Insertion of Selenium, Tellurium, or Arsenic Atoms into Borane Cage Compounds using Element Oxide Reagents

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Summary The $B_{11}H_{14}^-$ ion reacts with $NaHSeO_3$ or TeO_2 in heptane–water to produce $B_{11}H_{11}Se$ or $B_{11}H_{11}Te$ and $B_{10}H_{12}CH^-$ reacts with As_2O_3 to form 1,2-$B_{10}H_{10}CHAs$.

DURING the past few years a number of examples of insertion of nitrogen and sulphur units into borane and heteroatom borane cage structures by the use of $NaNO_2$ and $KHSO_3$ have been reported.[1,2] The insertion of S, Se, or Te into borane cages has previously been accomplished by the use of polychalconide ions.[3] The insertion of group 5A elements has generally been accomplished by the use of group 5A halides.[4]

We have found that $NaHSeO_3$, TeO_2, and As_2O_3 can be used as reagents for the insertion of Se, Te, and As, respectively, into certain borane and carbaborane anions.

Reaction of $NaB_{11}H_{14}$ with an excess of $NaHSeO_3$ or solid TeO_2 in water–heptane under nitrogen for 24 h produced $B_{11}H_{11}Se$ (**1**) (*ca.* 18% yield) or $B_{11}H_{11}Te$ (**2**) (*ca.* 25% yield), respectively. The products were isolated from the heptane layer which was changed several times during the course of the reaction. Compounds (**1**) and (**2**) have also been prepared by the reaction of $B_{10}H_{12}Se$ or $B_{10}H_{12}Te$ with $Me_3N{\cdot}BH_3$ in refluxing xylenes. Purification of (**1**) was accomplished by sublimation at 70 °C (0·1 Torr) on to a water-cooled probe, m.p. 390—395 °C (decomp., sealed tube, uncorrected). Compound (**2**) was purified by crystallization from $CHCl_3$, m.p. *ca.* 480 °C (rapid decomp.). The high resolution mass spectra exhibit peaks at *m/e* 212·1044 (M^+) corresponding to the $^{11}B_{11}{}^{1}H_{11}{}^{80}Se$ ion (calc. 212·1051) and *m/e* 262·0917 (M^+) corresponding to the $^{11}B_{11}{}^{1}H_{11}{}^{130}Te$ ion (calc. 262·0952) for (**1**) and (**2**), respectively. The ^{11}B n.m.r. spectra of (**1**) and (**2**) (see Table) are very similar to that reported previously for $B_{11}H_{11}S$.[5] We propose, therefore, that (**1**) and (**2**) have *closo*, nearly-icosahedral cage structures.

TABLE. 70·6 MHz ^{11}B n.m.r. data for (**1**)—(**3**).

Compound	Relative intensity	δ/p.p.m.[a] (J_{BH}/Hz)
(**1**)[b]	1:5:5	22·9(142), *ca.* −3·5, −4.4(139)
(**2**)[c]	1:10	22·3(142), −4·3[d]
(**3**)[e]	1:2:2:2:1	0·6(176), −5·3(173), −10·3(161), *ca.* −12·5, −39·5(154)

[a] Relative to $BF_3{\cdot}OEt_2$ = 0 p.p.m., with positive values downfield of the standard. [b] Solvent $CHCl_3$. [c] Solvent Me_2CO. [d] Unsymmetrical doublet. [e] Solvent heptane.

Reaction of K(7,8-$B_9C_2H_{12}$) with an excess of $NaHSeO_3$, using the procedure described for the preparation of (**1**) and (**2**), over a period of 7 days, produced $B_8C_2H_{10}Se$ (**3**)† (*ca.* 2% yield) which was purified by sublimation at 70 °C (0·1 Torr) on to a water-cooled probe, m.p. 269—272 °C; high resolution mass spectrum: *m/e* 202·0709 (M^+) corresponding to the $^{11}B_8{}^{12}C_2{}^{1}H_{10}{}^{80}Se$ ion (calc. 202·0693). The ^{11}B n.m.r. spectrum of (**3**) is very similar to that of B_8C_2-

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† Satisfactory C and H analyses were obtained for (**3**).

$H_{10}S$.[2] The 26 valence electron count[6] suggests that (**3**) has a *nido* structure. The structure may be that of an icosahedron missing one vertex. An *X*-ray study is underway.

Reaction of $Na[B_{10}H_{12}CH]$ with solid As_2O_3 in 0·03 M aqueous KOH–heptane for 12 h produced 1,2-$B_{10}H_{10}CHAs$ (*ca.* 5% yield) which was identified by comparison of its low resolution mass spectrum and ^{11}B n.m.r. spectrum with those of an authentic sample.[7]

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