Using the latter assignment, the 36 electrons needed to achieve the rare gas configuration of krypton are contributed in the following manner: $Mn^+$ has 24 electrons, six electrons are donated from the three carbonyl ligands and six electrons are donated from the metal–hydrogen–boron bridges. In this way, each Mn–H–B unit can be considered as a two-electron three-center bond, a common convention used to describe the bonding in electron-deficient boron hydrides.[17] The second bookkeeping method, Wade's rules,[18] focuses attention on the boron hydride fragment. The number of skeletal bonding electrons can be counted as follows: six electrons are contributed by the $B–H_{terminal}$ groups (two electrons per BH), five electrons are donated by the bridging hydrogen atoms in the molecule (one electron per Mn–H–B and one electron per B–H–B), and an additional electron comes from the $(CO)_3Mn^0$ [18] moiety, giving a total of 12 cage bonding electrons in the system. There are two electron pairs in excess of the one pair per vertex atom [the manganese atom and the three boron atoms form the four vertices of the system (bridge hydrogen atoms contribute electrons to the skeletal bonding framework but cannot be counted as vertices)]. Thus $(CO)_3MnB_3H_8$ can be considered to be a nido species derived from a trigonal bipyramid via removal of an apical vertex. The third structural categorization method uses a model suggested by Glidewell.[19] The number of skeletal bonding electrons in the system is counted by Wade's method, as outlined above, giving a total of 12 cage electrons for $(CO)_3MnB_3H_8$. According to Glidewell's method, a distorted tetrahedron of $C_{3v}$ symmetry (and a p-orbital basis set) has $A_1' + E' + A' + E''$ bonding molecular orbitals and will achieve a closed shell configuration with 12 cage electrons.

The crystal packing and the nature of the toluene disorder on the inversion centers are shown in the stereoscopic projection

Table VI. Comparison of $(CO)_3MnB_3H_8$ to Bidentate $B_3H_8^-$ Complexes and to Free $B_3H_8^-$

| | $(CO)_3MnB_3H_8$ | $[(CO)_4CrB_3H_8]^-$ [c] | $(Ph_3P)_2CuB_3H_8$ [d] | $Be(B_3H_8)_2$ [e] | $B_4H_{10}$ [f] | $B_3H_8^-$ [g] |
|---|---|---|---|---|---|---|
| Bond,[a] Å | | | | | | |
| B(1)–B(2) and B(2)–B(3) | 1.725 (9) | 1.82 (1) | 1.82 (2) | 1.834 (4) | 1.845 (2) | 1.77 |
| B(1)–B(3) | 1.748 (9) | 1.78 (1) | 1.76 (1) | 1.766 (3) | 1.750 | 1.80 |
| $B–H_{terminal}$ | 0.99 (10)–1.11 (6) | 1.07 (7)–1.22 (9) | 1.0 (1)–1.3 (1) | 1.05 (2)–1.14 (2) | 1.03 (4)–1.17 (4) | 1.05–1.20 |
| B(1)–H(5) and B(3)–H(6) | 1.20 (4) | 1.29 (6) | 1.21 (6) | 1.17 (2) | 1.21 (3) | *m* |
| [B(2)–H(4)][b] | [1.21 (5)] | | | | | |
| B(1)–H(7) and B(3)–H(8) | 1.20 (6) | 1.15 (7) | 1.16 (9) | 1.12 (2) | 1.21 (3) | 1.2 |
| B(2)–H(7) and B(2)–H(8) | 1.36 (6) | 1.43 (7) | 1.52 (9) | 1.34 (2) | 1.37 (10) | 1.5 |
| M–H(5) and M–H(6) | 1.69 (4)[h] | 1.78 (6)[i] | 1.85 (5)[j] | 1.50 (2)[k] | 1.37 (10)[l] | *m* |
| [M–H(4)][b] | 1.69 (5)[h] | | | | | |
| Angle, Deg | | | | | | |
| B(2)–B(1)–B(3) and B(1)–B(3)–B(2) | 59.6 (4) | 60.8 | 60.8 | 61.2 (1) | 61.7 | 59.5 |
| B(1)–B(2)–B(3) | 60.9 (4) | 58.4 | 58.5 | 57.5 (1) | 56.6 | 61.1 |
| B(1)–H(7)–B(2) and B(2)–H(8)–B(3) | 84 (4) | 89 (4) | 82 (5) | 96 (1) | 92 | 81 |
| B(1)–H(5)–M and B(3)–H(6)–M | 103 (3)[h] | 104 (4)[i] | 99 (3)[j] | 94 (1)[k] | 92[l] | *m* |
| [B(2)–H(4)–M][b] | [105 (3)][h] | | | | | |
| H(5)–B(1)–H(7) and H(6)–B(3)–H(8) | 107 (4) | 89 (4) | 101 (4) | 99 (1) | 96 | *m* |
| [H(4)–B(2)–H(7) and H(4)–B(2)–H(8)][b] | [106 (4)] | | | | | |
| H(2)–B(2)–H(4) | 109 (4) | 115 (6) | 110 (7) | 122 (2) | 125 | *m* |
| H(7)–B(2)–H(8) | 139 (4) | 134 (5) | 144 (5) | 133 (1) | 135 | 145 |
| H(5)–M–H(6) | 94 (2)[h] | 101 (4)[i] | 103 (2)[j] | 125 (1)[k] | 135[l] | *m* |
| [H(4)–M–H(5) and H(4)–M–H(6)][b] | [92 (2)][h] | | | | | |
| Dihedral Angle between Planes, Deg | | | | | | |
| B(1)B(2)B(3) to B(1)MB(3) | 78.3[h] | 118.5[i] | 119.3[j] | 115.0 (2)[k] | 118.1[l] | *m* |

[a] The numbering systems in the various literature citations have been altered so that the bond and angle designations listed here are internally consistent. For each of the complexes listed here the values reported in the table are averages assuming $C_s$ symmetry for the $B_3H_8^-$ unit (i.e., a mirror plane through B(2) and the midpoint of the B(1)–B(3) bond). [b] The values in brackets are unique to the tridentate $B_3H_8^-$ ligand. [c] Reference 4a. [d] Reference 9d. [e] Reference 13. [f] C. E. Nordman and W. N. Lipscomb, *J. Chem. Phys.*, 21, 1856 (1953). [g] Reference 14. [h] M = Mn. [i] M = Cr. [j] M = Cu. [k] M = Be. [l] M = B. [m] Unavailable or not symmetry related to $(CO)_3MnB_3H_8$.

**Table VII.** Deviation of Selected Atoms from Selected Planes

| Plane | Atom | Deviation of atom from plane, Å | Atom | Deviation of atom from plane, Å |
|---|---|---|---|---|
| MnB(1)B(2) | H(1) | 0.172 | H(5) | −0.568 |
| | H(2) | −0.293 | H(7) | −0.847 |
| | H(4) | −0.364 | | |
| MnB(1)B(3) | H(1) | 0.529 | H(6) | 0.490[a,b] |
| | H(3) | 0.471 | H(7) | −1.140 |
| | H(5) | 0.425[a,b] | H(8) | −1.126 |
| MnB(2)B(3) | H(2) | 0.245 | H(6) | 0.369 |
| | H(3) | −0.078 | H(8) | 0.756 |
| | H(4) | 0.561 | | |
| B(1)B(2)B(3) | H(1) | −0.621 | H(5) | 1.123 |
| | H(2) | −0.660 | H(6) | 1.106 |
| | H(3) | −0.732 | H(7) | −0.275[c,d] |
| | H(4) | 1.146 | H(8) | −0.282[c,d] |

[a] In $(Ph_3P)_2CuB_3H_8$ these bridge hydrogens are 0.38 and 0.40 Å above the CuB(1)B(3) plane.[9d] [b] In $Be(B_3H_8)_2$ these bridge hydrogens are displaced an average of 0.092 Å above the BeB(1)B(3) plane.[13] [c] In $(Ph_3P)_2CuB_3H_8$ these bridge hydrogens are +0.2 and −0.8 Å out of the plane defined by the boron atoms. [d] In $Be(B_3H_8)_2$ these bridge hydrogens are an average of 0.026 Å out of the B(1)B(2)B(3) plane.

of the unit cell in Figure 3. The $(CO)_3MnB_3H_8$ exists as discrete molecules and exhibits normal van der Waals packing with the cocrystallized toluene molecules. The closest distance of 3.202 Å is between carbonyl oxygen atoms of adjacent molecules, while the closest toluene nonbonding distance is 3.753 Å from the toluene methyl carbon C(1) and B(2) of an adjacent molecule.

**Acknowledgment.** This work has been supported in part by grants from the National Science Foundation.

**Registry No.** $(CO)_3MnB_3H_8$, 53801-96-0; $(CO)_4MnB_3H_8$, 53801-97-1.

**Supplementary Material Available:** A listing of observed and calculated structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

## References and Notes

(1) D. F. Gaines and S. J. Hildebrandt, *J. Am. Chem. Soc.*, **96**, 5574 (1974). The solution structure of $(CO)_3MnB_3H_8$ is discussed in greater detail in ref 3.
(2) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds", McGraw-Hill, New York, N.Y., 1969.
(3) D. F. Gaines and S. J. Hildebrandt, *Inorg. Chem.*, companion paper in this issue.
(4) "International Tables for X-Ray Crystallography", Vol. I, 2nd ed, The Kynoch Press, Birmingham, England, 1965, p 99.
(5) Programs used in the structural determination and refinement included ORFLS and ORFFE, the W. P. Busing, K. O. Martin, and H. A. Levy least-squares and error analysis programs; and ORTEP 2, the C. K. Johnson thermal ellipsoid plotting program. All other crystallographic programs used were written by J.C.C.
(6) $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $R_2 = [\sum w_i(|F_o| - |F_c|)^2/\sum w_i|F_o|^2]^{1/2}$. The standard deviation of an observation of unit weight is defined as $[w_i(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, where $m$ is the number of observations and $n$ is the number of parameters fitted to the data.
(7) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964).
(8) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(9) (a) L. J. Guggenberger, *Inorg. Chem.*, **9**, 367 (1970); (b) F. Klanberg, E. L. Muetterties, and L. J. Guggenberger, *ibid.*, **7**, 2272 (1968); (c) S. J. Lippard and D. A. Ucko, *ibid.*, **7**, 1051 (1968); (d) S. J. Lippard and K. M. Melmed, *ibid.*, **8**, 2755 (1969); (e) E. L. Muetterties, W. G. Peet, P. A. Wegner, and C. W. Alegranti, *ibid.*, **9**, 2447 (1970); (f) F. Klanberg and L. J. Guggenberger, *Chem. Commun.*, 1293 (1967); (g) D. F. Gaines and J. H. Morris, *ibid.*, 626 (1975); (h) H. Beall, C. H. Bushweller, W. J. Dewkett, and M. Grace, *J. Am. Chem. Soc.*, **92**, 3484 (1970); (i) C. H. Bushweller, H. Beall, M. Grace, W. Dewkett, and H. Bilofsky, *ibid.*, **93**, 2145 (1971); (j) J. Borlin and D. F. Gaines, *ibid.*, **94**, 1367 (1972); (k) S. Hermanek and J. Plesek, *Collect. Czech. Chem. Commun.*, **31**, 177 (1966).
(10) An additional mode of bonding, π-borallyl, is encountered when the ligand is $B_3H_7^{2-}$: (a) A. R. Kane and E. L. Muetterties, *J. Am. Chem. Soc.*, **93**, 1041 (1971); (b) L. J. Guggenberger, A. R. Kane, and E. L. Muetterties, *ibid.*, **94**, 5665 (1972).
(11) (a) H. D. Kaesz, W. Fellmann, G. R. Wilkes, and L. F. Dahl, *J. Am. Chem. Soc.*, **87**, 2753 (1965); (b) J. W. Lott, D. F. Gaines, H. Shenhav, and R. Schaeffer, *ibid.*, **95**, 3042 (1973); (c) J. C. Calabrese, M. B. Fischer, D. F. Gaines, and J. W. Lott, *ibid.*, **96**, 6318 (1974); (d) J. W. Lott and D. F. Gaines, *Inorg. Chem.*, **13**, 2261 (1974); (e) D. F. Gaines, J. W. Lott, and J. C. Calabrese, *ibid.*, **13**, 2419 (1974).
(12) (a) L. F. Dahl and R. E. Rundle, *Acta Crystallogr.*, **16**, 419 (1963); (b) S. J. LaPlaca, W. C. Hamilton, J. A. Ibers, and A. Davison, *Inorg. Chem.*, **8**, 1928 (1969).
(13) J. C. Calabrese, D. F. Gaines, S. J. Hildebrandt, and J. H. Morris, *J. Am. Chem. Soc.*, **98**, 5489 (1976).
(14) C. R. Peters and C. E. Nordman, *J. Am. Chem. Soc.*, **82**, 5738 (1960).
(15) W. N. Lipscomb, "Boron Hydrides", W. A. Benjamin, New York, N.Y., 1963, p 110.
(16) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed, Wiley, New York, N.Y., 1972, p 683.
(17) W. N. Lipscomb, "Boron Hydrides", W. A. Benjamin, New York, N.Y., 1963, Chapter 2.
(18) K. Wade, *Adv. Inorg. Chem. Radiochem.*, **18**, 1 (1976).
(19) C. Glidewell, *Inorg. Nucl. Chem. Lett.*, **11**, 761 (1975).

---

Contribution from the Department of Chemistry,
University of Wisconsin, Madison, Wisconsin 53706

# Syntheses and Properties of Some Neutral Octahydrotriborate(1−) Complexes of Chromium-, Manganese-, and Iron-Group Metals

DONALD F. GAINES* and STEVEN J. HILDEBRANDT

*Received August 30, 1977*

Reaction of selected complexes of the type $L_n(CO)MX$ with salts and derivatives of $B_3H_8^-$ has produced $(CO)_4MnB_3H_8$, $(CO)_4ReB_3H_8$, $(\eta^5\text{-}C_5H_5)(CO)FeB_3H_8$, $(H)(CO)_3FeB_3H_8$, $(\eta^5\text{-}C_5H_5)(CO)_2MoB_3H_8$, $(\eta_5\text{-}C_5H_5)(CO)_2WB_3H_8$, $[(C_6H_5)_3]P(CO)_3MnB_3H_8$, and $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2](CO)_2MnB_3H_8$. In these complexes $B_3H_8^-$ is a bidentate ligand via two M–H–B bridge hydrogen bonds. $(CO)_4MnB_3H_8$ undergoes reversible decarbonylation yielding $(CO)_3MnB_3H_8$, in which the $B_3H_8^-$ ligand is tridentate. $(CO)_4MnB_3H_8$ reacts with $Br_2$ and $Cl_2$ to produce $(CO)_4MnB_3H_7Br$ (or Cl), the halogen substitution occurring at the boron atom not bound to manganese. Detailed $^{11}B$ and $^1H$ NMR studies of these complexes reveal their structures and some examples of interesting selective intramolecular hydrogen exchange phenomena.

## Introduction

Several main-group and transition-metal complexes containing the octahydrotriborate(1−) ligand, $B_3H_8^-$, have been reported during the last decade. Representative examples include $[(C_6H_5)_3P]_2CuB_3H_8$,[1] $(C_5H_5)_2TiB_3H_8$,[2a] $[(CO)_4Cr\text{-}B_3H_8^-]$,[2] $(CH_3)_2GaB_3H_8$,[3] and $Be(B_3H_8)_2$.[4] Single-crystal x-ray studies of three[1c,2c,4b] of these complexes show that the bidentate $B_3H_8^-$ ligand is bound to metals via two M–H–B three-center two-electron bridge hydrogen bonds from adjacent boron atoms. Spectroscopic studies suggest similar static structures for all $M\text{–}B_3H_8$ complexes except $(CO)_3MnB_3H_8$, vide infra. Some of the complexes have low barriers to partial

0020-1669/78/1317-0794$01.00/0 © 1978 American Chemical Society