Preparation and *X*-Ray Crystal Structures of 5,10-Dibromo-*nido*-decaborane(14)

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Summary The first example of a facially substituted dihalogeno-*nido*-decaborane(14), 5,10-$B_{10}H_{12}Br_2$, has been obtained from the reaction of Br_2 with $Me_2SnB_{10}H_{12}$; its structure has been determined by *X*-ray crystallography.

Although basal- [B(1)—B(4)][1] and monofacial- [B(5)—B(10)] halogen substituted *nido*-decaboranes(14) are known,[2] the more synthetically interesting decaboranes dihalogen substituted in the facial positions were unknown until now. We have prepared and characterized the first example of such a compound, 5,10-$B_{10}H_{12}Br_2$ (**1**).

Br_2 (2 mol. equiv.) reacts cleanly with $Me_2SnB_{10}H_{12}$[3] in CS_2 at −78 °C to form Me_2SnBr_2 and $B_{10}H_{12}Br_2$ as major products along with $B_{10}H_{14}$, $B_{10}H_{13}Br$, and $B_{10}H_{11}Br_3$ as minor products. Removal of CS_2, $B_{10}H_{14}$, and Me_2SnBr_2 at 25 °C *in vacuo*, followed by sublimation of remaining materials at 80 °C yields pure, crystalline 5,10-$B_{10}H_{12}Br_2$ (**1**) (yield *ca.* 70%), which gave satisfactory analytical data. Compound (**1**) is soluble in $CHCl_3$, C_6H_6, and CS_2. The most intense mass spectral peaks occur at *m/e* 275 ($B_{10}Br_2H_x^+$; 100%), 181 (31), 169 (15), and 101 (17). The 32·1 MHz ^{11}B n.m.r. spectrum of (**1**) exhibits (relative to BF_3–OEt_2) a complex pattern of overlapped resonances (maxima at δ −15·7, −11·1, and −5·9 p.p.m.; area 6), a doublet at δ 4·3 p.p.m., (J 165 Hz, area 2), and a doublet at δ 35·8 p.p.m., (J 160 Hz, area 2).

A single crystal of (**1**), obtained by its slow sublimation *in vacuo* at 100 °C was subjected to *X*-ray analysis. *Crystal data:* monoclinic, space group $P2_1/c$, a = 13·323(3), b = 7·416(3), c = 24·890(8) Å, β = 153·61(1)°, Z = 4 (20 °C, Mo-K_α). Intensities were measured using a Syntex P$\bar{1}$ automated diffractometer. The positions of bromine and boron were established from the three-dimensional Patterson map using standard heavy-atom techniques. Hydrogen atoms were located from a Fourier difference map. 1440 significant reflections were used in refinement (R_1

$= 0{\cdot}051$; $R_2 = 0{\cdot}053$, anisotropic temperature factors; no absorption correction).

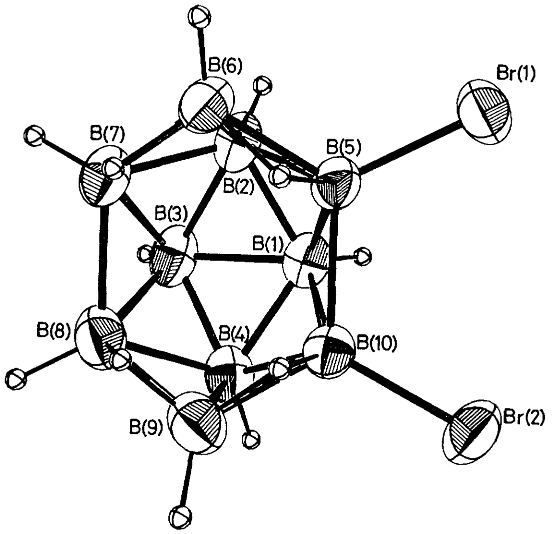

FIGURE. Structure of 5,10-$B_{10}H_{12}Br_2$, (**1**): B(1)–B(5), 1·942(8); B(2)–B(10), 1·940(8); B(1)–B(3), 1·78(1); B(1)–B(2), 1·78(1); B(1)–B(5), 1·72(1); B(2)–B(6), 1·73(1); B(2)–B(5), 1·77(1); B(2)–B(7), 1·79(1); B(5)–B(6), 1·80(1); B(6)–B(7), 1·78(1); B(5)–B(10), 2·00(1); B(7)–B(8), 1·95(1); B(6)–H(6,7), 1·27(9); B(7)–H(6,7), 1·14(9); B–H (terminal) average, 1·07(9) Å; ∠ Br(1)–B(5)–B(1), 122·6(5); Br(1)–B(5)–B(2), 125·9(5); Br(1)–B(5)–B(6), 119·3(5); Br(1)–B(5)–B(10), 117·3(4)°.

The structure analysis establishes that (**1**) is substituted at the B(5) and B(10) positions of the B_{10} cage and that the molecule has C_s symmetry; the structure of (**1**) is shown in the Figure. Except for lengthening of the B(5)–B(10) bond relative to B(7)–B(8), the bromine substituents on the cage edge cause relatively little distortion of the B_{10}-cage from that observed in unsubstituted decaborane(14), $B_{10}H_{14}$.[4]

The reaction of Br_2 with $Me_2SnB_{10}H_{12}$ proceeds according to the stoicheiometry in equation (1), and can be classed as an oxidative cleavage reaction.

$$Me_2SnB_{10}H_{12} + 2Br_2 \rightarrow 5,10\text{-}B_{10}H_{12}Br_2 + Me_2SnBr_2 \qquad (1)$$

The reaction shows a clear kinetic preference for substitution at B(5) and B(10). At −78 °C, the product is almost exclusively 5,10-$B_{10}H_{12}Br_2$. Only traces of other, so far uncharacterized, monobromodecaborane(s), tribromodecaborane(s), and other isomeric dibromodecaborane(s) are observed. The isomeric dibromodecaborane(s), although not characterized completely, are clearly disubstituted in the facial [B(5)—B(10)] positions, indicating that there is a competing tendency for bromine migration to B(6), B(9) and/or B(7), B(8) positions.

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