1,2-Bisdichloroboryl-1-vinylborylethane

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COYLE and RITTER[1] have recently reported addition of diboron tetrahalides to monovinylmetal halides to give substituted 1,2-bis(dihalogenoboryl)ethyl derivatives; previous studies of the addition of diboron tetrahalides to vinylmetal compounds containing more than one vinyl group have been inconclusive. We now report restricted 1 : 1 addition of diboron tetrachloride to trivinylborane; reaction of equimolar amounts in a sealed tube at room temperature and in absence of solvent gives quantitatively the low-melting point solid compound $(CH_2:CH)_2B{\cdot}CH(BCl_2){\cdot}CH{\cdot}CH_2{\cdot}BCl_2$ (I), in which two vinyl groups are retained. Chemical evidence for (I) was obtained by elemental analysis, evolution of ethylene (2 mol.) with propionic acid and of ethylene and ethane (1 mol.) on acid hydrolysis and pyrolysis (release of ethane by these methods is characteristic of dihalogenoborylethanes)[2]. The ^1H n.m.r. spectrum of (I) in carbon tetrachloride showed the expected doublet and triplet for the ethane protons, with the vinyl multiplet at τ — 8·50 (relative to Me_4Si); the i.r. spectrum of (I) showed the expected C=C stretching band at 1600 cm.$^{-1}$. When set aside with boron trichloride, (I) yielded chlorodivinylborane (1 mol.) and a solid having ^1H n.m.r. and i.r. spectra identical with those of 1,1,2-tris(dichloroboryl)-ethane,[1] which indicated the exchange

$$(CH_2:CH)_2B{\cdot}CH(BCl_2)CH_2{\cdot}BCl_2 + BCl_3 \rightarrow (CH_2:CH)_2BCl + (BCl_2)_2CH{\cdot}CH_2{\cdot}BCl_2$$

Treatment of (I) with an excess of trimethylamine in a sealed tube under pressure at 120° and in absence of solvent yielded acetylene (1 mol.) with uptake of trimethylamine (3 mol.). Fractional sublimation of the solid products gave BCl_3,NMe_3 and a second trimethylamine adduct containing no chlorine; this second adduct yielded ethylene (2 mol.) with hydrogen chloride and its i.r. spectrum showed the strong B–H stretching absorption at 2360 cm.$^{-1}$, indicating that this adduct was trimethylamine–divinylborane. The residue from the reaction had the composition $[Me_3N,BCl]_n$. These facts suggest that the reaction of (I) with trimethylamine is

$$(CH_2:CH)_2B{\cdot}CH(BCl_2){\cdot}CH_2{\cdot}BCl_2 + 3Me_3N \rightarrow$$

$$Me_3N{\cdot}BCl_3 + Me_3N{\cdot}BH(CH:CH_2)_2 + \frac{1}{n}[Me_3N{\cdot}BCl]_n + C_2H_2$$

Acceptance of donor molecules by dichloroboryl groups attached to carbon is usually followed by disproportionation to give adducts containing BCl_3 and BCl groups, as observed here. Significantly, however, acceptance of trimethylamine by the divinylboryl group is followed by rupture of the divinylboryl–carbon bond and acquisition of a hydrogen atom, and not by disproportionation. This suggests that the reaction of (I) with boron trichloride occurs *via* divinylboryl-dichloroboryl exchange rather than simple vinyl-chlorine exchange; it is implied that, while the attachment of two vinyl groups to boron is strong, the attachment of a third non-vinyl group is correspondingly weak.

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