

## The Synthesis and Molecular Structure of a Metalloborane Zwitterion $\text{Mn}(\text{CO})_3[\text{B}_9\text{H}_{12}\{\text{O}(\text{CH}_2)_4\text{NEt}_3\}]$

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**Summary** Reaction of  $\text{Mn}(\text{CO})_3[\text{B}_9\text{H}_{12}(\text{THF})]$  with triethylamine produces the zwitterion  $\text{Mn}(\text{CO})_3[\text{B}_9\text{H}_{12}\{\text{O}(\text{CH}_2)_4\text{NEt}_3\}]$ , the structure of which has been determined by X-ray crystallography.

RECENTLY we reported the first examples of a new series of air-stable metalloboranes in which the metal, manganese, appeared to be bonded to the borane framework by a sigma-type bond and by metal-hydrogen-boron bridge bonds to two other boron atoms.<sup>1</sup> We report here the reaction of one of these metalloboranes with triethylamine and the characterization of the unexpected product.

In refluxing tetrahydrofuran (THF),  $\text{Mn}(\text{CO})_3[\text{B}_9\text{H}_{12}(\text{THF})]$  reacts with triethylamine to produce a moderate yield (27%) of a product (I) that was initially thought to be  $\text{Mn}(\text{CO})_3[\text{B}_9\text{H}_{12}(\text{NEt}_3)]$ . However, the <sup>11</sup>B n.m.r. spectrum of (I) consisted of a singlet at -21.8 p.p.m. and seven BH doublets ranging from -14.8 to +36.0 p.p.m. ( $\text{BF}_3 \cdot \text{OEt}_2$  reference), suggesting that the reaction had produced a material having very low symmetry. The product initially expected would have had a plane of symmetry, as does the starting material, and a maximum of six different boron environments. The <sup>1</sup>H n.m.r. spectrum of (I) contained four types of bridge hydrogens, two in the B-H-B region ( $\tau$ 10.99 and 13.05) and two in the Mn-H-B region ( $\tau$ 20.80 and 21.78). Further, a quartet at 6.30 and a related triplet at 8.83 (with fine structure arising from <sup>14</sup>N coupling) appeared to be very similar to ethyl group resonances observed for tetraethylammonium salts.<sup>2</sup> Other CH resonances were observed but could not be assigned. As these data did not lead to an unambiguous structural assignment, a single-crystal X-ray study was initiated.

**Crystal data:** Crystallization of (I) from  $\text{CH}_2\text{Cl}_2$ -heptane produced orange-red plates in the triclinic space group  $P\bar{1}$ ;  $a = 10.018(2)$ ,  $b = 12.843(3)$ ,  $c = 9.305(2)$  Å,  $\alpha = 99.661-$

$(15)^\circ$ ,  $\beta = 94.543(14)^\circ$ ,  $\gamma = 96.918(15)^\circ$ ,  $U = 1165.54(35)$  Å<sup>3</sup>,  $D_m = 1.207$  g cm<sup>-3</sup>,  $D_c = 1.201$  g cm<sup>-3</sup> for  $Z = 2$  (421.65). A total of 3307 data were measured at room temperature on a Syntex P1 auto-diffractometer using monochromated Cu-K $\alpha$  radiation. Of the 1857 independent observations 1803 had  $I > 2\sigma(I)$  and were used in the structure analysis.

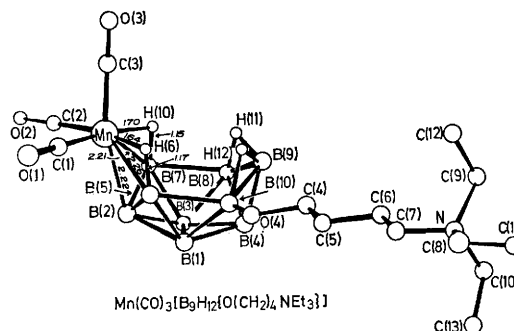


FIGURE. The molecular structure of  $\text{Mn}(\text{CO})_3[\text{B}_9\text{H}_{12}\{\text{O}(\text{CH}_2)_4\text{NEt}_3\}]$ . Terminal hydrogen atoms on B(1)-B(9) and C(4)-C(13) have been eliminated for clarity.

The structure was solved using conventional heavy atom techniques. After several cycles of full-matrix least-squares refinement, a difference electron density function revealed positions for all hydrogen atoms. Subsequent refinement of the crystal absorption corrected data including hydrogen positions and anisotropic temperature factors for all non-hydrogen atoms finally yielded  $R_1 = 0.056$  and  $R_2 = 0.061$ . The molecular structure of (I), shown in the Figure, is that of a zwitterion in which the formal positive charge is on the nitrogen atom and the negative charge is considered

to be delocalized over the  $MnB_9$  framework. Several important interatomic distances are shown on the Figure. Other distances are similar to those expected from previous structural studies of metal carbonyls,  $B_{10}H_{14}^3$  and alkyl ammonium salts.<sup>4</sup>

Cleavage of complexed THF by an amine and formation of a zwitterion appears to be unprecedented in borane and metalborane chemistry. The shift of the boron-oxygen linkage from B(2) in the reactant  $Mn(CO)_3[B_9H_{12}(THF)]$  to

B(10) in the product indicates that a complex rearrangement occurs during the course of the reaction. Further studies of this unusual type of reaction and rearrangement are in progress.

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<sup>1</sup> J. W. Lott, D. F. Gaines, H. Shenhav, and R. Schaeffer, *J. Amer. Chem. Soc.*, in the press.

<sup>2</sup> D. F. Hillenbrand, personal communication.

<sup>3</sup> J. S. Kasper, C. M. Lucht, and D. Harker, *Acta Cryst.*, 1950, **3**, 436.

<sup>4</sup> L. B. Handy, J. K. Ruff, and L. F. Dahl, *J. Amer. Chem. Soc.*, 1970, **92**, 7312.