

## NIDO - HETEROBORANES

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**Abstract** - A new nido-6-CB<sub>9</sub>H<sub>12</sub><sup>-</sup> ion has been prepared and used for the synthesis of various monocarbaboranes and their derivatives. Protonation of the anion in the presence of Lewis bases (L = Me<sub>2</sub>S, MeCN and PPh<sub>3</sub>) yields a series of nido-9-L-6-CB<sub>9</sub>H<sub>13</sub> compounds. Twofold proton abstraction from 6-CB<sub>9</sub>H<sub>12</sub><sup>-</sup> by strong bases and a subsequent reaction with cyclopentadiene and MCl<sub>2</sub> · 6 H<sub>2</sub>O (M = Co, Fe) results in the formation of mixed eleven-vertex closo-[1-(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)M<sup>III</sup>η<sup>6</sup>-(2-CB<sub>9</sub>H<sub>10</sub>)]<sup>-</sup> complex anions containing the CB<sub>9</sub>H<sub>10</sub><sup>3-</sup> ligand. Acid degradation of 6-CB<sub>9</sub>H<sub>12</sub><sup>-</sup> yields uncharged nido-4-CB<sub>8</sub>H<sub>14</sub> which smoothly dehydrogenates to nido-4-(or 7-)CB<sub>8</sub>H<sub>12</sub> at elevated temperatures. The 4-CB<sub>8</sub>H<sub>14</sub> carborane reacts with water solution of K<sub>2</sub>CO<sub>3</sub> to produce the 4-CB<sub>8</sub>H<sub>13</sub><sup>-</sup> ion and with symmetrically substituted acetylenes R<sub>2</sub>C<sub>2</sub> (R = Me, Ph) under the formation of B-Me-5,6-R<sub>2</sub>-5,6-C<sub>2</sub>B<sub>8</sub>H<sub>10</sub> nido-dicarbaboranes. The latter reaction involves an extraordinary rearrangement of the skeletal CH<sub>2</sub> group to the terminal position. Specific procedures have been developed for preparing other nine-vertex nido-heteroboranes: 4-NB<sub>8</sub>H<sub>13</sub>, 6,8-CSB<sub>7</sub>H<sub>11</sub>, and 6,8-S<sub>2</sub>B<sub>7</sub>H<sub>9</sub> having structures with an open hexagonal face. Structures of all compounds are suggested on basis of both spectral and X-ray diffraction studies.

## INTRODUCTION

The intent of this paper is to present an overview in the study of nido-heteroboranes carried out in our Institute since the second meeting at Leeds in 1974. A systematic study of intermediate dicarbaboranes (Ref. 1) revealed novel synthetic routes and many interesting features of this class of compounds. As a consequence of this development, some predictions have been made and general stability rules formulated (Ref. 1-4). In order to make more generalizations, we extended our interest to less investigated groups of open heteroboranes containing carbon, nitrogen or sulphur atoms in the borane framework. Special attention has been paid to the synthesis and reactions of parent intermediate monocarbaboranes, azaboranes, and dithiaboranes. (see Note a).

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Note a. The nomenclature term nido- is generally used for all open-cage compounds (Ref. 5) as a common denotation of both nido- and arachno- series (Ref. 2-4). In order to distinguish this nomenclature ambiguity in special cases, the denotation nido- and arachno- is used in the text for compounds having  $2n + 4$  and  $2n + 6$  skeletal electrons, respectively ( $n$  = number of cage-atoms).

ADVANCES IN CHEMISTRY OF NIDO - MONOCARBABORANES

Nido-monocarbaboranes and their derivatives of the general formulae  $CB_{n-1}H_{n+3}$  (nido-series) or  $CB_{n-1}H_{n+5}$  (arachno-series) represent less investigated group of the borane family. Three general types of compounds, comprising the missing link between boranes and dicarbaboranes, have been characterized in the last few years. The preparation and extensive chemistry of  $CB_{10}H_{13}$  and its derivatives was mostly developed by Knoth and Todd *et al.* (Ref. 6-13). Less extensive is the chemistry of nido- $CB_5$  (Ref. 14-18) and  $CB_9$  (Ref. 6, 13) compounds. Completely unknown remained the group of 7- to 9-vertex monocarbaboranes. A more detailed survey on this field was given (Ref. 19, 20) elsewhere.

Preparation and chemistry of 6-carba-nido-decaborate(12)

Knoth (6, 13) showed that treatment of 6- $NMe_3CB_9H_{11}$  (1) in boiling tetrahydrofuran with sodium metal, followed by subsequent hydrolysis, afforded the closo-1- $CB_9H_{10}^-$  ion (see Fig. 1) in a low yield.

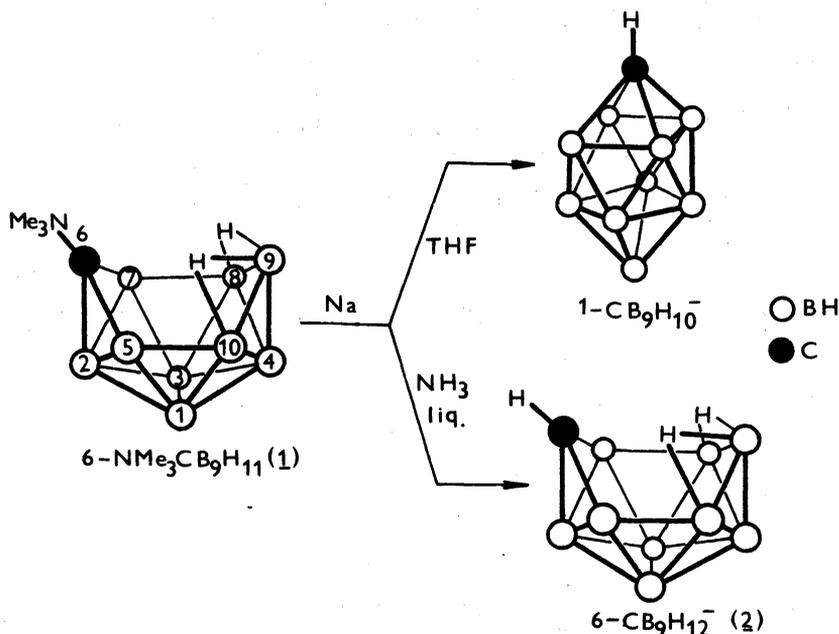


Fig. 1. Preparation and structure of the nido-6- $CB_9H_{12}^-$  ion.

In liquid ammonia, we have obtained (Ref. 21) ca. 80 % of the nido-6- $CB_9H_{12}^-$  ion, isoelectronic with  $B_{10}H_{12}^{2-}$ . The structure, shown in Fig. 1, is in agreement with the  $^{11}B$  n.m.r. spectrum of (2) exhibiting six doublets of relative area 2:1:2:2:1:1 and with the  $^1H$  n.m.r. spectrum which shows the skeletal CH,  $NMe_4^+$ , and BHB bridge signals of relative intensities 1:12:2 and  $\delta$  values 5.4, 3.4, and -3.7 p.p.m. (relative to tetramethylsilane). The CH signal shows a distinct splitting to a symmetrical quartet after the  $^{11}B$  decoupling, probably due to CH spin coupling with three adjacent BH protons. The same effect was detected by Onak (22) in several small 5- to 7-vertex dicarbaboranes and by Grimes (23) on the FT  $^1H$  n.m.r. study of small metallocarbaboranes. Considering the above results and our recently

formulated n.m.r. rules (Ref. 24), we suggested for (1) which exhibits similar  $^{11}\text{B}$  n.m.r. spectrum as (2), a new structure differing from that proposed by Knoth (13) in positions of both hydrogen bridges. Moreover, Knoth's structure cannot be represented by any topological valence formula (Ref. 25).

Synthesis of 9-ligando-6-carba-nido-decaboranes(13). In the presence of Lewis bases, the anion (2) reacts with anhydrous hydrogen chloride to produce a new class of arachno-9-L-6- $\text{CB}_9\text{H}_{13}$  (3) compounds (L =  $\text{Me}_2\text{S}$ , MeCN and  $\text{PPh}_3$ ) in a high yield (Ref. 26).

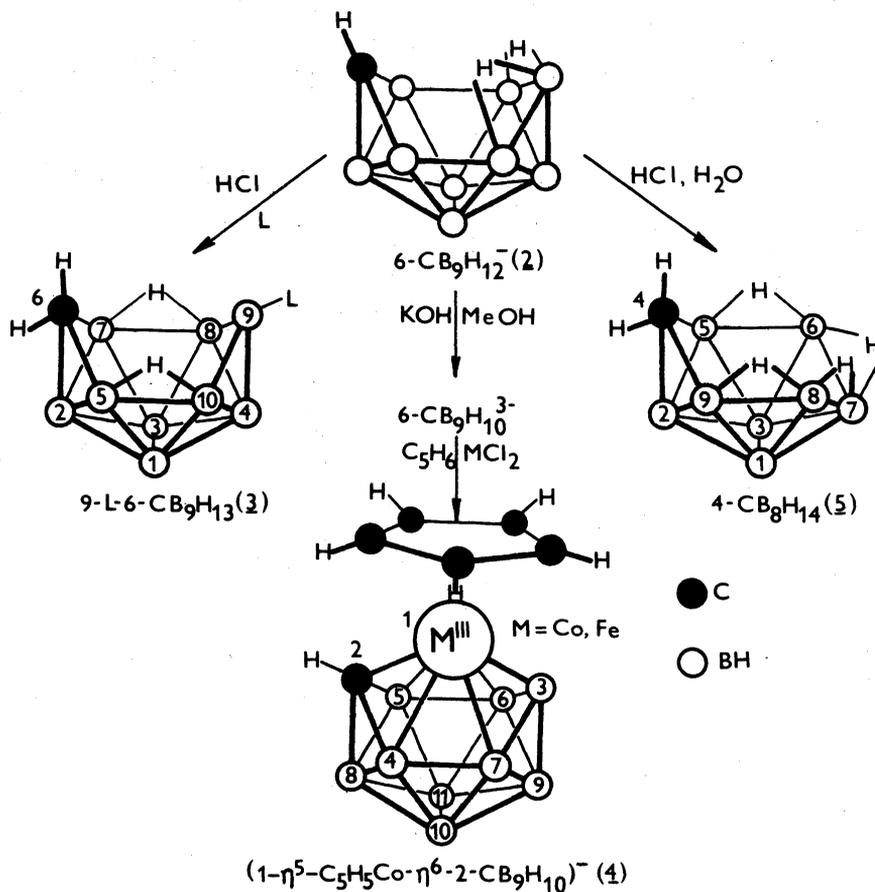


Fig. 2. Typical reactions of the nido-6- $\text{CB}_9\text{H}_{12}^-$  ion.

The synthetic pathway involves a proton addition to (2) followed by the attack of a Lewis base at the position 9 (see Fig. 2) without a significant movement of skeletal atoms. Similar 1:1:2:1:2:2 patterns of doublets were found in the  $^{11}\text{B}$  n.m.r. spectra of compounds (3). The assignment of particular signals was made by comparing the obtained  $^{11}\text{B}$  n.m.r. spectra with those of  $6,9\text{-C}_2\text{B}_8\text{H}_{14}$  (Ref. 27) and  $6,9\text{-L}_2\text{B}_{10}\text{H}_{12}$  (Ref. 28). The  $^1\text{H}$  n.m.r. spectra of (3) consist of narrow ligand CH signals, two finely split peaks of both equatorial and axial CH groups, and broad hydrogen bridge signals. When  $^{11}\text{B}$  decoupled, the signal assigned to the axial CH group was found to be distinctly split to a symmetrical heptet, probably due to a coupling with three adjacent BH and one equatorial CH protons. Mass spectra show distinct peaks corresponding to  $\text{L}^+$  and  $\text{CB}_9\text{H}_{13}^+$  molecular ions, due to an apparent fragmentation during the mass spectral experiment. Despite of this, however, all attempts to obtain the  $\text{CB}_9\text{H}_{13}$  carborane by thermal decomposition of (3) failed. All above results are consistent with the structure shown in Fig. 2, isoelectronic with the  $\text{B}_{10}\text{H}_{14}^{2-}$  ion.

Compounds (3) represent the first example of arachno-ten-vertex monocarbaboranes and complete the missing link between the 6,9-C<sub>2</sub>B<sub>8</sub>H<sub>14</sub> and 6,9-L<sub>2</sub>-B<sub>10</sub>H<sub>12</sub> compounds.

Synthesis of mixed eleven-vertex complexes of the CB<sub>9</sub>H<sub>10</sub><sup>3-</sup> ion. Treatment of the NMe<sub>4</sub><sup>+</sup> salt of the anion (2) and cyclopentadiene with MCl<sub>2</sub>·6H<sub>2</sub>O (M = Co, Fe) in the concentrated methanolic potassium hydroxide results in the formation of blue-green and violet, air-stable complexes, (C<sub>5</sub>H<sub>5</sub>M<sup>III</sup>CB<sub>9</sub>H<sub>10</sub>)<sup>-</sup>NMe<sub>4</sub><sup>+</sup> (4), [(4a), M = Co; (4b), M = Fe], in ca. 55 % yield (Ref. 29). The structure of (4a), shown in Fig. 2, is in agreement with the <sup>11</sup>B n.m.r. spectrum which consists of four doublets of relative area 1:4:3:1. The <sup>1</sup>H n.m.r. spectrum of (4a) exhibits three singlets at δ 5.06, 3.6, and 3.12 p.p.m. which are due to the cyclopentadienyl, skeletal CH group and tetramethylammonium resonances. The <sup>1</sup>H n.m.r. spectrum of (4b) shows only one singlet at δ 3.17 p.p.m. assigned to the NMe<sub>4</sub><sup>+</sup> protons. As expected, no other signals were found either in <sup>1</sup>H or <sup>11</sup>B n.m.r. spectrum of the paramagnetic complex (4b). Of other possibilities, the symmetrical eleven-vertex closo-1-[η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>M<sup>III</sup>-η<sup>6</sup>-(2-CB<sub>9</sub>H<sub>10</sub>)]<sup>-</sup> structure (see Fig. 2) containing the skeletal CH group at the lowest (Ref. 4), and the C<sub>5</sub>H<sub>5</sub>M<sup>2+</sup> vertex at the highest (Ref. 30) co-ordinate position, is consistent with the above mentioned results. Presented results are in agreement with the synthetic pathway involving twofold bridge proton abstraction from (2) under the formation of the 6-CB<sub>9</sub>H<sub>10</sub><sup>3-</sup> ligand having six electrons in the hexagonal open face, required for complexing the central M<sup>III</sup> ion. Both compounds, (4a) and (4b), isoelectronic with B<sub>11</sub>H<sub>11</sub><sup>2-</sup>, complete the series of mixed cyclopentadienyl complexes with CB<sub>7</sub>H<sub>8</sub><sup>3-</sup> (Ref. 31), CB<sub>8</sub>H<sub>9</sub><sup>3-</sup> (Ref. 32, 33) and CB<sub>10</sub>H<sub>11</sub><sup>3-</sup> (Ref. 33) ligands, reported before. Despite of many efforts, all attempts to prepare analogous nickel compounds have been unsuccessful.

#### Preparation and chemistry of 4-carba-nido-nonaborane(14)

Treatment of (2) with hydrochloric acid in the presence of ferric chloride afforded white, sublimable crystals of 4-CB<sub>8</sub>H<sub>14</sub> (5), m.p. 45-46 °C, stable under nitrogen. Due to a high yield (ca. 90 %), this compound became one of the most accessible carboranes at all. The suggested structure (Ref. 21), shown in Fig. 2, is consistent with the <sup>11</sup>B n.m.r. spectrum exhibiting the 1:1:2:2:2 patterns of doublets, and the <sup>1</sup>H n.m.r. spectrum containing two CH (equatorial and axial) and two BHB bridge signals of relative area 1:1:2:2. As in the case of compounds (3), the signal of the axial CH group is distinctly split to a symmetrical heptet after the <sup>11</sup>B decoupling. It is noteworthy, that carborane (5) undergoes easy dehydrogenation during the mass spectral analysis, showing an intense peak at m/e 112, corresponding to the <sup>12</sup>C<sup>11</sup>B<sub>8</sub><sup>1</sup>H<sub>12</sub><sup>+</sup>, and only a small peak (ca. 3 %) of the <sup>12</sup>C<sup>11</sup>B<sub>8</sub><sup>1</sup>H<sub>14</sub><sup>+</sup> at m/e 114. Considering these results, the structure with the CH<sub>2</sub> group and four hydrogen bridges in a hexagonal open face has been suggested for carborane (5). The same structure was found for 4-NB<sub>8</sub>H<sub>13</sub> (Fig. 4) by X-ray diffraction analysis (Ref. 34). Compound (5), isoelectronic with B<sub>9</sub>H<sub>14</sub><sup>-</sup>, represent the first example of the parent arachno-monocarbaborane. Its formation from the anion (2) can be explained easily by the hydrolytic removal of the B(9) atom.

Preparation of 4-carba-nido-nonaborate(13). The carborane (5) dissolves rapidly in the water solution of potassium carbonate from which the CB<sub>8</sub>H<sub>13</sub><sup>-</sup>NMe<sub>4</sub><sup>+</sup> (6) salt was precipitated. The original carborane can be regenerated by the treatment of (6) with hydrochloric acid. The <sup>11</sup>B n.m.r. spectrum of

(6) shows five doublets of relative area 2:1:1:2:2, and the  $^1\text{H}$  n.m.r. spectrum exhibits five singlets of relative intensities 12:1:1:2:1, reading upfield, attributable to the  $\text{NMe}_4^+$  protons, equatorial and axial CH group, and two types of hydrogen bridges. These data support the symmetrical structure of (6) with three adjacent bridging hydrogens and one  $\text{CH}_2$  group in the open pentagonal face (Fig. 3).

Synthesis of 4-(7-) carba-nido-nonaborane(12). The carborane (5) undergoes an easy dehydrogenation (Ref. 35) when sublimed through a hot tube at 250-350°C and  $10^{-2}$  Torr, affording in ca. 90 % yield a new monocarbaborane  $\text{CB}_8\text{H}_{12}$  (7) which is stable under nitrogen.

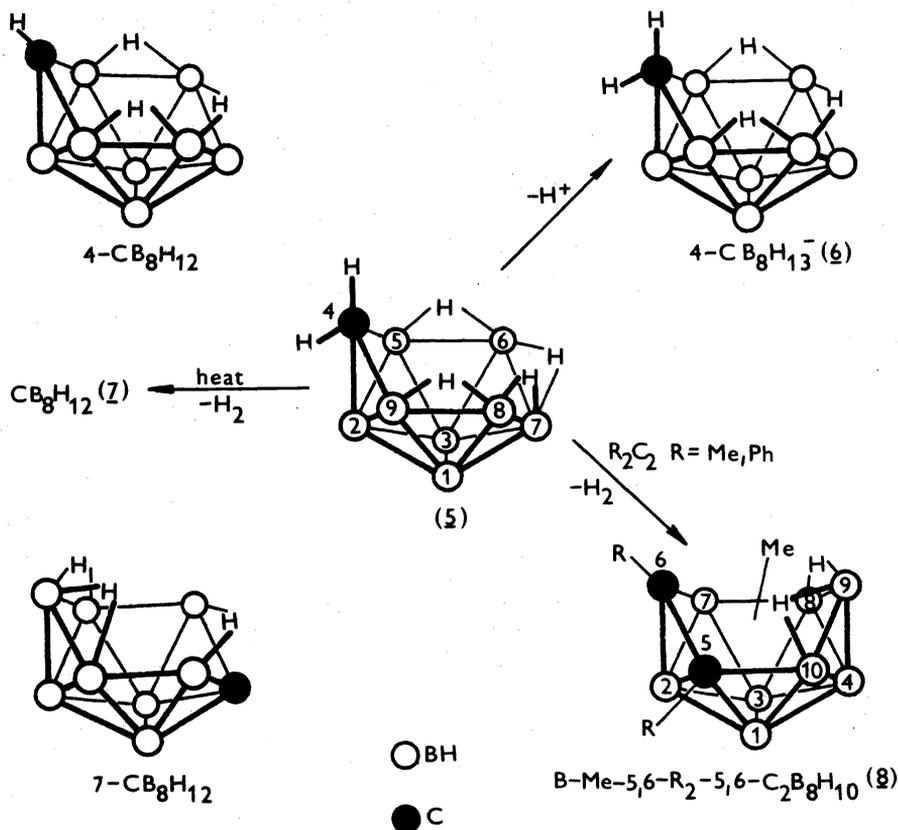


Fig. 3. Reactions of the nido-4-CB<sub>8</sub>H<sub>14</sub>.

Its  $^{11}\text{B}$  n.m.r. spectrum, consisting of separate 1:2:2:2:1 patterns of doublets, and the  $^1\text{H}$  n.m.r. spectrum, showing signals of the skeletal CH group and two types of hydrogen bridges of relative intensities 1:2:1, indicate the symmetrical structure with two identical and one different hydrogen bridges, and one skeletal CH group within the nine vertex nido-skeleton. At present, it is difficult to decide between the two most probable structures, 4- or 7-CB<sub>8</sub>H<sub>12</sub> (see Fig. 3). The formation of both structures is possible under the experimental conditions, and the definitive solution will bring the X-ray diffraction study. Both alternative structures of (7) show a restriction of the six-membered open face to the five-membered one by connecting the non-adjacent B(6)-B(8) atoms in (5), by a hydrogen bridge. This observation, together with the recent demonstration of the 3,4-Me<sub>2</sub>-3,4-C<sub>2</sub>B<sub>7</sub>H<sub>9</sub> structure (Ref. 36), indicate that the open pentagonal face is preferred to the hexagonal one in the nine-vertex nido-boranes or hetero-boranes.

Acetylene insertion reactions. According to our recent results, carborane (5) reacts at 120°C with symmetrically substituted acetylenes,  $R_2C_2$  ( $R = \text{Me}, \text{Ph}$ ), to produce B-methyl-C,C'-dialkyl derivatives of the nido-5,6- $C_2B_8H_{12}$  (Ref. 37-40) [(8a),  $R = \text{Me}$ , and (8b),  $R = \text{Ph}$ ] and one molecule of hydrogen. This reaction involves an extraordinary rearrangement of the skeletal  $CH_2$  group to the terminal position (see Fig. 3) as the Me substituent. The  $^1H$  n.m.r. spectrum of (8a) shows two sharp singlets of both Me-C groups at  $\delta$  1.66 and 1.72 p.p.m., one broader singlet of the Me-B group at  $\delta$  0.73 p.p.m., and two different BHB bridge resonances at  $\delta$  -2.1 and -2.35 p.p.m. Similar results were observed with (8b) which exhibits the Me-B resonance at  $\delta$  0.73 p.p.m. The  $^{11}B$  n.m.r. spectra of both compounds have a typical shape of the 5,6- $C_2B_8H_{12}$  spectrum (Ref. 37-40) showing two separate doublets and a less resolved multiplet composed of one singlet and five doublets. Due to the complexity of these spectra, it is still impossible to determine the position of the Me-B group unambiguously.

#### SYNTHESIS OF NEW NINE - VERTEX HETEROBORANES BY DEGRADATIVE INSERTION

Our first venture into this area was the synthesis of two dicarba-aza-nido-boranes,  $NC_2B_8H_{11}$  and  $NC_2B_8H_{13}$  (Ref. 41), based on the degradative insertion of one nitrogen atom into the 7,8- $C_2B_9H_{12}^-$  molecule. Similar process was published later by Stanko *et al.* (Ref. 42), who prepared the analogous nido-10-S-7,8- $C_2B_8H_{10}$  by the reaction of 7,8- $C_2B_9H_{12}^-$  with potassium hydrosulphite. Our effort to extend the concept of the degradative insertion to other borane systems resulted in the preparation of a family of new nine-vertex nido-heteroboranes.

#### Preparation of 4-aza-nido-nonaborane(13)

The reaction of sodium nitrate with decaborane (14) in tetrahydrofuran followed by acidification with gaseous hydrogen chloride afforded a new azaborane (9) in ca. 30 % yield as an air sensitive liquid, b.p. 60°C at  $10^{-2}$  Torr, m/e 125.1802 (calc. for  $NB_9H_{12}$  125.1807). However, the  $^{11}B$  n.m.r. spectrum showed only eight doublets of relative intensities 1:2:1:2:2 and indicated the formula  $NB_8H_{13}$  rather than  $NB_9H_{12}$ . The X-ray structure determination (Ref. 34) confirmed the 4- $NB_8H_{13}$  structure shown in Fig. 4. The structure of this first uncharged parent azaborane can be described as an iso- $B_9H_{15}$  cage with the ninth boron position replaced by a nitrogen and with two bridging hydrogens missing.

#### Preparation of 6-carba-8-thia-nido-nonaborane(11) and 6,8-dithia-nido-nonaborane(9)

The synthesis (Ref. 42) of both compounds, (10) and (11), based on the treatment of anions (13)-9,11- $C_2B_{10}H_{13}^-$  (Ref. 44) and 6-SB $_9H_{12}^-$  (Ref. 45) with potassium pyrosulphite and hydrochloric acid, is demonstrated in Fig. 4. The  $^{11}B$  n.m.r. spectrum of (10) consisted of two overlapped 2:1 doublets and four doublets of intensity 1, while the spectrum of (11) exhibited five doublets of relative area 2:1:2:1:1. The  $^1H$  n.m.r. spectrum of (10) shows four singlets of equal intensity located at  $\delta$  0.47, ca. -1.2, -1.25, and -3.0 p.p.m., attributable to the equatorial and axial CH groups, and two different bridging hydrogens. The spectrum of (11) shows one singlet at  $\delta$  -1.1 p.p.m., assigned to two equivalent hydrogen bridges. The UV spectra of (10) and (11) exhibit maxima at 240 ( $\epsilon = 3660$ ) and 230 ( $\epsilon = 3430$ ) nm, respectively. It is noteworthy, that all above characteristics of compounds (10) and (11) are very similar to that of 6,8- $C_2B_7H_{13}$  (12) (Ref. 46). On the basis of these results, we propose the same 2532 topological valence structure for compounds (10) - (12) involving the sulphur atom with two exohedral electron pairs (see Fig. 5), equivalent to both  $BH_2^-$  or  $CH_2$  group. The

sulphur atom thus contributes two orbitals and two electrons for the skeletal bonding.

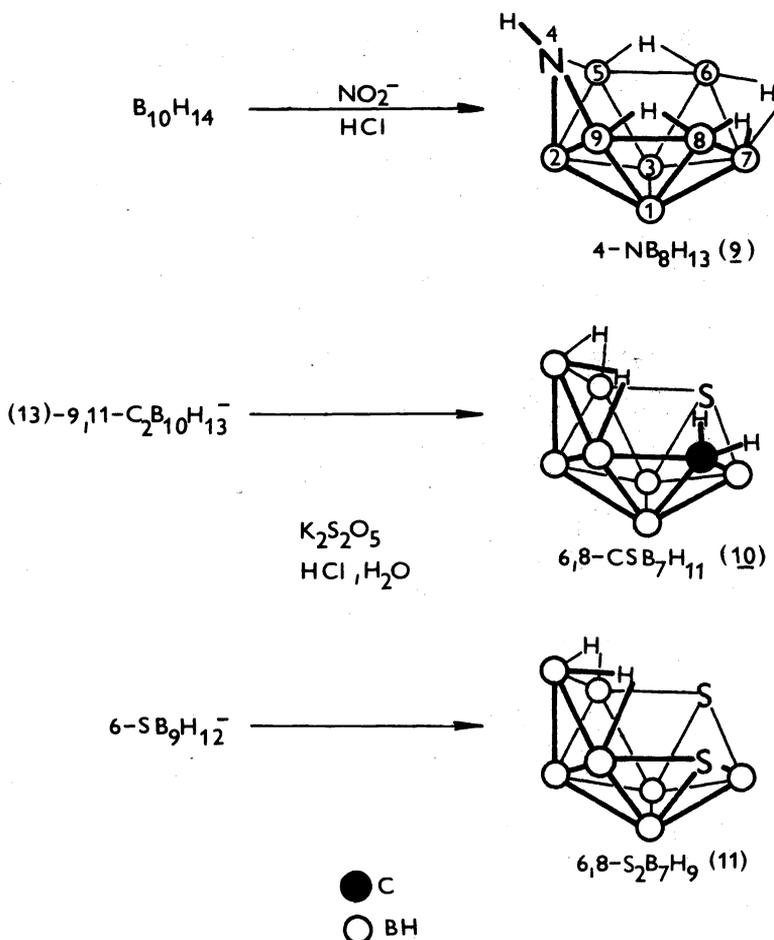


Fig. 4. Synthesis and structure of new nine-vertex nido-heteroboranes.

Following this idea, we assign the arrangement with two exohedral ligands ( $\underline{X}$  or  $\underline{X-H}$ ) on the "ambiguous" heteroatom X even to compounds  $NB_8H_{13}$  (Ref. 34) and  $SB_9H_{12}^-$  (Ref. 45), i.e. generally to compounds with the skeletal oxidation state  $2n + 6$  (arachno-compounds).

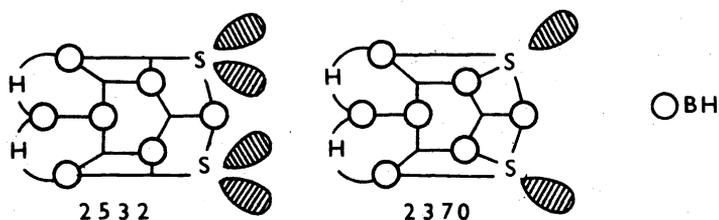


Fig. 5. Alternative topological valence structures of the nido-6,8- $S_2B_7H_9$ .

On the other hand, for  $SB_9H_{11}$  (Ref. 45),  $SB_{10}H_{12}$  (Ref. 45),  $NC_2B_8H_{11}$  (Ref. 41), and  $SC_2B_8H_{10}$  (Ref. 42), i.e. for compounds with the skeletal oxidation

state  $2n + 4$  (nido-series) we suggest the structure with one exohedral ligand on the ambiguous atom (X or X-H). This problem with closo-compounds was solved earlier by Rudolph and Pretzer (3) who favoured the only possible arrangement with one exohedral ligand.

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