NINE-VERTEX POLYHEDRAL MONOTHIABORANE CHEMISTRY.* THE FIRST *nido* THIANONABORANE: ISOLATION AND CHARACTERIZATION BY NMR OF THE [*nido*-9-SB_8H_9]$^-$ ANION, AND ITS CONVERSION TO COMPOUNDS OF THE 6-L-*arachno*-4-SB_8H_{10} SERIES (WHERE L = SMe_2 AND PYRIDINE)

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Deprotonation of 6(*exo*)-(SMe_2)-*arachno*-4-SB_8H_{10} either by sodium hydride or sodium metal leads to the isolation in high-yield of the [*nido*-9-SB_8H_9]$^-$ anion, which has been characterized by ^{11}B and ^1H NMR spectroscopy. The *nido* anion can be reconverted to compounds of the 6(*exo*)-L-*arachno*-4-SB_8H_{10} series (where L = SMe_2 and pyridine) by reaction with Lewis bases (L) followed by acidification with trifluoroacetic acid.

Our two groups have been interested for some time in the chemistry of cluster thia[1 – 5] and dithiaboranes[6], and in their metallated analogues[7 – 12], i.e. in compounds that incorporate one or two sulfur atoms in the polyhedral borane framework. Of particular interest in this area have been the nine-vertex thiaboranes, of which we first characterized the *arachno* compounds 4-SB_8H_{12} (refs[2,3]), 6(*exo*)-L-4-SB_8H_{10} (where L = SMe_2, PPh_3, MeCN, MeNC, and tertiary amines)[4], and 4,6-$S_2B_7H_9$ (ref.[5]). Now we would like to present the reactions leading to the isolation of the first representative of the *nido* nine-vertex family of monothiaboranes, the [*nido*-9-SB_8H_9]$^-$ anion, and we also describe its reconversion to compounds of the 6(*exo*)-L-*arachno*-4-SB_8H_{10} type. The schematic structures and numbering systems for the nine-vertex *arachno* and *nido* compounds encountered in this work are in structures *I* and *III* below.

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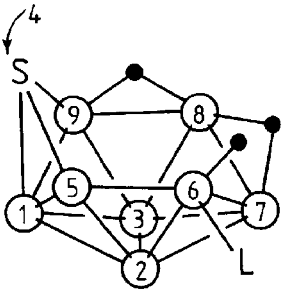
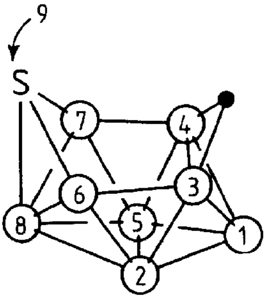
RESULTS AND DISCUSSION

Syntheses

Treatment of 6(*exo*)-(SMe_2)-*arachno*-4-SB_8H_{10} (*I*, ref.[4]) with either sodium hydride or metallic sodium in tetrahydrofuran (THF) at room temperature, followed by heating at reflux, led to the formation of an anionic compound that we isolated with tetrabutyl- and tetramethylammonium countercations. The anion was characterized as [*nido*-9-$SB_8H_9]^-$ (*II*), the first example of a *nido* nine-vertex thiaborane system, by NMR spectroscopy.



I



II

The formation of compound *II* from *I* is consistent with the stoichiometries as in Eqs (*1*) and (*2*), which represent a straighforward *arachno* to *nido* transformation with no significant movement of cage atoms in the original framework of *I*.

$$\underset{I}{(SMe_2)SB_8H_{10}} + H^- \longrightarrow \underset{II}{[SB_8H_9]^-} + H_2 + SMe_2 \qquad (1)$$

$$\underset{I}{(SMe_2)SB_8H_{10}} + Na \longrightarrow \underset{II}{[SB_8H_9]^-} + 1/2\,H_2 + SMe_2 \qquad (2)$$

The reaction between anion *II* (reaction scale ca 1 mmol) and either dimethyl sulfide or pyridine in dichloromethane, followed by treatment with trifluoroacetic acid and purification by thin-layer chromatography (TLC) on silica gel, led to the isolation of the corresponding 6(*exo*)-L-*arachno*-4-SB_8H_{10} compounds (where L = SMe_2 or pyridine) in yields of 97 and 58%, respectively. The reaction is consistent with the stoichiometry as in Eq. (*3*), and thus represents a direct *nido* to *arachno* conversion reaction, i.e. a process that is effectively the reverse of that in Eqs (*1*) and (*2*):

$$[SB_8H_9]^- + L + H^+ \longrightarrow LSB_8H_{10} . \qquad (3)$$

From the mechanistic viewpoint, this reaction is consistent with an attack by base L at the {BH(3)} vertex in structure *II*. This is associated with the attachment of a proton at the B(4) position [which becomes B(8) in structure *I*] to generate the B(7)–H–B(8)–H–B(9) bridging system.

NMR Measurements

The measured NMR parameters for the [*nido*-9-SB_8H_9]$^-$ anion (*II*) are given in Table I, and selected features, together with other data for comparison, are presented in Fig. 1. The ^{11}B NMR spectrum of *II* (see Table I and Fig. 1) consists of five doublets with relative intensities 1 : 2 : 2 : 2 :1, thus indicating nine-vertex arrangement of C_s symmetry as in structure *II*. The corresponding ^{1}H NMR spectrum, combined with ^{1}H-{^{11}B(selective)} measurements[13], revealed the same relative intensity patterns for the signals of terminal protons, and in addition there was one broad high-field resonance of relative intensity 1, consistent with a bridging hydrogen atom. The arrangement of the cluster {BH} units and the bridging hydrogen atom as in structure *II* was also confirmed by two-dimensional [^{11}B-^{11}B]-COSY (ref.[14]) measurements that also allowed all resonances to be assigned unambiguously to the individual cluster {BH}

TABLE I
Measured NMR parameters for the [*nido*-9-SB_8H_9]$^-$ anion (*II*) at 294 – 297 K

Assignment	δ(^{11}B)[a]	*J*(^{11}B-^{1}H)	Observed [^{11}B-^{11}B]-COSY correlations[b]	δ(^{1}H)[c]
BH(1)	+22.2	155	2,5 s; 3,4 s	+5.07
BH(6,7)	+2.6	144	2,5 m; 3,4 s	+2.63
BH(2,5)	–7.0	138	1 s; 3,4 m; 6,7 m; 8 s	+2.01
BH(3,4)	–34.1	136	1 s; 2,5 m; 6,7 s; 8 s	+0.55
BH(8)	–37.8	164	2,5 s	+0.06
μH(3,4)	–	–	–	–4.50

[a] Tetrabutylammonium salt in $CDCl_3$. [b] Measured under conditions of complete {^{1}H(broadband noise)} decoupling; s stronger, m intermediate. [c] Tetramethylammonium salt in CD_3CN, assignments by ^{1}H-{^{11}B(selective)} measurements[13].

vertices. [^{11}B-^{11}B]-COSY correlations (see Table I) are observed for all adjacent boron sites except for the linkages between the $^{11}B(6,7)$ and $^{11}B(8)$ nuclei that flank the heteroatomic {S} vertex. An interesting feature is the $^{11}B(1)$ resonance, of which the positioning at lowest-field appears to contradict the previously proposed NMR cluster assignment rules[15], as also does the corresponding binary-borane $[B_9H_{12}]^-$ anion *III* (see Fig. 1).

The 22-electron nine-vertex [*nido*-9-SB_8H_9]$^-$ structure *II* is formally isostructural and isoelectronic with the hypothetical borane congener {*nido*-B_9H_{10}}$^{3-}$ (i.e. a doubly deprotonated structure *III*), from which *II* can be notionally derived by the replacement of the $\{BH(9)\}^{2-}$ group by the isoelectrolobal neutral {S} unit. Anion *II* is thus isoelectronic, but not isostructural, with the previously reported borane anion [*nido*-B_9H_{12}]$^-$

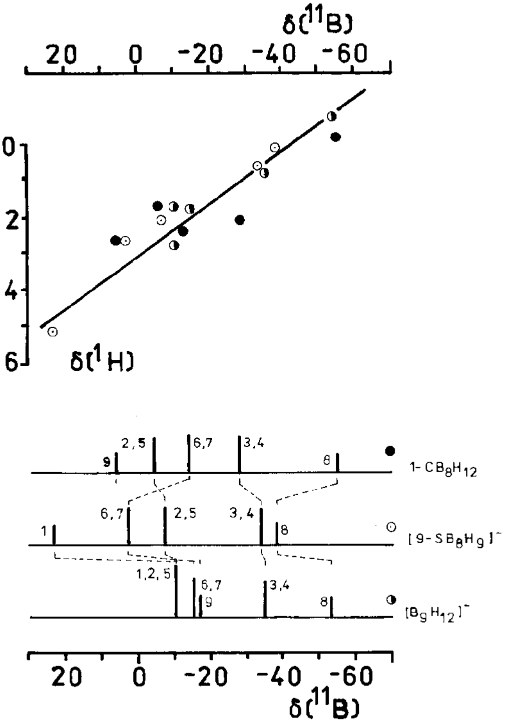
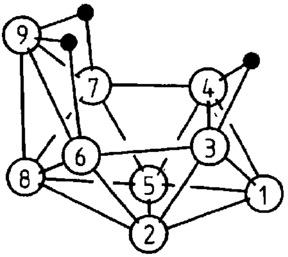


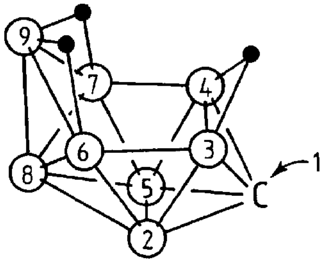
FIG. 1

NMR data for [*nido*-9-SB_8H_9]$^-$$NBu_4^+$ (*II*, ❍) together with those for the [*nido*-B_9H_{12}]$^-$ anion (*III*, ❍, data from ref.[26]) and *nido*-1-CB_8H_{12} (*IV*, ●, data from ref.[20]) for comparison. The top diagram plots $\delta(^1H)$ versus $\delta(^{11}B)$ for BH(*exo*) units for compounds *II*, *III*, and *IV*. The line drawn has a slope $\delta(^1H)$: $\delta(^{11}B)$ 1 : 14, intercept +3.1 in $\delta(^1H)$. The bottom diagrams are stick representations of the chemical shifts and relative intensities in the ^{11}B spectra of all three compounds. The hatched lines drawn connect equivalent positions in the three compounds

(*III*, ref.[16]), and with the neutral monocarbaborane *nido*-1-CB_8H_{12} (*IV*, refs[17 – 20]). This last carborane *IV* differs from *II* in the positioning of the heteroatomic cage unit, in that in *IV* it is located in the least connectivity[21,22] 1-position. The difference can be attributed to the explicit tendency of carborane *IV* to adopt the same arrangement of interboron hydrogen bridges as in structure *III*, thus forcing the carbon atom off the open face, while in structure *II* there is only one bridging hydrogen that can be easily accommodated between boron positions in the open pentagonal face, and so there is no need for the S heteroatom to move off the open face and adopt a less convenient higher co-ordinate position (1).



III



IV

A useful insight into the cluster NMR properties of the parent (i.e. unsubstituted) representatives of the series of nine-vertex *nido* boranes and heteroboranes that have so far been characterized is provided by Fig. 1. The bottom diagrams are stick representations of the ^{11}B chemical shifts and relative intensities for [*nido*-9-SB_8H_9]$^-$ (*II*) and for the structurally similar isoelectronic compounds *III* and *IV*. The most straightforward comparison is afforded by the pure binary boron hydride anion [B_9H_{12}]$^-$ (*III*), this comparison reveals marked downfield shifts of the ^{11}B(8) ($\Delta\sigma$ ca −15 ppm) and ^{11}B(6,7) ($\Delta\sigma$ ca −18 ppm) resonances (adjacent to the sulfur centre) and the high downfield shift for the B(1) atom ($\Delta\sigma$ ca −33 ppm), which is antipodal[15] to S(9). Inspection of Fig. 1 also reveals a general similarity of the ^{11}B NMR patterns of *II* with the equivalent shielding patterns of carborane *IV*, the most striking differences for *IV* being associated with the different cluster position of the heteroatomic {CH} unit and with the presence of two more hydrogen bridges. The ^{1}H shielding variations of anion *II* are found to parallel the ^{11}B shielding changes (Fig. 1, uppermost diagram) with the slope of the correlation being similar to those of the other related *nido* nine-vertex species *III* and *IV*. The general $\delta(^{11}B) : \delta(^1H)$ correlation slope of ca 14 : 1, with intercept 3.1 ppm in $\delta(^1H)$, is in accord with previous observations[20].

EXPERIMENTAL

Tetrahydrofuran (THF) was distilled from sodium diphenylketyl, and dichloromethane from calcium hydride, prior to use. Analytical thin-layer chromatography (TLC) was performed using Silufol (Kavalier, Votice) sheets (silica gel on Al foil, detection by I_2 vapour, followed by spray with 2% aqueous $AgNO_3$). The sample of 6(*exo*)-(SMe_2)-*arachno*-4-SB_8H_{10} (*I*) was made by the literature method[4]. NMR spectroscopy was performed as described in other recent papers from our laboratories[19,23,24] with chemical shifts δ being given in ppm to high frequency (low field) of Ξ = 32.083 971 MHz (nominally F_3BOEt_2) for ^{11}B (quoted ±0.5 ppm) and Ξ = 100 MHz ($SiMe_4$) for ^1H (quoted ±0.05 ppm), Ξ being defined as in ref.[25].

Preparation of [*nido*-9-SB_8H_9]$^-$[NBu_4]$^+$ (*II*)

A solution of 6(*exo*)-(SMe_2)-*arachno*-4-SB_8H_{10} (*I*) (4.9 g; 26 mmol) in THF (50 cm^3) was stirred with sodium hydride or, alternatively, with sodium metal (ca 50% suspensions in mineral oil; ca 1.0 g; 42 mmol) for 2 h at ambient temperature and then refluxed for another 3 h (hydrogen evolution). The mixture was then filtered in vacuo and the filtrate treated with a solution of tetrabutylammonium chloride (7.5 g; 27 mmol) in water (50 cm^3). The THF was evaporated (rotatory evaporator) to give a white precipitate, which was filtered off, washed with water (25 cm^3) and hexane (10 cm^3), and then dried in vacuo. The crude product thus obtained (7.6 g; 20 mmol; 80% yield) can be crystallized from a concentrated solution in dichloromethane that is overlayered by an equivalent volume of hexane, to give a white crystalline product, characterized as [*nido*-9-SB_8H_9]$^-$[NBu_4]$^+$ (*II*) by NMR spectroscopy (see Table I). Similar treatment of the above aqueous solution with an equivalent amount of 1 mol dm^{-3} aqueous tetramethylammonium chloride gave the [NMe_4]$^+$ salt of *II* (yield 72%) on recrystallization from aqueous acetone.

Conversion of [*nido*-9-SB_8H_9]$^-$[NBu_4]$^+$ (*II*) into 6-(SMe_2)-*arachno*-4-SB_8H_{10} (*I*)

Dimethyl sulfide (1 cm^3) was added to a solution of [*nido*-9-SB_8H_9]$^-$[NBu_4]$^+$ (*II*; 100 mg; 0.27 mmol) in dichloromethane (5 cm^3), the mixture was treated with trifluoroacetic acid (1 cm^3), and then stirred for 2 h. The more volatile components were then evaporated (rotatory evaporator) and the residue applied to preparative TLC plates [Silica (Fluka type GF 254), 200 × 200 × 1 mm on glass, prepared from a water slurry and dried at ca 80 °C in air]. Development with dichloromethane gave one band (R_F = 0.76), which was removed from the plate and extracted with dichloromethane (ca 20 cm^3). Evaporation of the extract gave a white crystalline solid (49 mg; 95%), which was identified as 6(*exo*)-(SMe_2)-*arachno*-4-SB_8H_{10} (*I*) by NMR spectroscopy[4].

Conversion of [*nido*-9-SB_8H_9]$^-$[NBu_4]$^+$ (*II*) into 6(*exo*)-(py)-*arachno*-4-SB_8H_{10}

Pyridine (1 cm^3) was added to a solution of [*nido*-9-SB_8H_9]$^-$ [NBu_4]$^+$ (*II*; 370 mg; 1 mmol) in dichloromethane (5 cm^3), the mixture was treated with trifluoroacetic acid (1 cm^3), and then stirred for 1 h. Procedure was then as in the preceding experiment, and isolation of the TLC band at R_F 0.67 gave a pale yellow compound (121 mg; 58%) which was identified as 6(*exo*)-(py)-*arachno*-4-SB_8H_{10} by NMR spectroscopy[4].

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REFERENCES

1. Plesek J., Hermanek S.: J. Chem. Soc., Chem. Commun. *1975*, 127.
2. Base K., Gregor V., Hermanek S.: Chem. Ind. (London) *1979*, 743.
3. Base K., Wallbridge M. G. H., Greenwood N. N., Jones J. H., Kennedy J. D., Stibr B.: Polyhedron *8*, 2089 (1989).
4. Holub J., Stibr B., Kennedy J. D., Thornton-Pett M., Jelinek T.: Inorg. Chem., submitted.
5. Bown M., Fontaine X. L. R., Kennedy J. D.: J. Chem. Soc., Dalton Trans. *1988*, 1467.
6. Plesek J., Hermanek S., Janousek Z.: Collect. Czech. Chem. Commun. *42*, 785 (1977).
7. Base K., Stibr B., Zakharova I. A.: Synth. React. Inorg. Met.-Org. Chem. *10*, 509 (1980).
8. Ferguson J., Jennigs M. C., Lough A. J., Coughlan S., Spalding T. R., Kennedy J. D., Fontaine X. L. R., Stibr B.: J. Chem. Soc., Chem. Commun. *1990*, 891.
9. Bown M., Fontaine X. L. R., Greenwood N. N., Kennedy J. D.: Z. Anorg. Allg. Chem. *602*, 17 (1991).
10. Nestor K., Fontaine X. L. R., Greenwood N. N., Kennedy J. D., Thornton-Pett M.: J. Chem. Soc., Dalton Trans *1991*, 2657.
11. Coughlan S., Spalding T. R., Ferguson G., Gallagher A., Lough A. J., Fontaine X. L. R., Kennedy J. D., Stibr B.: J. Chem. Soc., Dalton Trans. *1992*, 2865.
12. Jones J. H., Fontaine X. L. R., Greenwood N. N., Kennedy J. D., Thornton-Pett M., Stibr B., Langhoff H.: J. Organomet. Chem. *445*, C15 (1993).
13. Fontaine X. L. R., Kennedy J. D.: J. Chem. Soc., Dalton Trans. *1987*, 1573.
14. Hutton W. C., Venable T. L., Grimes R. N.: J. Am. Chem. Soc. *106*, 29 (1984).
15. Hermanek S.: Chem. Rev. *92*, 325 (1992), and references therein.
16. Graybill B. M., Ruff J. K., Hawthorne M. F.: J. Am. Chem. Soc. *83*, 2669 (1961); Jacobsen G. B., Meina G. D., Morris J. H., Thomson C., Andrews S. J., Reed D., Welch A. J., Gaines D. F.: J. Chem. Soc., Dalton Trans. *1985*, 1645.
17. Base K., Hermanek S., Stibr B.: Chem. Ind. (London) *1977*, 951.
18. Base K., Stibr B., Dolansky J., Duben J.: Collect. Czech. Chem. Commun. *46*, 2345 (1981).
19. Hermanek S., Fusek J., Stibr B., Plesek J., Jelinek T.: Polyhedron *5*, 1873 (1986).
20. Jones J. H., Stibr B., Kennedy J. D., Lawrence A. D., Thornton-Pett M.: J. Chem. Soc., Dalton Trans. *1993*, 1269.
21. Williams R. E.: Inorg. Chem. *10*, 210 (1971).
22. Willians R. E.: Adv. Inorg. Chem. Radiochem. *18*, 67 (1976).
23. Bown M., Plesek J., Base K., Stibr B., Fonatine X. L. R., Greenwood N. N., Kennedy J. D.: Magn. Reson. Chem. *27*, 947 (1989).
24. Fontaine X. L. R., Kennedy J. D., McGrath M., Spalding T. R.: Magn. Reson. Chem. *29*, 711 (1991).
25. McFarlane W.: Proc. R. Soc. London, A *306*, 185 (1968).
26. Beckett M. A., Bown M., Fontaine X. L. R., Greenwood N. N., Kennedy J. D., Thornton-Pett M.: J. Chem. Soc., Dalton Trans. *1986*, 1969.

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