

A *nido*-6-manganadecaborane salt

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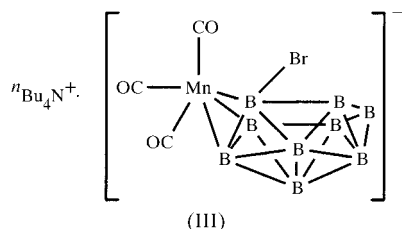
Received 8 August 2000

Accepted 6 December 2000

A new manganadecaborane has been isolated as a previously unsuspected product from the reaction of $[\text{Mn}(\text{CO})_5\text{Br}]$ with $\text{K}[\text{B}_9\text{H}_{14}]$. The anion of tetrabutylammonium 5-bromo-6,6,6-tricarbonyl-6-manganadodecahydrodecaborate(1-), $(\text{C}_{16}\text{H}_{36}\text{N})[\text{Mn}(\text{B}_9\text{H}_{12}\text{Br})(\text{CO})_3]$, has a *nido* cage structure. The Mn atom is bonded through three B—Mn bonds of similar length [2.221 (4), 2.224 (3) and 2.236 (3) Å] and two bridging H atoms. The position of the bromo substituent breaks the twofold symmetry of the cage found in simple analogues, and this is reflected in the B—B bond parameters.

Comment

Reactions between $[\text{Mn}(\text{CO})_5\text{Br}]$ and $\text{K}[\text{B}_9\text{H}_{14}]$ have been shown to produce a range of *nido*-metalloboranes, including salts of the $[\text{6}-(\text{CO})_3\text{-6-Mn}(\text{B}_9\text{H}_{13})]^-$ anion and the neutral isomeric species $[\text{2}-(\text{thf})\text{-6}-(\text{CO})_3\text{-6-Mn}(\text{B}_9\text{H}_{12})]$, (I), and $[\text{5}-(\text{thf})\text{-6}-(\text{CO})_3\text{-6-Mn}(\text{B}_9\text{H}_{12})]$, (II) (where thf is tetrahydrofuran; Lott *et al.*, 1973; Lott & Gaines, 1974). In our hands, the reaction also produces the previously unknown bromo-substituted anion $[\text{5-Br-6}-(\text{CO})_3\text{-6-Mn}(\text{B}_9\text{H}_{12})]^-$, which we have isolated and characterized as the tetra-*n*-butylammonium salt, (III).



Crystallographic analysis of the dark-red crystals obtained showed (III) to consist of discrete cations and anions which are separated by at least van der Waals distances. Although the *n*-butyl arms of the cation are rotationally disordered, the metalloborane anion seems to be unaffected. Fig. 1 shows that the coordination geometry about Mn1 to be quasi-octahedral with the two bridging H atoms *trans* to carbonyl ligands. The main distortion from idealized geometry is the C1—Mn1—B2 angle of 161.4 (1)°. The terdentate bonding of the borane cage to manganese through only three B atoms is relatively unusual and can be described as arising from a formal neutral

$[\text{Mn}(\text{CO})_3]$ vertex which contributes one electron and three orbitals to the cluster bonding (Kennedy, 1986). The only relevant compounds found in a search of the Cambridge Structural Database (Allen & Kennard, 1993) were (I), (II), and the related zwitterion $[\text{8}-(\text{C}_2\text{H}_5)_3\text{N}(\text{CH}_2)_4\text{O}]\text{-6}-(\text{CO})_3\text{-6-Mn}(\text{B}_9\text{H}_{12})$, (IV) (Gaines *et al.*, 1974), although similar interactions have been proposed for other compounds (see, for example, Fischer & Gaines, 1979). These three compounds display non-symmetrical bonding to the metal, as is shown by both their B5—B2 and B2—B7 distances [1.764 (6) and 1.807 (6) Å for (II), and 1.783 (9) and 1.816 (10) Å for (IV)] and by their Mn—B bond lengths [ranges 2.206 (5)—2.232 (4) and 2.209 (6)—2.262 (7) Å for (II) and (IV), respectively]. A related Mo compound which also has a five-substituted halogen atom similar to (III), *i.e.* $[\text{5-Cl-6}-(\text{CO})_2\text{-6}-(\text{PPhMe}_2)_2\text{-6-Mo}(\text{B}_9\text{H}_{12})]$ (Greenwood *et al.*, 1986), also shows non-symmetrical bonding. This contrasts with the more symmetrical bonding mode of (III) (see Table 1). The B5—Br1 distance of 2.025 (3) Å lies near the upper limit found for B—Br bonds (range of 1.881–2.052 Å for 3652 fragments), presumably as a consequence of electron withdrawal by the metal. The overall geometry of the boron cage is similar to that of $\text{B}_{10}\text{H}_{14}$ (Brill *et al.*, 1971), but the two long B—B bonds, B5—B10 and B7—B8, are now different from each other [1.994 (5) and 2.027 (6) Å] due to the unsymmetrical position of the halide substituent. The remaining B—B bond lengths range from 1.713 (5) to 1.801 (5) Å.

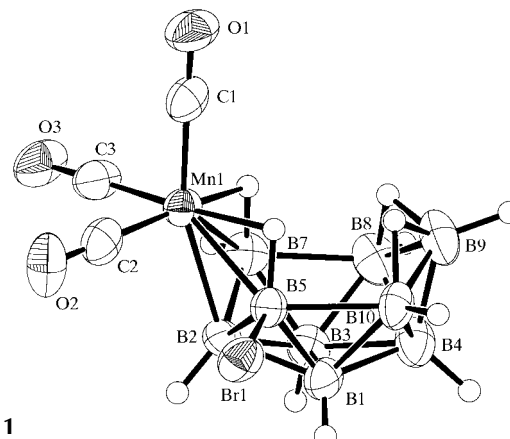


Figure 1
ORTEP (Johnson, 1976) view of the anion of (III) with non-H atoms shown with 50% probability ellipsoids and H atoms as small spheres of arbitrary size.

Experimental

Compound (III) was synthesized by adaption of the method of Lott & Gaines (1974) and was recrystallized from a water, ethanol and CH_2Cl_2 solution by slow evaporation.

Crystal data

$(\text{C}_{16}\text{H}_{36}\text{N})[\text{Mn}(\text{B}_9\text{H}_{12}\text{Br})(\text{CO})_3]$
 $M_r = 570.72$
 Monoclinic, $P2_1/n$
 $a = 11.7469$ (1) Å
 $b = 18.2581$ (2) Å
 $c = 14.5558$ (1) Å
 $\beta = 101.352$ (1)°
 $V = 3060.79$ (5) Å³
 $Z = 4$

$D_x = 1.239$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 34786 reflections
 $\theta = 1.81$ – 27.48 °
 $\mu = 1.757$ mm⁻¹
 $T = 150$ (2) K
 Plate, dark red
 $0.20 \times 0.20 \times 0.05$ mm

Data collection

Nonius KappaCCD diffractometer
 φ and ω scans to fill Ewald sphere
 Absorption correction: multi-scan
 (Blessing, 1997)
 $T_{\min} = 0.71$, $T_{\max} = 0.92$
 34786 measured reflections
 6964 independent reflections

5105 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.053$
 $\theta_{\max} = 27.48^\circ$
 $h = -15 \rightarrow 15$
 $k = -22 \rightarrow 23$
 $l = -18 \rightarrow 18$
 Intensity decay: $<2\%$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.143$
 $S = 1.03$
 6964 reflections
 353 parameters
 H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0796P)^2 + 1.8574P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.02 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.52 \text{ e } \text{\AA}^{-3}$
 Extinction correction: *SHELXL97*
 (Sheldrick, 1997)
 Extinction coefficient: 0.0048 (7)

Table 1

Selected bond lengths (Å).

Br1—B5	2.025 (3)	B2—B5	1.789 (4)
Mn1—C2	1.789 (4)	B2—B7	1.797 (5)
Mn1—C3	1.793 (3)	B3—B8	1.736 (6)
Mn1—C1	1.802 (3)	B3—B7	1.748 (5)
Mn1—B7	2.221 (4)	B3—B4	1.801 (5)
Mn1—B2	2.224 (3)	B4—B9	1.713 (6)
Mn1—B5	2.236 (3)	B4—B8	1.769 (7)
B1—B5	1.737 (5)	B4—B10	1.782 (5)
B1—B10	1.753 (5)	B5—B10	1.994 (5)
B1—B3	1.768 (5)	B7—B8	2.027 (6)
B1—B2	1.777 (5)	B8—B9	1.773 (5)
B1—B4	1.785 (6)	B9—B10	1.784 (6)
B2—B3	1.771 (5)		

The cation disorder was modelled by treating seven of the C atoms as split across two sites [occupancies 0.735 (4) and 0.265 (4)]. The atoms of the minor component were refined isotropically. H atoms of the borane cage were positioned as found in difference syntheses and were then allowed to ride on their parent B atoms with only their U_{iso} values refined. H atoms of the cation were placed in calculated

positions and in a riding mode for the major disorder component but were omitted from the minor disorder component. The methyl-group orientations were obtained by refining torsional parameters. The largest residual electron-density peaks all lie in the vicinity of the disordered cation and have values of 1.02, 0.65 and 0.50 e Å⁻³.

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); software used to prepare material for publication: *SHELXL97*.

We thank the EPSRC X-ray crystallography service at the University of Southampton for data collection.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1569). Services for accessing these data are described at the back of the journal.

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