X-Ray Crystallographic Determination of the Molecular Structure of $B_9C_2H_{12}AlMe_2$, a Non-rigid Aluminio-carborane Derivative

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Summary Determination of the molecular structure of $B_9C_2H_{12}AlMe_2$ by single-crystal *X*-ray diffraction techniques, shows that the aluminium atom is involved in bonding only to *two* boron atoms of the $B_9C_2H_{12}$ icosahedral fragment: ^{11}B n.m.r. studies suggest that, in solution, the molecule undergoes rapid intramolecular rearrangements.

THE preparation of the aluminio-carborane species $B_9C_2H_{11}$-AlR and $B_9C_2H_{12}AlR_2$ (R = Me, Et) has been reported recently.[1] A structural study of $B_9C_2H_{11}AlEt$ has shown the aluminium atom to be symmetrically bonded to the pentagonal B_3C_2 face of a 1,2-dicarbollide ligand.[1] We now report a low temperature *X*-ray diffraction study on $B_9C_2H_{12}AlMe_2$, and some results on its unusual tautomeric nature.

Crystal data: $C_4H_{18}B_9Al$, $M = 190{\cdot}54$, triclinic, $a = 7{\cdot}46$, $b = 6{\cdot}46$, $c = 6{\cdot}99$ Å, $\alpha = 115{\cdot}4$, $\beta = 97{\cdot}0$, $\gamma = 87{\cdot}6°$, $D_c = 1{\cdot}05$ g cm^{-3}, $Z = 1$, space group $P1$ (C_1^1; No. 1). (The density was not measured, due to the great air- and moisture-sensitivity of the compound.)

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Preliminary studies showed the crystals to decompose in an X-ray beam within *ca.* 1 h at room temperature. The crystallographic analysis was therefore carried out at $-100°$, using the conventional cold N_2-stream technique. Single-crystals were sealed into Lindemann glass capillary tubes and diffraction data for the levels 0—6*kl* and *h*0—2*l* were collected photographically with a Weissenberg camera. All data were corrected for absorption ($\mu = 10{\cdot}1$ cm^{-1} for Cu-K_α radiation) and the structure was solved using Fourier and isotropic least-squares refinement techniques. All non-hydrogen atoms have been located, the present discrepancy index being $R = 0{\cdot}16$ for 902 independent non-zero reflections. [We attribute the rather high R value to two principal causes: (i) significant decomposition of crystals even at $-100°$; (ii) insufficiently precise temperature control (from one Weissenberg layer to the next) on our home-built cooling system.] A difference-Fourier map yielded no information as to the positions of hydrogen atoms.

The geometric arrangement of aluminium, carbon, and boron atoms is illustrated in the Figure.

Distances of the aluminium atom from the five atoms on the open pentagonal face are: Al–B(7) = 2·33(2), Al–B(8) = 2·28(2), Al–C(2) = 3·65(2), Al–C(1) = 4·36(2), and Al–B(4) = 3·90(2) Å. The aluminium–methyl distances are Al–Me(1) = 1·93(2) and Al–Me(2) = 1·94(2) Å [*cf.* Al–Et = 1·930(6) Å in $B_9C_2H_{11}AlEt$[1]]. Angles around the aluminium atom are: Me(1)–Al–Me(2) = 131(1), B(7)–Al–B(8) = 47(1), Me(1)–Al–B(7) = 110(1), Me(2)–Al–B(7) = 111(1), Me(1)–Al–B(8) = 112(1), Me(2)–Al–B(8) = 112(1)°. The dihedral angle between the planes B(7)–Al–B(8) and B(7)–B(8)–B(4)–C(1)–C(2) is 129·5°. The molecule is 7,8-μ-dimethylaluminio-1,2-dicarba-*nido*-undecaborane(13).

Mean distances within the icosahedral 1,2-dicarbollide cage are: B–B = 1·81, B–C = 1·69, and C(1)–C(2) = 1·51(2) Å. This last distance is considerably shorter than that normally found in bis(*pentahapto*-dicarbollide) metal[2] complexes, *i.e.*, *ca.* 1·605 Å in $(B_9C_2H_{11})_2Ni^{IV}$,[3] 1·636 Å in $(Me_2B_9C_2H_9)_2Ni^{IV}$[4] or 1·625 Å in $[(B_9C_2H_{10})_2S_2CH]Co^{III}$,[5] and similar to values found for the "slipped" bis(*trihapto*-1,2-dicarbollide)metal[2] species of d^8 and d^9 electronic configuration, in which the C_2 fragment of the open B_3C_2 face is not involved in bonding to the metal atom {*cf.* C–C = 1·53(1) Å in $[B_9C_2H_{11})_2Cu^{II}]^{2-}$[6] and 1·49(3) Å in $[(B_9C_2H_{11})_2Cu^{III}]^{-}$[7]}.

There is no direct (crystallographic) information on the location of the hydrogen atoms of the $B_9C_2H_{12}$ cage. However, it is evident that six hydrogens are associated with the open pentagonal (B_3C_2) face. The long B–Al distances [av. = 2·31(2) Å], the unusually small B(7)–Al–B(8) angle [47(1)°], and the fact that the aluminium atom lies outside the rim of the open face near the position normally occupied by terminal boron protons, leads us to conclude that, in the solid state, the aluminium is probably bound to the cage by two hydride bridges, B(7)–H–Al and B(8)–H–Al [*cf.*, B ··· Al = 2·15 Å in $Al(BH_4)_3$[8,9]].

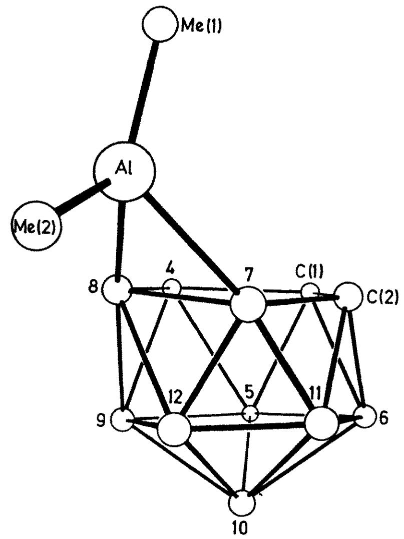

FIGURE. *The solid-state geometry of* 7,8-μ-*dimethylaluminio*-1,2-*dicarba*-nido-*undecaborane*(13). *The probable location of hydrogen atoms is: terminal hydrogens on all cage atoms except* B(7) *and* B(8) *and three hydrogen bridges* [B(7)–H–Al, B(8)–H–Al, B(8)–H–B(4)].

Both high resolution ^1H and ^{11}B n.m.r. and i.r. spectra of the compound support this conclusion. In addition, a temperature dependent ^{11}B n.m.r. spectrum [in which resonances for the pairs B(4) and B(7), B(5) and B(11), and B(9) and B(12) are each equivalent at room temperature, but separate at lowered temperatures, while resonances for B(6), B(8), and B(10) are not appreciably temperature dependent] lead us to conclude that the dimethylaluminium moiety and a bridging proton between B(8) and B(4) [located at τ 13·6 p.p.m. in a ^1H n.m.r. spectrum] are in rapid exchange at room temperature.

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