Reactions of Decaborane with Adducts of Aluminium and Gallium Hydride

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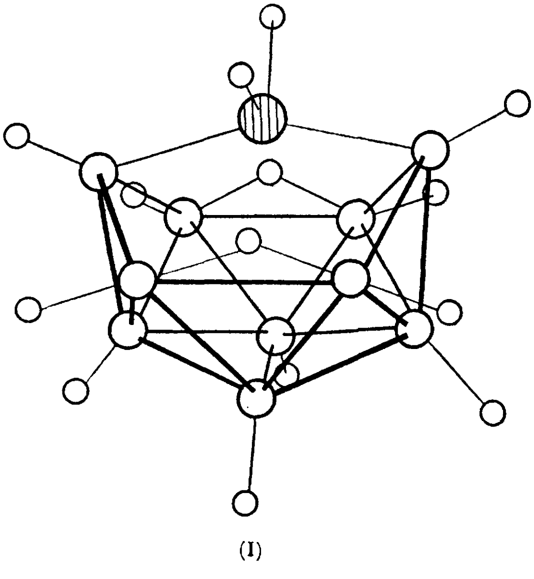
DECABORANE is known to react with triethylamine–borane[1] according to Equation 1 to give the triethylammonium salt of the icosahedral anion $B_{12}H_{12}^{2-}$. Under milder conditions only one boron atom is added and appreciable yields of the anion $B_{11}H_{14}^{-}$ are obtained by Equation 2. Reactions of decaborane with trimethylamine–alane, Me_3NAlH_3, and trimethylamine–gallane, Me_3NGaH_3, were therefore investigated in an attempt to prepare novel hydride anions containing both boron and aluminium, or boron and gallium.

Decaborane reacts quantitatively with trimethylamine–alane in ether at room temperature according to Equation 3 (n = 1·5—2). The product was isolated as a fine, white powder; it is stable under dry nitrogen but is extremely reactive towards water and other hydrolytic solvents. Because of the variable amount of ether, absolute analysis figures varied slightly but the atom ratios B : Al : N were always constant and correspond to the values 10·0 : 1·00 : 1·00.

Structure (I) is suggested for the anion. This is the first report of a compound containing a direct Al–B bond and also the first report of a 6,9-bridged derivative of the dianion $B_{10}H_{14}^{2-}$ (II). Adducts of the type $B_{10}H_{12}L_2$ normally have the ligands, L, substituting the external 6,9-hydrogen atoms;[2] in (I) it can be seen that the internal 6,9-hydrogen atoms of $B_{10}H_{14}^{2-}$ have been substituted by a bridging AlH_2^+ group. This structure is consistent not only with the analytical data but also with the



(I)

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[1] N. N. Greenwood and J. H. Morris, *Proc. Chem. Soc.*, **1963**, **338**.

[2] W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, **1963**.

infrared spectrum, the topological theory of boranes,[2] and studies of the reactions of partially deuterated decaborane and trimethylamine–alane.

The same product was formed when decaborane reacted with an equimolar quantity of trimethylamine–monochloroalane, Me_3NAlH_2Cl, in ether; no gas was evolved but hydrogen chloride was retained quantitatively in solution as required by Equation 4.

$$2Et_3NBH_3 + B_{10}H_{14} + [Et_3NH^+]_2[B_{12}H_{12}]^{2-} + 3H_2 \qquad (1)$$

$$Et_3NBH_3 + B_{10}H_{14} = [Et_3NH^+][B_{11}H_{14}]^- + H_2 \qquad (2)$$

$$Me_3NAlH_3 + B_{10}H_{14} + nEt_2O = [Me_3NH^+][B_{10}H_{12}AlH_2^-]nEt_2O + H_2 \qquad (3)$$

$$Me_3NAlH_2Cl + B_{10}H_{14} + nEt_2O = [Me_3NH^+][B_{10}H_{12}AlH_2^-]nEt_2O + HCl \qquad (4)$$

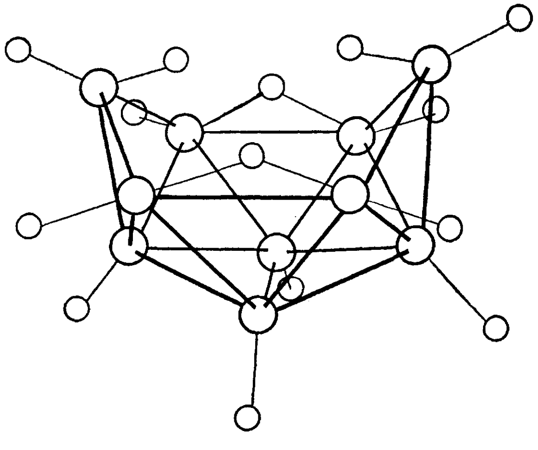
$$[B_{10}H_{12}AlH_2]^- + 3H_2O = [B_{10}H_{15}]^- + Al(OH)_3 + H_2 \qquad (5)$$

$$[Me_3NH]^+[B_{10}H_{15}] = [Me_3NH]^+[B_{10}H_{13}]^- + H_2 \qquad (6)$$

$$[Me_3NH^+][B_{10}H_{15}]^- = B_{10}H_{14} + Me_3N + H_2 \qquad (7)$$

$$Me_3NGaH_3 + B_{10}H_{14} = [Me_3NH]^+[B_{10}GaH_{16}]^- \qquad (8)$$

Salts of the anion (I) react explosively with water but under controlled conditions hydrolysis proceeds according to Equation 5. It is notable that only one molar equivalent of hydrogen is evolved from the AlH_2 unit, the second mole being retained in the borane anion. The product isolated was $[Me_3NH]^+[B_{10}H_{15}]^-$ and this loses hydrogen readily. The reaction can be written[3] as in Equation 6. The $B_{10}H_{15}^-$ anion was identified by its infrared and ultraviolet spectra and by its interconversion[3] with $B_{10}H_{14}^{2-}$. The $B_{10}H_{13}^-$ anion was also readily confirmed by its ultraviolet spectrum[2].



(II)

When an alcoholic solution of $Me_3NHB_{10}H_{15}$ was passed down a cation-exchange column, hydrogen was evolved and decaborane was recovered in 80% yield from the eluant. (Equation 7). This remarkable sequence indicates that the B_{10} unit remains intact throughout the whole series of reactions 3, 5, and 7.

The reaction of decaborane with trimethylamine–gallane in ether at room temperature proceeds according to Equation 8. No hydrogen is evolved and the product is obtained as a fine, white powder which is stable under dry nitrogen. The compound contains no solvent and analyses correctly for C, B, N, and Ga. The reaction also proceeds in benzene solution but is slower and the product is less pure. The anion $B_{10}GaH_{16}^-$ is relatively unreactive to water and other hydroxylic solvents and can be recovered unchanged from solution in 1M-hydrochloric acid. This is the first report of a gallium hydride derivative which is so stable towards hydroxylic reagents.

The compound $[Me_3NH][B_{10}GaH_{16}]$ is a 1 : 1 electrolyte in ethanol. The anion is considered to be the first example of a 6,9-bridged derivative of the dianion $B_{10}H_{16}^{2-}$; the two hydrogen atoms have been replaced by a bridging GaH_2^+ unit involving direct Ga–B bonds to give $[B_{10}H_{14}GaH_2^-]$. This structure is consistent with the infrared spectrum. Alternatively the anion could be a derivative of $B_{10}H_{14}^{2-}$ analogous to (I) but with the direct Al–B bonds replaced by three-centre Ga–H–B bonds. However, this possibility is considered less likely on the basis of steric requirements and the hydrolytic stability of the compound.

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[3] R. Schaeffer and F. Tebbe, *Inorg. Chem.*, 1964, 3, 1638.

[4] J. Dupont and M. F. Hawthorne, *Chem. and Ind.*, 1962, 405.

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