Preparation of Electron-rich Heteroatom-containing Boranes

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Summary The syntheses of $B_9C_2H_{11}AsPh$ and $B_8H_8As_2S$ are described; these are the first examples of a new class of electron-rich heteroatom-containing boranes.

Reduction of *closo*-carboranes with sodium naphthalide in a suitable solvent forms the synthetically useful, electron-rich $B_nC_2H_{n+2}{}^{2-}$ ions (n = 6—10).[1] We report here our initial studies on a new class of neutral heteroatom analogues of the electron-rich $B_9C_2H_{11}{}^{2-}$ and $B_{10}C_2H_{12}{}^{2-}$ ions Formally, a BH unit in $B_{10}C_2H_{12}{}^{2-}$ can be replaced with AsR^{2+} to generate the isoelectronic but neutral molecule, $B_9C_2H_{11}$-AsR. Thus, addition of phenyldichloroarsine to a suspension in toluene of $Na_2(1,2\text{-}B_9C_2H_{11})$ afforded yellow, sublimable $B_9C_2H_{11}AsPh$ (I), m.p. 125—127°, in low yield. The high-resolution mass spectrum of (I) had a cut-off at *m/e* 286·1288 corresponding to the $^{12}C_8{}^1H_{16}{}^{75}As^{11}B_9{}^+$ ion (calculated *m/e* 286·1304). The *CC'*-dimethyl analogue, $B_9H_9C_2Me_2AsPh$, m.p. 120—121°, was also prepared and characterized.† The room temperature ^{11}B n.m.r. spectrum of (I) was unexpectedly simple containing doublet resonances at −5·2, −3·1, +0·8, +4·0, +13·9, and +16·9 p.p.m. (BF_3,OEt_2 = 0 p.p.m.) with relative areas 1:2:1:2:2:1 respectively. The ^1H n.m.r. spectrum at room temperature of (I) [$(CD_3)_2CO$] contained one broad singlet (2H) at τ 5·77 due to the carborane CH protons. At −40°, it showed two broad singlets at τ 5·55 and 5·93. This suggests that (I) is fluxional at room temperature as is the similar *nido*-molecule $Me_2AlB_9C_2H_{12}$.[2]

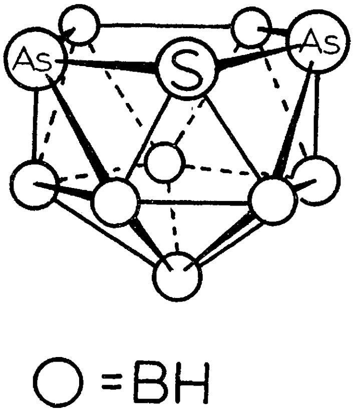

Figure. Proposed structure of $B_8H_8As_2S$.

We have found that reaction of $Cs_2B_{10}H_{14}$ with excess of arsenic trichloride and triethylamine results in the unusual insertion of two arsenic atoms into the boron cage to form the known molecule, $1,2\text{-}B_{10}H_{10}As_2$.[3] A similar reaction occurs between $CsB_9H_{12}S$, arsenic trichloride, and triethylamine in acetonitrile solution to give the white, sublimable, air-sensitive $B_8H_8As_2S$ (II) in low yield. The mass spectrum of (II) had a cut-off at *m/e* 278 corresponding to the $^{11}B_8{}^1H_8{}^{75}As_2{}^{32}S^+$ parent ion. The ^{11}B n.m.r. spectrum of (II) contained doublets at −9·8, −7·4, −1·3, +0·4, and +30·3 p.p.m. with relative areas 2:1:2:2:1 respectively. This spectral pattern is consistent with the *nido*-structure shown in the Figure. Compound (II) is isoelectronic with the electron-rich $B_9C_2H_{11}{}^{2-}$ ion which is also believed to have a *nido*-structure similar to that in the Figure.

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† Satisfactory elemental analyses were obtained for the three new compounds described here.

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