Mercury–Boron Derivatives of Decaborane

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HITHERTO, no compounds containing mercury–boron σ-bonds have been reported.[1] In a comprehensive study[2,3] of the formation of Group II metallo-boron derivatives of decaborane, the reactions of mercuric and methylmercuric halides with decaborane ($B_{10}H_{14}$), sodium decaboranate ($NaB_{10}H_{13}$), and decaboranylmagnesium iodide ($B_{10}H_{13}MgI$)[4] were investigated.

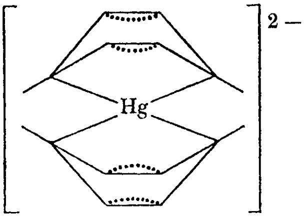
Mercuric chloride was found to metallate decaborane in diethyl ether according to the reaction:

$$B_{10}H_{14} + n\text{HgCl}_2 = B_{10}H_{14-n}(\text{HgCl})_n + n\text{HCl}$$

where $n = 7,8$ depending on the period of reaction. Interestingly, mercuric bromide was reduced to mercurous bromide by decaborane in diethyl ether, and both mercuric chloride and bromide were reduced to the mercurous state by decaborane in tetrahydrofuran.

Methylmercuric chloride did not react with decaborane in diethyl ether although the corresponding bromide and iodide were slowly reduced to mercurous bromide and iodide respectively. Methylmercuric halides did react with sodium decaboranate in diethyl ether to form the appropriate sodium halide (50—80% yield), but mercury was also deposited and the reaction was not a satisfactory route to mercury–boron derivatives of decaborane.

The rates of reaction of methylmercuric halides (MeHgX, X = Cl, Br, I) with decaboranylmagnesium iodide were in the order Cl > Br $\gg$ I as expected from the polarities of the respective mercury–halogen bonds, and this is further evidence consistent with the suggestion[4] that decaboranylmagnesium iodide is best regarded as $B_{10}H_{13}^{\delta-}\ MgI^{\delta+}$. The reaction products were air-sensitive, orange crystalline solids of the type $Mg_6(B_{20}H_{24}Hg)X_{10},x\text{Et}_2O$ [*e.g.*, for X = Cl, Found: B, 12·4; Cl, 19·8; Hg, 11·1; Mg, 7·7. $Mg_6(B_{20}H_{24}Hg),11\text{Et}_2O$ requires: B, 12·35; Cl, 20·2; Hg, 11·4; Mg, 8·3%]. The compound dissolved without reaction in water or ethanol to form an orange solution (λ_{max} = 305 mμ) containing stoicheiometric amounts of magnesium, $[(B_{10}H_{12})_2Hg]^{2-}$, and halide ions and from which the orange tetramethylammonium salt $(Me_4N)_2(B_{10}H_{12})_2\,Hg$ (λ_{max} 305 mμ in MeCN) could be precipitated. [Found (after recrystallisation from acetonitrile–ether): C, 16·4; H, 8·0; B, 36·5; Hg, 34·0; N, 4·6. $(Me_4N)_2B_{20}H_{24}Hg$ requires: C, 16·3; H, 8·15; B, 36·7; Hg, 34·0; N, 4·75%]. The original products can therefore be formulated $Mg[(B_{10}H_{12})_2Hg],5MgX_2,x\text{Et}_2O$.



The infrared spectrum of $[(B_{10}H_{12})_2Hg]^{2-}$ in the range 4000–400 cm.$^{-1}$ was identical to that reported[2] for $[(B_{10}H_{12})_2Cd]^{2-}$ or $[(B_{10}H_{12})_2Zn]^{2-}$, but in the range 400–200 cm.$^{-1}$ each dianion exhibited a single, definitive absorption as follows: ν (cm.$^{-1}$) = 225 $[(B_{10}H_{12})_2Hg]^{2-}$, 235 $[(B_{10}H_{12})_2Cd]^{2-}$, 278 $[(B_{10}H_{12})_2Zn]^{2-}$: these may be assigned to the antisymmetric metal–boron stretching vibration of the tetrahedral MB_4 unit assuming $[(B_{10}H_{12})_2Hg]^{2-}$ has the structure shown, analogous to that suggested[2] for $[(B_{10}H_{12})_2Cd]^{2-}$, or $[(B_{10}H_{12})_2Zn]^{2-}$. (The structure convention depicting only the 5,6,7,8,9,10 boron atoms of the decaborane cluster has previously been described.)[5]

The ^{11}B n.m.r. spectrum of $[(B_{10}H_{12})_2Hg]^{2-}$ at 20 Mc./sec. consisted of a large unsymmetrical doublet at 410 c./sec. and a small symmetrical doublet at 1010 c./sec. relative to trimethyl borate.

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