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Cage-Expansion and -Contraction Reactions of *nido*-6-SB_9H_{11}: Improved Synthetic Routes to *nido*-7-$SB_{10}H_{12}$ and *arachno*-4-SB_8H_{12}

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Improved synthetic routes have been developed for the preparation of *nido*-7-$SB_{10}H_{12}$ and *arachno*-4-SB_8H_{12}. Good yields (>60%) of *nido*-7-$SB_{10}H_{12}$ can be obtained by acidification of the anion that is formed either by the reaction of *nido*-6-SB_9H_{11} with $NaBH_4$ under reflux conditions or by the reaction of *nido*-$SB_9H_{10}^-$ with BH_3·THF. *arachno*-4-SB_8H_{12} can be obtained in moderate yields (~20%) either by oxidative degradation of the *arachno*-$SB_9H_{12}^-$ anion or by base degradation of *arachno*-9-L-6-SB_9H_{11} (L = Et_2S or Et_3N).

Introduction

The first polyhedral thiaboranes were reported 20 years ago,[1] but the chemistry of these compounds has developed slowly in comparison with that of their isoelectronic carborane analogues because of the inaccessability of most of the cage systems. We report here the development of improved synthetic routes to both *nido*-7-$SB_{10}H_{12}$ and *arachno*-4-SB_8H_{12}, starting with the readily available thiaborane *nido*-6-SB_9H_{11}.

Experimental Section

All manipulations were carried out by using standard high-vacuum or inert-atmosphere techniques as described by Shriver.[2]

Materials. The compounds *nido*-6-SB_9H_{11},[3] *arachno*-$SB_9H_{12}^-$,[4] *arachno*-9-Et_2S-6-SB_9H_{11},[1] and *arachno*-9-Et_3N-6-SB_9H_{11},[1] were prepared according to previously reported methods. Methylene chloride was dried over calcium chloride. Dioxane and tetrahydrofuran were freshly distilled from sodium benzophenone. Diethyl sulfide, triethylamine, and borane–tetrahydrofuran were purchased from Aldrich and used as received. Ferric chloride hexahydrate and sodium borohydride were obtained from EM Science. Anhydrous HCl (Matheson) was purified by vacuum fractionation through a −110 °C trap.

Syntheses of *nido*-7-$SB_{10}H_{12}$. Reaction of *nido*-6-SB_9H_{11} with $NaBH_4$. A 100 mL three-neck round-bottom flask equipped with a reflux condenser and nitrogen bubbler was charged with 0.50 g (3.52 mmol) of freshly sublimed *nido*-6-SB_9H_{11}, 0.27 g (7.0 mmol) of vacuum-dried $NaBH_4$, and 50 mL of dried dioxane under nitrogen. The reaction mixture was then heated at mild reflux, whereupon H_2 was evolved. After the mixture was stirred overnight, the evolution of H_2 was complete; however, the best results were obtained when heating was continued for at least 36 h. The reaction mixture was then chilled to 15 °C, resulting in the formation of a milky slurry, which was filtered through a coarse frit. The pale yellow precipitate was then dissolved in 5 mL of water. To this solution was added 20 mL of methylene chloride, and the combined mixture was treated with excess (~5 mL) 5 N aqueous HCl at −5 °C. The methylene chloride layer was removed and the solvent evaporated. Sublimation of this material at 60 °C under high vacuum followed by vacuum-drying gave 0.34 g (2.24 mmol, 63.6% yield) of pure *nido*-7-$SB_{10}H_{12}$, which was identified by comparison of its ^{11}B NMR and IR spectra with those of an authentic sample.

When the above reaction was run in THF solvent, the reaction was complete in a shorter time (overnight) with comparable yields; however, because of the solubility of $NaBH_4$ in THF, purification of the product was more difficult.

Reaction of *nido*-$SB_9H_{10}^-$ with BH_3·THF. A 100-mL round-bottom flask fitted with a vacuum stopcock was charged with 0.50 g (3.52 mmol) of *nido*-6-SB_9H_{11}, excess NaH (0.17 g, 7 mmol), and ~20 mL of tetrahydrofuran. The flask was then slowly warmed to room temperature in vacuo, whereupon H_2 was evolved. After gas evolution ceased (~2 h), the resulting yellow solution was filtered and transferred to a three-neck flask fitted with a dropping funnel and reflux condenser. Dioxane (~20 mL) was added to the solution, which was then heated to reflux, followed by the dropwise addition of 10 mL of a 1 M solution of BH_3·THF. The solution was then heated at reflux overnight. Analysis of the reaction solution at this point by ^{11}B NMR indicated the exclusive formation of the *nido*-$SB_{10}H_{11}^-$ anion. The reaction mixture was next cooled to room temperature and reduced in volume to ~20 mL by rotary evaporation. Addition of 10 mL of chilled dioxane to the concentrate resulted in the formation of a white precipitate, which was collected on a coarse frit. The solid was then dissolved in 5 mL of water. To this solution was added 20 mL of methylene chloride, and the combined mixture was then treated with excess (~5 mL) 5 N aqueous HCl at −5 °C. The methylene chloride layer was separated and the solvent removed by rotary evaporation to give the crude product. Further sublimation at 60 °C under vacuum gave 0.37 g (2.39 mmol) of *nido*-7-$SB_{10}H_{12}$, a 68% yield based on consumed *nido*-6-SB_9H_{11}.

Syntheses of *arachno*-4-SB_8H_{12}. From *arachno*-$SB_9H_{12}^-$. In a 250-mL three-neck round-bottom flask equipped with a dropping funnel and nitrogen bubbler, a 25-mL aqueous ~1 M solution[3] of *arachno*-$SB_9H_{12}^-$ was added dropwise under nitrogen to 20 mL of an aqueous solution containing 6.80 g of $FeCl_3$·$6H_2O$. Pentane (~50 mL) was then layered on top of the solution, and 20 mL of 12.2 N HCl was added dropwise at −5 °C. After 30 min of stirring at room temperature, hydrogen gas evolution had subsided and the aqueous layer had turned from orange-yellow to pale blue. The pentane layer was then removed, washed with water (3 × 15 mL), and dried over $MgSO_4$. Evaporation to dryness gave a pale yellow solid. Sublimation at 40 °C afforded 0.39 g of *arachno*-4-SB_8H_{12} (2.98 mmol), which was characterized by comparison of its NMR spectra with those previously reported.[4,5] Unreacted *arachno*-$SB_9H_{12}^-$ was recovered from the water solution by precipitation with Me_4NCl (1.42 g (6.56 mmol) of $Me_4N^+SB_9H_{12}^-$). The overall yield of *arachno*-4-SB_8H_{12}, based on consumed *arachno*-$SB_9H_{12}^-$, was 16.2%.

From *arachno*-9-Et_2S-6-SB_9H_{11}. In a 250-mL three-neck flask equipped with a reflux condenser and nitrogen bubbler, 2.95 g (12.7 mmol) of *arachno*-9-Et_2S-6-SB_9H_{11} was added under a nitrogen blanket to a solution made by dissolving 0.91 g (16.2 mmol) of potassium hydroxide in 50 mL of methanol. The white suspension gradually changed to yellow as the solution was heated to reflux. Heating was continued overnight; then the solution was cooled to room temperature and the solvent vacuum-evaporated. The solid was then dissolved in 5 mL of *deaerated* water. Addition of a concentrated aqueous tetramethylammonium chloride solution resulted in the precipitation of crude product. Subsequent recrystallization from acetonitrile and acetone and vacuum-drying gave 0.83 g (4.1 mmol) of $Me_4N^+SB_8H_{11}^-$ (32.3% yield). The salt was next suspended in 20 mL of methylene chloride and the mixture cooled at −78 °C while 10 mmol of anhydrous HCl was added. The solution was stirred for 15 min, and then the volatiles were removed by vacuum evaporation. Sublimation of the resulting solid at 40 °C gave 0.41 g of *arachno*-4-SB_8H_{12} (3.13 mmol, 24.6% yield based on starting *arachno*-9-Et_2S-6-SB_9H_{11}, 21% based on *nido*-6-SB_9H_{11}).

From *arachno*-9-Et_3N-6-SB_9H_{11}. In a similar apparatus as described above, 3.15 g (12.9 mmol) of *arachno*-9-Et_3N-6-SB_9H_{11} was added under a nitrogen blanket to a solution made by dissolving 0.95 g (17 mmol) of potassium hydroxide in 50 mL of methanol. After overnight reflux the volatiles were removed by vacuum evaporation. The solid was then dissolved in 5 mL of *deaerated* water. Addition of a concentrated aqueous tetramethylammonium chloride solution resulted in the precip-

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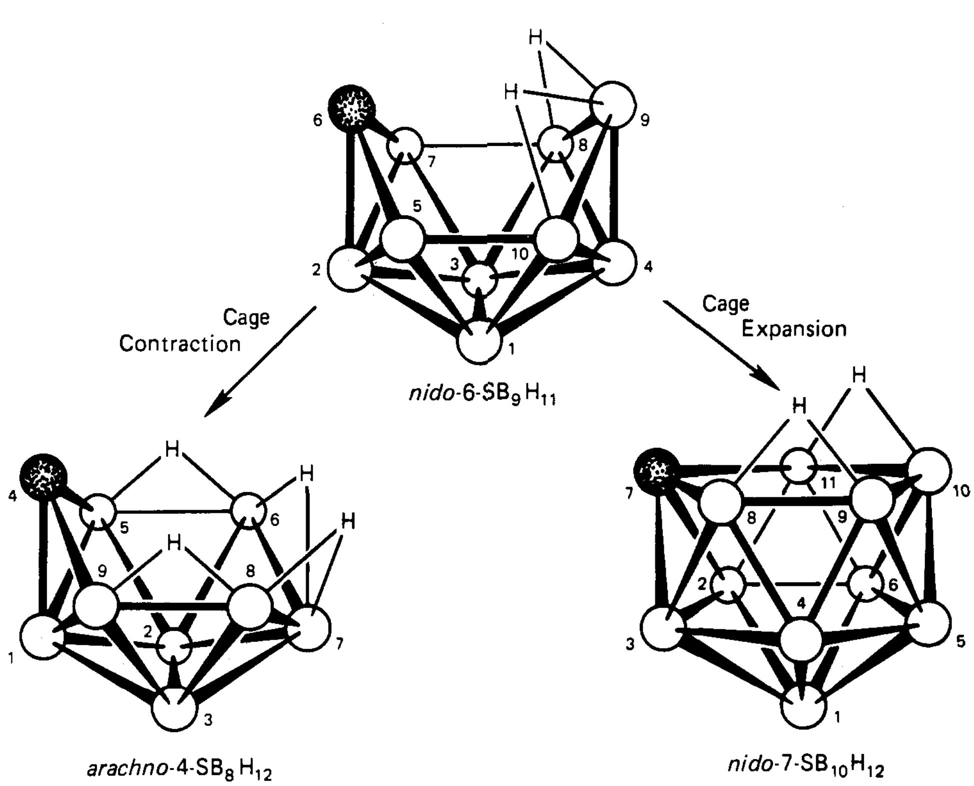

Figure 1. Proposed structures and cage numbering for *nido*-6-SB_9H_{11}, *nido*-7-$SB_{10}H_{12}$, and *arachno*-4-SB_8H_{12}.

itation of crude product. Subsequent recrystallization from acetonitrile and acetone and vacuum-drying gave 0.79 g (3.87 mmol) of $Me_4N^+SB_8H_{11}^-$ (30.0% yield). The salt was then suspended in 20 mL of methylene chloride and the mixture cooled at −78 °C while 10 mmol of anhydrous HCl was added. The solution was stirred for 15 min, and then the volatiles were removed by vacuum evaporation. Sublimation of the resulting solid at 40 °C gave 0.38 g of *arachno*-4-SB_8H_{12} (2.88 mmol, 22.3% based on starting *arachno*-9-Et_3N-6-SB_9H_{11}, 19% based on *nido*-6-SB_9H_{11}).

Results and Discussion

The compound *nido*-6-SB_9H_{11} can be prepared in nearly quantitative yields[1] from the reaction of decaborane(14) with aqueous ammonium polysulfide and is therefore a useful starting material for the synthesis of other thiaborane cage systems. The fact that *nido*-6-SB_9H_{11} is isoelectronic and isostructural with $B_{10}H_{14}$ suggested the possibility that it might undergo either cage-expansion or cage-contraction reactions, as shown in Figure 1, similar to those observed for $B_{10}H_{14}$ and thus serve as a precursor to SB_{10} and SB_8 cluster systems.

For example, it has been shown that decaborane(14) will react with $NaBH_4$ to give the *nido*-$B_{11}H_{14}^-$ anion in good yields.[6,7]

$$B_{10}H_{14} + NaBH_4 \xrightarrow[R_2O]{90\ ^\circ C} Na^+B_{11}H_{14}^- + 2H_2 \qquad (1)$$

We have found that *nido*-6-SB_9H_{11} undergoes an analogous reaction to give the *nido*-$SB_{10}H_{11}^-$ anion:

$$6\text{-}SB_9H_{11} + NaBH_4 \xrightarrow[\text{dioxane}]{\text{reflux}} Na^+SB_{10}H_{11}^- + 2H_2 \qquad (2)$$

The anion can then be converted to the neutral thiaborane by acidification with aqueous HCl in methylene chloride to give a ~60% yield of *nido*-7-$SB_{10}H_{12}$, based on consumed *nido*-6-SB_9H_{11}.

It was originally suggested that reaction 1 occurs via a two-step process involving the reactions

$$B_{10}H_{14} + NaBH_4 \xrightarrow{R_2O} Na^+B_{10}H_{13}^- + H_2 + H_3B{\cdot}OR_2 \qquad (3)$$

$$Na^+B_{10}H_{13}^- + H_3B{\cdot}OR_2 \rightarrow Na^+B_{11}H_{14}^- + H_2 + R_2O \qquad (4)$$

A similar pathway may be proposed for the production of *nido*-7-$SB_{10}H_{12}$ from *nido*-6-SB_9H_{11}, as shown in (5) and (6), and

$$6\text{-}SB_9H_{11} + NaBH_4 \xrightarrow{\text{dioxane}} Na^+SB_9H_{10}^- + H_2 + H_3B{\cdot}\text{dioxane} \qquad (5)$$

$$Na^+SB_9H_{10}^- + H_3B{\cdot}\text{dioxane} \rightarrow Na^+SB_{10}H_{11}^- + H_2 + OR_2 \qquad (6)$$

indeed, ^{11}B NMR spectra taken during the reaction indicated the initial formation of *nido*-$SB_9H_{10}^-$, followed by the gradual appearance of resonances due to *nido*-$SB_{10}H_{11}^-$.

Such a pathway would also be entirely consistent with Shore's work,[8] which demonstrated that many borane anions readily react with diborane to give cage-expansion products. These observations further suggested that an alternate route to *nido*-$SB_{10}H_{11}^-$ based on direct borane addition to *nido*-$SB_9H_{10}^-$ could be developed. It was subsequently demonstrated that reaction 7 results in the exclusive formation *nido*-$SB_{10}H_{11}^-$:

$$SB_9H_{10}^- + H_3B{\cdot}THF \xrightarrow[\text{dioxane}]{\text{reflux}} SB_{10}H_{11}^- + H_2 + THF \qquad (7)$$

Acidification of the anion then resulted in production of *nido*-7-$SB_{10}H_{12}$ in 68.0% yield.

As is shown in the Figure 1, *nido*-7-$SB_{10}H_{12}$ has been proposed to adopt a structure based on an icosahedron missing one vertex, with the sulfur occupying a position on the open face.[1] Such a structure can be derived from *nido*-6-SB_9H_{11} in a straightforward manner, consistent with the syntheses outlined above, by the addition of a –BH unit to, for example, the S-B7-B8-B9 edge of the molecule. It has also been shown[1] that the two bridging hydrogens of *nido*-7-$SB_{10}H_{12}$ can be removed to generate the isostructural anion, *nido*-$SB_{10}H_{10}^{2-}$. This anion is isoelectronic with the dicarbollide anion, *nido*-$C_2B_9H_{11}^{2-}$, and has been shown to form similar types of transition-metal π-complexes;[1,9] however,

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because of its relative inaccessibility, its chemistry has not yet been extensively developed.

The best previous synthesis of *nido*-7-$SB_{10}H_{12}$ has been via the pyrolytic disproportionation of $CsB_9H_{12}S$, which gives ~40% yields.[1] The compound has also been obtained in 22% yield by acidification of the $Et_3NH^+SB_{10}H_{11}^-$ salt, formed from the reaction of *arachno*-9-L-6-SB_9H_{11} and Et_3NBH_3.[1] Thus, the synthetic routes based on reactions 2 and 7 offer considerable advantages in yields, ease of reaction, and product separation.

The thiaborane *arachno*-4-SB_8H_{12} was first prepared via the multistep synthetic route outlined in (8) in ~5.0% yields by Pretzer and Rudolph but was originally incorrectly formulated as *nido*-4-SB_8H_{10}.[3]

$$\text{6-SB}_9\text{H}_{11} \xrightarrow{\Delta} \text{1-SB}_9\text{H}_9 \xrightarrow{\text{OH}^-} \text{SB}_8\text{H}_{11}^- \xrightarrow{\text{H}^+} \text{4-SB}_8\text{H}_{12} \qquad (8)$$

Baše, Heřmánek, and Gregor[5] later showed that the compound actually has two additional bridge hydrogens and that the correct formula is *arachno*-4-SB_8H_{12}. The compound is thus proposed to have a structure based on an eleven-vertex polyhedron missing the six-coordinate vertex and one adjacent four-coordinate vertex, as has been determined for the isoelectronic cage system *arachno*-4-NB_8H_{13}.[10] The Czech group has also reported[5] an improved preparation of the compound based on the reaction sequence shown in (9), which gives the compound in 15% yields.

$$\text{B}_{10}\text{H}_{14} + \text{KHSO}_3 \xrightarrow[\text{20 °C}]{\text{H}_2\text{O}} \xrightarrow{\text{dilute HCl}} \text{4-SB}_8\text{H}_{12} \qquad (9)$$

We have found that *arachno*-4-SB_8H_{12} can be conveniently obtained in ~20% yields from *nido*-6-SB_9H_{11} by either of two different synthetic routes. The first method involves the oxidative degradation[11] of the *arachno*-$SB_9H_{12}^-$ anion and yields the neutral compound directly as indicated in (10).

$$\text{SB}_9\text{H}_{12}^- + \text{FeCl}_3 \xrightarrow[\text{pentane}]{\text{aq HCl}} \text{4-SB}_8\text{H}_{12} + \text{FeCl}_2 + \text{HCl} + \text{H}_2 + \text{B(OH)}_3 \qquad (10)$$

Thus, when aqueous *arachno*-$SB_9H_{12}^-$ was treated with a stoichiometric amount of acidic aqueous $FeCl_3$ and the reaction mixture extracted with pentane, *arachno*-4-SB_8H_{12} was obtained as the only product, which upon sublimation was obtained in 16.2% yield. The compound is isolated as a white volatile solid that decomposes to intractable materials upon moderate heating.

It has previously been shown that *arachno*-4-SB_8H_{12} can be deprotonated to the *arachno*-$SB_8H_{11}^-$ anion by reaction with, for example, triethylamine. Due to the difficult and poor-yield routes to *arachno*-4-SB_8H_{12}, it has been impractical to develop the chemistry of *arachno*-$SB_8H_{11}^-$. Thus, a reasonable synthetic route to *arachno*-$SB_8H_{11}^-$ that does not go through *arachno*-4-SB_8H_{12} would be highly desirable.

We have found that simple base degradation as outlined in (11) of either *arachno*-9-Et_2S-6-SB_9H_{11} or *arachno*-9-Et_3N-6-SB_9H_{11} gives ~30% yields of *arachno*-$SB_8H_{11}^-$ (isolated as the tetramethylammonium salt).

$$\text{9-L-6-SB}_9\text{H}_{11} + \text{OH}^- + \text{CH}_3\text{OH(excess)} \rightarrow \text{SB}_8\text{H}_{11}^- + \text{L} + \text{B(OCH}_3)_3 \qquad (11)$$

The *arachno*-9-L-6-SB_9H_{11} compounds are isoelectronic with *arachno*-6,9-$L_2B_{10}H_{12}$, and reaction (11) can be considered analogous to the previously reported alcoholysis reactions of *arachno*-6,9-$L_2B_{10}H_{12}$, which give *arachno*-6-LB_9H_{13} in good yields:

$$\text{6,9-L}_2\text{B}_{10}\text{H}_{12} + 3\text{ROH} \rightarrow \text{6-LB}_9\text{H}_{13} + \text{B(OR)}_3 + \text{L} + \text{H}_2 \qquad (12)$$

Reaction 11 thus provides a convenient route to *arachno*-$SB_8H_{11}^-$, which should allow future investigations of the chemistry of this cage system. Alternatively, the anion can be protonated to give the neutral thiaborane with overall yields from *nido*-6-SB_9H_{11} being in the range of ~20%.

In summary, the results presented above have demonstrated the close similarity of the chemistries of the isoelectronic cage systems $B_{10}H_{14}$ and *nido*-6-SB_9H_{11}, as well as new pathways to *nido*-7-$SB_{10}H_{12}$, *arachno*-4-SB_8H_{12}, and their corresponding anions. Work further exploring the reactivity of these thiaborane clusters is now in progress and will be reported in future publications.

Acknowledgment. We thank the National Science Foundation and the Army Research Office for the support of this research.

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