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Synthesis of Heteroatom Boranes Containing Two Arsenic Atoms

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Treatment of $KB_9H_{12}S$ or $KB_{10}H_{11}Se$ with As_2O_3 in basic solution formed $B_8H_8As_2S$ and $B_8H_8As_2Se$, respectively. Base degradation of $B_8H_8As_2S$ followed by reaction with $C_5H_5^-$ and $CoCl_2$ formed $B_7H_7As_2SCo(C_5H_5)$. Reaction of $B_7C_2H_{13}$ with AsI_3 and triethylamine formed $B_7C_2H_9As_2$ in moderate yield.

Introduction

Previously we have reported that reaction of $Na[B_{10}H_{12}CH]$ with As_2O_3 in aqueous potassium hydroxide formed the known closo molecule 1,2-$B_{10}H_{10}CHAs$.[1] We have also found that this reagent which is derived from arsenious acid will react with decaborane in aqueous solution to form $K[B_{10}H_{12}As]$ and subsequently with further arsenic insertion will form 1,2-$B_{10}H_{10}As_2$. These latter two arsaboranes have been previously prepared from decaborane by using arsenic trichloride and various bases.[2] In this report we describe the synthesis, characterization, and some chemistry of $B_8H_8As_2Se$ and $B_7C_2H_9As_2$ as well as some chemistry of the previously reported[3] $B_8H_8As_2S$.

Experimental Section

General Procedures and Instrumentation. All reactions were run under an atmosphere of prepurified nitrogen. Melting points were obtained in sealed, evacuated capillaries and are uncorrected. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y.

Boron-11 NMR spectra at 70.6 MHz were obtained with a Varian HR-220 spectrometer and were externally referenced to $BF_3{\cdot}O(C_2H_5)_2$. High-resolution mass spectral data were obtained on an AEI MS-902 spectrometer. Infrared data were obtained as a KBr disk on a Perkin-Elmer 283 instrument.

$B_8H_8As_2S$. The potassium salt[4] $KB_9H_{12}S$ (50 mL of a 0.1 M solution) was placed in a 250-mL flask fitted with a nitrogen inlet and a magnetic stirring bar. In a separate reaction KOH (2.8 g) was dissolved in 15 mL of degassed water. As_2O_3 (10 g) was added and the mixture refluxed for 15 min. The arsenic solution was then added to the $K^+B_9H_{12}S^-$ solution with rapid stirring. The reaction mixture was stirred at room temperature for 8 h under a nitrogen atmosphere. The aqueous solution was then extracted with three 20-mL portions of hexane. The hexane fractions collected were evaporated to dryness. The remaining black residue was redissolved in hexane; the solution was filtered to remove insoluble materials and again evaporated to dryness, yielding 0.1 g (7% yield) of white crystalline $B_8H_8As_2S$, mp 386–390 °C dec. The 70.6-MHz ^{11}B NMR spectrum (see Table I) was the same as previously reported.[3]

$B_8H_8As_2Se$. Decaborane(14) (5.0 g, 40 mmol) was placed in a flask fitted with a nitrogen inlet and a magnetic stirring bar. Fifty milliliters of deoxygenated water was added, and Na_2SeO_3 (7.0 g, 40 mmol) was slowly added with rapid stirring. The reaction was exothermic, and H_2 gas was evolved. After complete addition, the mixture was stirred for 12 h. Analysis of the reaction products in a separate experiment gave 37% yield of $B_{10}H_{11}Se^-$ (collected as the tetramethylammonium salt) and about 1% of $B_9H_9Se_2$. In a separate flask As_2O_3 (3.9 g, 20 mmol) was dissolved in an alkaline water solution (KOH, 1.2 g in 50 mL of H_2O) by boiling for 15 min. When the aqueous arsenic solution cooled, the solution containing $B_{10}H_{11}Se^-$ was added and the mixture allowed to stir for 48 h. Over the 2-day period the aqueous reaction mixture was extracted periodically with 25-mL portions of hexane. The hexane fractions were evaporated to dryness, and a yellow solid remained which was sublimed at 90–100 °C (10^{-2} torr) to give 0.1 g (1% yield) of $B_8H_8As_2Se$, mp 427–430 °C. Anal. Calcd for $B_8H_8As_2Se$: B, 26.74. Found: B, 26.61.

Table I. ^{11}B NMR Data for the Heteroatom Boranes Containing Two Arsenic Atoms

compd (solvent)	chem shift, ppm (J_{B-H}, Hz) [rel area]
$B_8H_8As_2S$ (CH_3CN)	10.3 (161) [2], 8.0 (156) [1], 1.8 (140) [2], 0.3 (156) [2], −30.0 (171) [1]
$B_8H_8As_2Se$ (heptane)	10.6 [2], 10.0 [1], 1.8 (156) [2], 0.7 (158) [2], −30.2 (161) [1]
$B_7H_7As_2SCo(C_5H_5)$ (CH_2Cl_2)	14.7 (146) [1], 7.0 (156) [2], 1.5 [1], 0.16 [1], −9.9 (156) [1], −23.3 (146) [1]
$B_7C_2H_9As_2$ (hexane)	−0.8 (144) [1], −1.0 [2], −4.1 [2], −14.3 (164) [1], −32.2 (146) [1]
$B_7C_2H_9As_2Co(C_5H_5)$ (CH_2Cl_2)	14.6 (142) [1], 5.6 (156) [1], ~2 [1], 1.5 [2], 0.0 [1], −18.9 (132) [1]

$B_7H_7As_2SCo(C_5H_5)$. Potassium hydroxide (0.14 g) was dissolved in 15 mL of methanol. To this solution was added $B_8H_8As_2S$ (0.73 g, 2.5 mmol), and the mixture was stirred at room temperature for 1 h. The orange solution was evaporated to dryness and the residue dissolved in 20 mL of THF. Triethylamine (2 mL) was added to the solution and the mixture stirred for 0.5 h, and then freshly cracked cyclopentadiene (1 mL) was added. Anhydrous cobalt(II) chloride (0.4 g, 3 mmol) was added and the mixture stirred for 18 h. The volatile components were removed under vacuum, and the residue was extracted with CH_2Cl_2. The extract was chromatographed on a 18 × 2 cm Florisil column using hexane and then CH_2Cl_2 as eluants. A white solid identified as $(C_2H_5)_3N{\cdot}BH_3$ by ^1H and ^{11}B NMR eluted first. This was followed by a red band of $B_7H_7As_2SCo(C_5H_5)$ obtained in very low yield. The 220-MHz ^1H NMR spectrum ($CDCl_3$ solvent) contained a single peak at 5.5 ppm assigned to the cyclopentadienyl ring.

$B_7C_2H_9As_2$. The carborane $B_7C_2H_{13}$[5] (0.244 g, 2 mmol) in 25 mL of THF was placed in a three-neck flask fitted with a reflux condenser and dropping funnel. Triethylamine (2 mL) was added to the solution, and then a solution of arsenic triiodide (1.9 g, 4 mmol) in 50 mL of THF was added slowly over 15 min. The mixture was then refluxed for 2 h. The volatile components were removed under vacuum, and the residue was extracted with several 25-mL portions of hexane. The hexane extract was washed with two 10-mL portions of 0.01 M KOH solution to remove any unreacted $B_7C_2H_{13}$. The hexane was then removed under vacuum and the $B_7C_2H_9As_2$ (0.19 g, 33% yield) obtained by sublimation at 90 °C (10^{-2} torr); mp 335–340 °C dec.

The infrared spectrum (KBr) contained absorptions at 3010 (w), 2560 (s), 1160 (m), 1123 (w), 1081 (m), 1068 (m), 967 (s), 949 (s), 906 (w), 880 (w), 838 (w), 768 (w), 746 (w), 737 (w), and 691 (w) cm^{-1}.

$B_7C_2H_9As_2Co(C_5H_5)$. A solution of $B_7C_2H_9As_2$ (0.044 g, 0.17 mmol) in 140 mL of dry THF was placed in a Vycor reaction tube. To the solution was added $(C_5H_5)Co(CO)_2$ (0.1 mL, 0.96 mmol) via syringe. The mixture was magnetically stirred under nitrogen and irradiated with a high-intensity mercury-vapor lamp for 22 h. The

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(1) Friesen, G. D.; Todd, L. J. *J. Chem. Soc., Chem. Commun.* **1978**, 349.
(2) Little, J. L.; Pao, S. S.; Sugathan, K. K. *Inorg. Chem.* **1974**, *13*, 1752.
(3) Siedle, A. R.; Todd, L. J. *J. Chem. Soc., Chem. Commun.* **1973**, 914.
(4) Plesek, J.; Hermanek, S.; Janousek, Z. *Collect. Czech. Chem. Commun.* **1977**, *42*, 785.
(5) Garrett, P. M.; George, T. A.; Hawthorne, M. F. *Inorg. Chem.* **1969**, *8*, 2008.

0020-1669/80/1319-2801$01.00/0

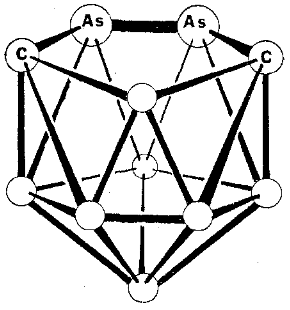

Figure 1. Proposed structure of $B_7C_2H_9As_2$.

solution was then opened to the air and stirred for another 3 h. Silica gel (0.04 g, 60–200 mesh) was added to the solution and the mixture evaporated to dryness under vacuum. The residue was chromatographed on a short silica gel column and eluted with methylene chloride. The material in the eluate was further purified by preparative thin-layer chromatography on a silica gel plate. Development with methylene chloride produced two strong bands. The second yellow band contained $B_7C_2H_9As_2Co(C_5H_5)$ in low yield; mp 264–265 °C dec. The ^1H NMR spectrum ($CDCl_3$) contained resonances at 5.2 (C_5H_5), 1.42 (carborane CH), and 1.17 ppm (carborane CH).

Results and Discussion

Thia and Selena Derivatives. A few years ago we[3] reported the synthesis of *nido*-$B_8H_8As_2S$ by the reaction of $K(B_9H_{12}S)$ with excess arsenic trichloride and triethylamine. In the present study we have found that this diarsathiaborane can be formed in slightly better yield by reaction of $K(B_9H_{12}S)$ with As_2O_3 in basic aqueous solution. This compound is thermally stable at 375 °C but melts with decomposition at 386 °C.

Previously we[6] and others[4,7] had demonstrated that the use of element oxide reagents was a fairly general method to insert heteroatoms into borane molecules. Reaction of $B_{10}H_{14}$ with Na_2SeO_3 formed $B_{10}H_{11}Se^-$ in 37% yield. Although this is not the highest yield method[8] for obtaining this selenaborane anion, it does provide another example of a synthesis using an element oxide reagent. Treatment of $K(B_{10}H_{11}Se)$ with As_2O_3 in basic solution resulted in degradation and multiple arsenic atom insertion to form yellow $B_8H_8As_2Se$ in low yield. The high-resolution mass spectrum contained a parent ion peak at *m/e* 325.8965 corresponding to the $^{11}B_8{}^1H_8{}^{75}As_2{}^{80}Se$ ion (*m/e* (calcd) 325.8969). The ^{11}B NMR spectrum of $B_8H_8As_2Se$ is very similar to that of the corresponding sulfur derivative (see Table I). One doublet of area 2 at 0.7 ppm in the spectrum is unusually sharp. This signal is probably due to the two equivalent boron atoms on the open face of the molecule that are flanked by heteroatoms. In this arrangement there would be less $^{11}B-^{11}B$ coupling than is experienced by other boron atoms in the molecule. An X-ray structure determination will be needed to locate the positions of the heteroatoms in the molecule. Base attacks on other neutral nido 11-atom heteroatom boranes (i.e., $B_9H_9Se_2$ and B_9H_9SSe) have led to the isolation of new lower molecular weight heteroatom borane molecules.[9] Reaction of $B_8H_8As_2S$ with KOH in methanol for a short time and then attempted trapping of degradation products as a cobalt complex employing triethylamine/C_5H_6/$CoCl_2$ produced red $B_7H_7As_2SCo(C_5H_5)$ in low yield. The high-resolution mass spectrum contained a parent ion peak at *m/e* 389.9082 corresponding to the $^{12}C_5{}^1H_{12}{}^{11}B_7{}^{75}As_2{}^{32}S^{59}Co$ ion (*m/e* (calcd) 389.9076). This represents another in a rapidly expanding number of relatively stable neutral nido 11-atom heteroatom boranes. An X-ray structure determination will be needed to determine the arrangement of heteroatoms in the framework. This result suggests that $B_7H_9As_2S$ might be isolated with carefully chosen experimental conditions.

Carborane Derivatives. Reaction of $B_7C_2H_{13}$ with arsenic triiodide and triethylamine formed white $B_7C_2H_9As_2$ in moderate yield. This compound exhibited a high-resolution mass spectrum parent ion peak at *m/e* 259.9783 corresponding to the $^{11}B_7{}^{12}C_2{}^1H_9{}^{75}As_2{}^+$ ion (*m/e* (calcd) 259.9788). The ^{11}B NMR spectrum contained five doublets with the relative areas 1:2:2:1:1 (see Table I) which suggests that there may be mirror-plane symmetry to the structure. The 220-MHz ^1H NMR spectrum contained one broadened singlet at 2.4 ppm which is assigned to the apparently equivalent CH groups. The molecule has $n + 2$ pairs of valence electrons, suggesting that it also has a nido 11-atom structure. Considering the known structure of the starting material $B_7C_2H_{13}$, simple proton abstraction and arsenic atom insertion into the open face of the carborane would form the tentatively proposed nido structure illustrated in Figure 1. The doublet at 0.8 ppm of unit area in the ^{11}B NMR spectrum is a very narrow signal and may be due to the one boron atom in the open face of the molecule which is flanked by carbon atoms and therefore is least broadened by $^{11}B-^{11}B$ (or $^{11}B-^{10}B$) spin–spin coupling.

This new type of molecule is isoelectronic with $B_7C_4H_{11}$, a member of the rapidly expanding tetracarbon carborane series. The $C_4B_7H_{11}$ molecule has not been isolated, although MC_4B_7 iron[10] and cobalt[11,12] metallocarborane derivatives have been reported. We have found that photolysis of $(C_5H_5)Co(CO)_2$ and $B_7C_2H_9As_2$ in THF formed $(C_5H_5)Co(B_7C_2H_9As_2)$ in very low yield. The appearance of two distinct CH resonances in the proton NMR spectrum and six resonances in the ^{11}B NMR spectrum suggests that this molecule has a very unsymmetrical structure. Further study is needed to completely characterize this cobalt complex.

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Registry No. $B_8H_8As_2S$, 51846-24-3; $B_8H_8As_2Se$, 74096-64-3; $B_7C_2H_9As_2$, 74081-79-1; $KB_9H_{12}S$, 63105-95-3; decaborane(14), 17702-41-9; $B_7C_2H_{13}$, 17653-38-2; $(C_5H_5)Co(CO)_2$, 12078-25-0; As_2O_3, 1327-53-3; Na_2SeO_3, 10102-18-8; $[Me_4N][B_{10}H_{11}Se]$, 61702-39-4; $KB_{10}H_{11}Se$, 74185-20-9; AsI_3, 7784-45-4.

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(6) Friesen, G. D.; Barriola, A. M.; Todd, L. J. *Chem. Ind.* (*London*) **1978**, 631.

(7) Plesek, J.; Stibr, B.; Hermanek, S. *Chem. Ind.* (*London*) **1974**, 662. Brattsev, V. A.; Knyazev, S. P.; Danilova, G. N.; Stanko, V. I. *Zh. Obshch. Khim.* **1975**, *45*, 1393.

(8) Little, J. L.; Friesen, G. D.; Todd, L. J. *Inorg. Chem.* **1977**, *16*, 869.

(9) Friesen, G. D.; Barriola, A.; Daluga, P.; Ragatz, P.; Huffman, J. C.; Todd, L. J. *Inorg. Chem.* **1980**, *19*, 458.

(10) Maxwell, W. M.; Bryan, R. F.; Grimes, R. N. *J. Am. Chem. Soc.* **1977**, *99*, 4008.

(11) Maxwell, W. M.; Wong, K.-S.; Grimes, R. N. *Inorg. Chem.* **1977**, *16*, 3094.

(12) Wong, K.-S.; Bowser, J. R.; Pipal, J. R.; Grimes, R. N. *J. Am. Chem. Soc.* **1978**, *100*, 5045.