

# DEGRADATION-INSERTION REACTIONS OF DECABORANE(14) WITH INORGANIC SALTS

Karel BAŠE

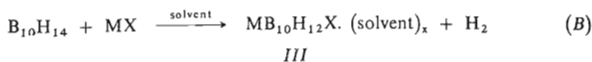
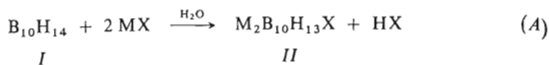
*Institute of Inorganic Chemistry,  
Czechoslovak Academy of Sciences, 250 68 Řež*

Received September 27th, 1982

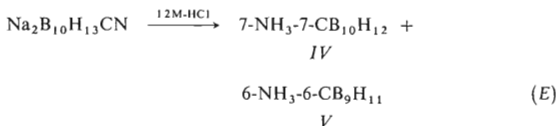
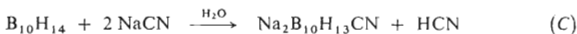
Decaborane(14) reacts with  $\text{NaNO}_2$  in tetrahydrofuran forming the  $[\text{9-tetrahydrofuran-6-NO}_2\text{B}_{10}\text{H}_{12}]^-$  salt which after protonization with concentrated  $\text{H}_2\text{SO}_4$  or diluted  $\text{HCl}$  affords azaboranes  $6\text{-NB}_9\text{H}_{12}$  and  $4\text{-NB}_8\text{H}_{13}$ , respectively. The  $6\text{-NB}_9\text{H}_{12}$  azaborane is hydrolyzed to the  $4\text{-NB}_8\text{H}_{13}$  azaborane and reacts with Lewis bases under the formation of the  $9\text{-L-6-NB}_9\text{H}_{12}$  ligand derivatives ( $\text{L} = (\text{CH}_3)_2\text{S}, \text{CH}_3\text{CN}, (\text{C}_6\text{H}_5)_3\text{P}$ ). By the reduction of  $9\text{-CH}_3\text{CN-6-NB}_9\text{H}_{12}$  with  $\text{LiAlH}_4$  in tetrahydrofuran the  $6\text{-NB}_9\text{H}_{13}^-$  anion was prepared. By an analogous reaction of decaborane(14) with  $\text{KHSO}_3$  in water and by a subsequent protonization of the formed intermediate with concentrated  $\text{H}_2\text{SO}_4$  or diluted  $\text{HCl}$  the thiaaboranes  $6\text{-SB}_9\text{H}_{11}$  and  $4\text{-SB}_8\text{H}_{12}$ , respectively, were prepared. The reaction of decaborane(14) with  $\text{Na}_2\text{SeO}_3$  in tetrahydrofuran followed by the protonization of the intermediate with diluted  $\text{HCl}$  afforded the  $7,8\text{-Se}_2\text{B}_9\text{H}_9$  species. Structures of all compounds were proposed on the basis of the  $^{11}\text{B}$  and  $^1\text{H}$  NMR spectra; in the case of  $4\text{-NB}_8\text{H}_{13}$ , the structure was determined by the X-ray diffraction analysis.

Heteroboranes represent a group of boron hydrides in which one or several boron atoms are substituted by a formally isoelectronic equivalent, *e.g.*  $\text{C}^+$ ,  $\text{N}^{2+}$ ,  $\text{P}^{2+}$ ,  $\text{As}^{2+}$ ,  $\text{S}^{3+}$ ,  $\text{Se}^{3+}$ ,  $\text{Te}^{3+}$ , *etc.* However, the number of general methods for preparation of heteroboranes, *i.e.* for introducing a heteroatom into the borane skeleton is very limited. Among them belong reactions of boranes with alkaline chalcogenides<sup>1-4</sup>, reactions of borane anions with halogenides of the *Va* group of the periodical table<sup>5,6</sup> and reactions of boranes with alkaline pseudohalogenides<sup>7,8</sup>.

Reactions of decaborane(14) with alkaline or ammonium salts of inorganic acids were studied in detail<sup>9</sup>. The course of the reaction depends on the reaction medium<sup>7-9</sup>: in an aqueous medium the reaction proceeds according to the equation (A), while in an anhydrous medium it follows the equation (B).



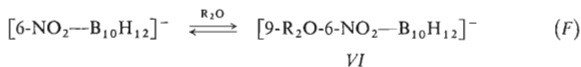
From the view of the preparation of heteroboranes, only the reaction of  $B_{10}H_{14}$  with the alkaline cyanide (C) and the subsequent protonization<sup>7,8</sup> of the formed intermediate (equations D, E) were studied. Degradation-insertion reactions of further boranes and heteroboranes with salts of inorganic acids have been described for a few cases only<sup>10,11,12</sup>.



Compounds *IV* and *V* are starting materials for the whole monocarbaborane chemistry<sup>7,8,13</sup>.

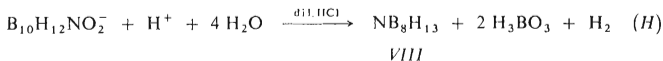
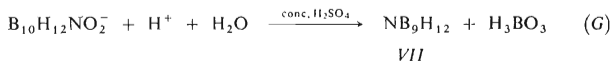
The aim of this study is the description of preparation conditions and of properties of the new medium heteroboranes which are starting compounds for the preparation of other heteroboranes and metalloheteroboranes. Further, an assumed course of the degradation-insertion reaction is discussed which seems to be a general method of the insertion of a heteroatom into borane or heteroborane skeletons.

The reaction of  $B_{10}H_{14}$  with  $NaNO_2$  in tetrahydrofuran proceeds according to the equation (B). Muetterties and coworkers<sup>14</sup> observed that in ether solution  $B_{10}H_{14}$  evolved in the presence of alkaline or ammonium MX salts one equivalent of hydrogen forming an appropriate  $B_{10}H_{12}X^-$  salt. They considered this reaction as an analogy of the early described reaction of  $B_{10}H_{14}$  with  $H^-$  in which  $B_{10}H_{13}^-$  resulted<sup>15</sup>. The mentioned  $B_{10}H_{12}X^-M^+$  salts were isolated in the form of solvates. An incomplete characterization makes, however, difficult to decide whether these products are ligand derivatives  $[9-R_2O-6-XB_{10}H_{12}]^-$  or the  $[6-XB_{10}H_{12}]^- \cdot (R_2O)_x$  solvates only. Due to the fact that the donor ability of an arbitrary ether is much lower than that of many other ligands it is possible to anticipate that in solutions the equilibrium (F) is present.



The existence of such an equilibrium could be a reason of the complexity of the <sup>11</sup>B NMR spectrum of the anion *VI* which is an analogy of the  $[9-(CH_3)_2S-6-CNB_{10}]^-$ .

$\cdot\text{H}_{12}]^-$  anion obtained earlier in the reaction of  $\text{B}_{10}\text{H}_{14}$  with NaCN in dimethyl sulfide<sup>7</sup>. In case that the reaction of decaborane(14) with MX salts proceeds in an aqueous or anhydrous medium under the formation of an *arachno*-system isoelectronic and isostructural with the *arachno*- $\text{B}_{10}\text{H}_{14}^{2-}$  anion (i.e. with the identical *styx* system<sup>16</sup>) it is possible to expect that in addition to NaCN also other salts will be able to insert a heteroatom into the borane skeleton, similarly as it occurs at the protonization of  $6\text{-CNB}_{10}\text{H}_{13}^{2-}$ . A degradation-insertion of the atom N into the borane skeleton occurs – depending on the conditions of the acid hydrolysis of the anion VI – under simultaneous removal of one or two B-atoms as demonstrated by equation (G) and (H), resp. and in Fig 1.



The *nido*-6- $\text{NB}_9\text{H}_{12}$  azaborane<sup>17</sup> is isoelectronic with  $\text{B}_{10}\text{H}_{12}^{2-}$ . Its <sup>1</sup>H and <sup>11</sup>B NMR spectra are very similar to those of the isoelectronic 6- $\text{CB}_9\text{H}_{12}$  and 6- $\text{SB}_9\text{H}_{11}$  heteroboranes<sup>13,18</sup> and are in the consonance with the proposed structure possessing an  $\text{NH}_{(s)}$  fragment in the 6-position and with two equivalent hydrogen bridges between the atoms B(8, 9) and B(9, 10) in the decaborane skeleton. The *arachno*-4- $\text{NB}_8\text{H}_{13}$  azaborane<sup>19,20</sup> is isoelectronic with  $\text{B}_9\text{H}_{14}^-$  and it is the first uncharged azaborane. Whereas the <sup>11</sup>B NMR spectrum showed an integral value of 8 B atoms, the mass spectrum exhibited surprisingly an edge mass corresponding to the  $\text{NB}_9\text{H}_{12}$  species, formed at an intermolecular reaction in the mass spectrometer. This discrepancy was solved by the X-ray structural analysis<sup>19</sup> which determined definitively the structure of the azaborane VIII. Azaborane VII subsides easily hydrolysis splitting the B(9) atom under the formation of the azaborane VIII (Fig 1). This type of hydrolysis is an analogy of the 6- $\text{CB}_9\text{H}_{12}$  and 6- $\text{HOB}_{10}\text{H}_{13}^{2-}$  anions degradation which affords 4- $\text{CB}_8\text{H}_{14}$  and  $\text{B}_9\text{H}_{14}^-$ , respectively. Azaborane VIII has the  $\text{NH}_{(s)}$  fragment in the lowest coordinated position 4 of the iso-nonaborane skeleton and bears two pairs of asymmetrical hydrogen bridges between the atoms B(5, 6), B(8, 9) and B(6, 7), B(7, 8) with shorter bonds pointing to the atoms B(6) and B(8). As it follows from quantum chemical studies<sup>21,22</sup>, the binding arrangement of the atom N can be demonstrated by means of fraction three-center bonds (Fig 2) with maximum electron density between the atoms N and B(5, 9). This kind of arrangement can be explained by a low disposition of the N atom to form multi-central bonds, which is probably caused by its high electronegativity.

The azaborane *VII* reacts in an almost quantitative yield with Lewis bases yielding the 9-L-6-NB<sub>9</sub>H<sub>12</sub> species *IXa*–*IXc* in which L = (CH<sub>3</sub>)<sub>2</sub>S (*IXa*), CH<sub>3</sub>CN (*IXb*), (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P (*IXc*). The bonding arrangement of these compounds is shown in Fig. 3. The bond B(9)–L splits, however, very easily both at an elevated temperature and in the solution. This is, why mass spectra of the compounds *IXa*–*IXc* show only signals

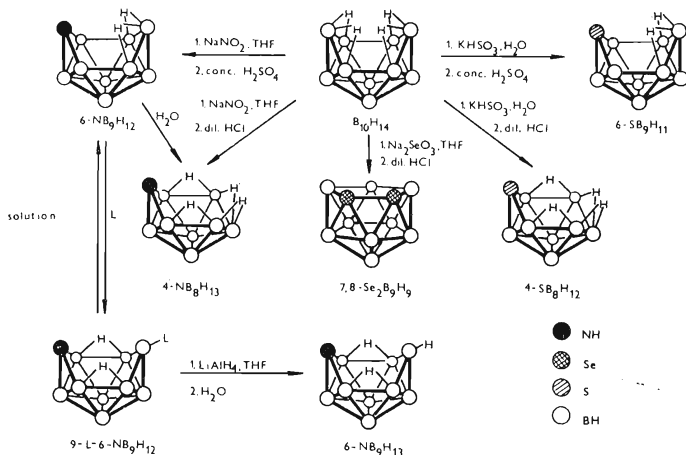


FIG. 1

Degradation-insertion reactions of decaborane(14) with inorganic salts

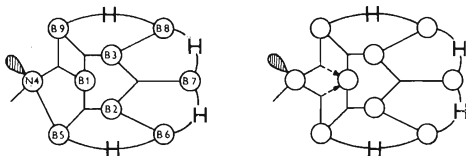
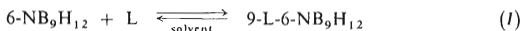


FIG. 2

Scheme of the bonding arrangement in the *arachno*-4-NB<sub>9</sub>H<sub>13</sub> molecule expressed by the styx notation and depicted by means of fractional three-center bonds

corresponding to the  $L^+$  and  $^{14}N^{11}B_9^1H_{12}^+$  species. Similarly, the  $^{11}B$  NMR spectra of these compounds exhibit signals which can be assigned to a mixture of compounds present in the equilibrium reaction (I) as illustrated in Fig. 1.



*IX*

This splitting was also confirmed by the UV spectra. In dichloromethane for compound *IXa* absorptions at  $\lambda_{\max}$  281 nm ( $\epsilon = 5\,358$ ) were found corresponding to compound *VII* together with a band at  $\lambda_{\max}$  234 nm ( $\epsilon = 13\,940$ ) appertaining to compound *IXa*. For the species *IXb* in dichloromethane only one band at  $\lambda_{\max}$  287 nm ( $\epsilon = 2\,103$ ) was observed corresponding exactly to the values of compound *VII* ( $\lambda_{\max}$  284 nm ( $\epsilon = 2\,105$ )). With compound *IXc* the UV spectra are distinctly complex due to the absorptions brought by triphenyl phosphine. In the IR spectra of compounds *VII* and *IXa*–*IXc* measured in tetrachloromethane or dichloromethane absorptions fitting to  $\nu(NH)_{\text{free}}$  and  $\nu(NH)_{\text{bond}}$ , were found while the IR spectra in KBr pellets were due to a hydrolysis measured only with *IXb* in which solely

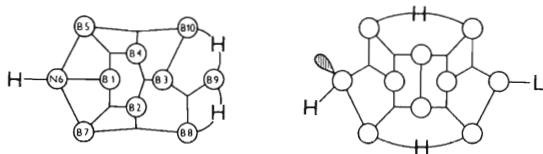


FIG. 3

Scheme of the bonding arrangement in the *nido*-6- $NB_9H_{12}$  and *arachno*-9- $L-NB_9H_{12}$  molecules expressed by the styx notation

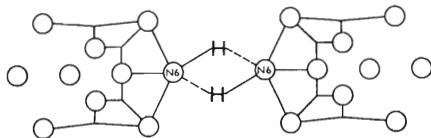


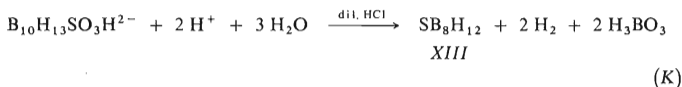
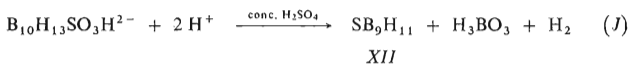
FIG. 4

Scheme of intermolecular hydrogen bridges between two *nido*-6- $NB_9H_{12}$  molecules

the band  $\nu(\text{NH})_{\text{free}}$  was observed whereas the band  $\nu(\text{NH})_{\text{bond}}$  was missing. Compound *IXb* exhibited in the IR spectrum a very weak band at  $2\,235\text{ cm}^{-1}$  corresponding to the  $\nu(\text{CN})$  vibration of the free acetonitrile ( $2\,240\text{ cm}^{-1}$ ); in KBr pellet this vibration has the value of  $2\,330\text{ cm}^{-1}$ . In accord with the IR spectra, in the Raman spectra of the solid compound *IXb* an intensive valence band of the CN valence vibration at  $2\,340\text{ cm}^{-1}$  was found. On the ground of the above results it is possible to state that the CN group lies in the plane of symmetry crossing the atoms N(6)–B(2, 4, 9). From the IR it is also possible to assume that in a solution compounds *VII* and *IX* (*IX* is dissociated to *VII*) form an intermolecular hydrogen bond as shown in Fig. 4.

The easy dissociation of the B(9)–L bond was utilized in the preparation of the pure azaborane *VII* by the sublimation of the ligand derivative *IXa*. The reaction of *IXb* with  $\text{LiAlH}_4$  in tetrahydrofuran afforded the *arachno*-6- $\text{NB}_9\text{H}_{13}^-$  anion the formation of which could be explained as a substitution of  $\text{CH}_3\text{CN}$  by the hydride anion. The formed azaborate anion, isolated in a high yield in the form of the tetramethyl ammonium salt was identified comparing the  $^{11}\text{B}$  NMR spectra with the published data<sup>1</sup>. The analysis of the  $^{11}\text{B}$  NMR spectra of the compound *X* has shown<sup>17</sup> that the high field doublet of intensity 4 at  $\delta$ -31.3 ppm is composed of a triplet of intensity 1 and of two doublets of the relative areas 2 : 1. This is in an agreement with the proposed structure of this anion possessing  $\text{NH}_{(s)}$  fragment in the position 6,  $\text{BH}_2$  group in the position 9 and two equivalent hydrogen bridges between atoms B(7, 8) and B(5, 10).

Similar results as in the azaborane series were achieved in the thiaborane group in which reactions of  $\text{B}_{10}\text{H}_{14}$  with  $\text{Na}_2\text{SO}_3$  and  $\text{K}_2\text{S}_2\text{O}_5$  were studied. Due to the fact that the expected transformation did not take place in tetrahydrofuran<sup>23</sup>, the reaction of  $\text{B}_{10}\text{H}_{14}$  with aqueous  $\text{KHSO}_3$  was studied and it was found to be strongly exothermic just at 343 K. If we assume the reaction pathway to proceed according to the equation (A), the nonidentified product<sup>24</sup> is  $[\text{B}_{10}\text{H}_{13}\text{SO}_3\text{H}]^{2-}$  (*XI*) which is isolable in the form of the tetramethyl ammonium salt. Due to a high reactivity of this intermediate its identification is difficult. Analogously to the degradation-N-insertion also here, in dependence on protonization conditions of the anion *IX*, one or two B atom/s are eliminated and the S-atom is incorporated according to the equations (J) and (K), respectively (see also Fig. 1).



Thiaborane *XII* was identified by the comparison of its  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectra with the literature data<sup>1,18</sup>. The formation of the thiaborane *XIII* is accompanied by the occurrence of the thiaborane *XII*, similarly as it is done with the protonization of the *arachno*-6- $\text{SB}_9\text{H}_{12}^-$  anion<sup>1,18</sup>. For the expected transformation of the thiaborane *XII* into the thiaborane *XIII*, which should be an analogy to the production of 4- $\text{CB}_8\text{H}_{14}$  and 4- $\text{NB}_8\text{H}_{13}$  (ref.<sup>13,19</sup>), no suitable conditions have been found. It is probably caused by a higher stability of 6- $\text{SB}_9\text{H}_{11}$  in comparison with 4- $\text{SB}_8\text{H}_{12}$  under the given reaction conditions. The structure of the thiaborane *XIII* was considered on the basis of a great similarity of its  $^{11}\text{B}$  NMR spectra with those of the isoelectronic and isostructural *arachno*-4- $\text{NB}_8\text{H}_{13}$  and *arachno*-4- $\text{CB}_8\text{H}_{14}$  species. All these monoheteroboranes of the general formula 4- $\text{XB}_8\text{H}_{12}$  ( $\text{X} = \text{CH}_2, \text{NH}, \text{S}$ ) subside an easy dehydrogenation or intermolecular reactions under elevated temperature even under the mass spectroscopy measurement conditions. A similar chemical behavior of these compounds has been also observed at the reaction with  $[(\text{C}_6\text{H}_5)_3\text{P}]_4\text{Pt}$  in which isoelectronic and isostructural *arachno*-platinaheteroboranes<sup>25</sup> arised. On the ground of the discussed spectral and chemical similarities an *arachno*-4- $\text{SB}_8\text{H}_{12}$  structure was proposed for the thiaborane *XIII* with the S atom in the position 4 of the iso-nonaborane skeleton having four hydrogen bridges between the atoms B(5,6), B(8,9) and B(6,7), B(7,8). The thiaborane *XIII* was prepared earlier in a different way<sup>18</sup> but was held for *nido*-4- $\text{SB}_8\text{H}_{10}$ .

Another reaction which leads to the insertion of a heteroatom into the borane skeleton is the reaction of  $\text{B}_{10}\text{H}_{14}$  with  $\text{Na}_2\text{SeO}_3$  in tetrahydrofuran followed by the protonization of the formed intermediate. During this reaction pathway, the insertion of two Se atoms into the borane skeleton<sup>26,27</sup> takes place under the formation of *nido*-7,8- $\text{Se}_2\text{B}_9\text{H}_9$  (*XIV*). A dissimilarity in the character of the product suggests a different reaction mechanism. The structure of the selenaborane *XIV* was suggested on the ground of its  $^{11}\text{B}$  NMR spectra. Almost simultaneously, the selenaborane *XIV* was prepared by Todd and coworkers<sup>4</sup> in another way.

## EXPERIMENTAL

The  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectra were recorded using a Varian XL-100 spectrometer and a JEOL FX 100 spectrometer (for compounds *VII* and *IX*). The mass spectra were determined with a LKB 9000 and with GC/MS HP-5985 A instrument for the *VII* and *IX*. IR spectra were recorded on a Beckman IR-20 A spectrometer, UV spectra were obtained on a Beckman Acta M-IV spectrometer. Raman spectra were recorded on a JEOL LR-1 spectrometer with the Ar-ion laser.  $^1\text{H}$  and  $^{11}\text{B}$  NMR  $\delta$  chemical shifts are related to tetramethyl silane and  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ , respectively. For the characterization of signals following symbols are used:  $\text{H}_{(b)}$  hydrogen bridge,  $\text{H}_{(t)}$  terminal hydrogen,  $\text{NH}_{(s)}$  skeletal NH fragment.

All reactions, if not mentioned otherwise, were carried out under argon by the vacuum-line technique. TLC was carried out on Silufol sheets (Kavalier, Votice, Czechoslovakia, using iodine vapour and subsequent spray with aqueous  $\text{AgNO}_3$  as the detection agents. The solvents

were dried by common laboratory methods. Melting points were obtained in sealed capillaries and are uncorrected.

#### 6-Aza-*nido*-decaborane(12), 6-NB<sub>9</sub>H<sub>12</sub> (VII)

a) To the suspension of NaNO<sub>2</sub> (6.9 g, 0.1 mol) in 50 ml of tetrahydrofuran was added dropwise the tetrahydrofuran solution of B<sub>10</sub>H<sub>14</sub> (I) (6.2 g, 0.051 mol; 50 ml; exothermic reaction, a gas evolution). The mixture was stirred for 5 h at 313 K. The tetrahydrofuran was distilled off, the residue was covered with hexane (50 ml) and under stirring 50 ml of concentrated H<sub>2</sub>SO<sub>4</sub> was added carefully within 3 h not to exceed the temperature of 300 K (exothermic reaction, gas evolution). When the reaction ceased, the hexane layer was separated, the solution concentrated to 20 ml and cooled down to 200 K. The separated product was quickly filtered, dried and purified by sublimation at 333–340 K/1.3 Pa. An amount of 3.41 g (54.5% related to I) of compound VII was obtained; m.p. 352–353 K, *m/z* 125 (corresponding to <sup>14</sup>N<sup>11</sup>B<sub>9</sub>H<sub>12</sub><sup>+</sup>). IR spectrum (tetrachloromethane): 3 340 (N—H<sub>free</sub>), 3 160 (N—H<sub>bond</sub>), 2 570 (B—H<sub>1</sub>), 1 950 (B—H—B) cm<sup>-1</sup>. UV spectrum (dichloromethane): λ<sub>max</sub> 284 nm (ε 2 105). <sup>1</sup>H NMR spectrum (100 MHz, hexadeuterobenzene): δ -3.2 (2 H, H<sub>(b)</sub>). <sup>11</sup>B NMR spectrum (32.1 MHz, hexadeuterobenzene): δ 14.0 (1 B, B<sub>(9)</sub>); 11.3 (2 B, B<sub>(1,3)</sub>); -1.8 (2 B, B<sub>(5,7)</sub>); -14.5 (2B, B<sub>(8,10)</sub>); -27.5 (1 B, B<sub>(2)</sub>); -32.9 ppm (1 B, B<sub>(4)</sub>).

b) 9-(CH<sub>3</sub>)<sub>2</sub>S-6-NB<sub>9</sub>H<sub>12</sub> (IXa) 3.4 g, 0.018 mol) was sublimed at 333 K/1.3 Pa. The sublimate was dissolved in a minimum amount of hexane, filtered and after cooling down to 200 K the precipitate was filtered off. The crude product was resublimed yielding 2.1 g (93% related to IXa) of the compound VII.

#### 4-Aza-*arachno*-nonaborane(13), 4-NB<sub>8</sub>H<sub>13</sub> (VIII)

The suspension of NaNO<sub>2</sub> in tetrahydrofuran was brought into reaction with B<sub>10</sub>H<sub>14</sub> similarly as in the previous experiment. After removing tetrahydrofuran by distillation, the residue was covered with hexane (50 ml) and 100 ml of 4M-HCl was added in portions under stirring (exothermic reaction, gas evolution). After cooling down to the ambient temperature the hexane layer was separated, dried with MgSO<sub>4</sub> and product mixture was separated by means of chromatography (silica gel; benzene-hexane 1 : 1). The solvents were removed by distillation in a vacuum evaporator and the liquid residue was distilled at 333 K/1.3 Pa yielding 1.75 g (29.8% related to I) of compound VIII; m.p. 273 K, *R<sub>F</sub>* (benzene-hexane 1 : 1) 0.27, *m/z* 125.1802 (corresponding to <sup>14</sup>N<sup>11</sup>B<sub>9</sub>H<sub>12</sub><sup>+</sup>, i.e. a product of an intermolecular reaction). IR spectrum (tetrachloromethane): 3 405 s (N—H); 2 570 vs, 2 590 vs, 2 610 vs (B—H<sub>1</sub>); 2 220 sh, w, 2 145 m, 2 100 sh, m, 2 060 sh, m (B—H—B) cm<sup>-1</sup>. <sup>1</sup>H NMR spectrum (100 MHz, hexadeuterobenzene): δ 3.0 (2 H, H<sub>(b1)</sub>); 1.18 (2 H, H<sub>(b2)</sub>); -2.94 ppm (1 H, NH<sub>(s)</sub>). <sup>11</sup>B NMR spectrum (32.1 MHz, hexadeuterobenzene): δ 7.8 (1 B, B<sub>(7)</sub>); -7.1 (2B, B<sub>(5,9)</sub>); -25.4 (1B, B<sub>(1)</sub>); -46.0 (2B, B<sub>(2,3)</sub>); -47.7 ppm (2B, B<sub>(6,8)</sub>).

#### 9-Dimethylsulfide-6-aza-*arachno*-decaborane(12), 9-(CH<sub>3</sub>)<sub>2</sub>S-6-NB<sub>9</sub>H<sub>12</sub> (IXa)

To the suspension of NaNO<sub>2</sub> (6.9 g, 0.1 mol) in 50 ml of tetrahydrofuran was added dropwise the tetrahydrofuran solution of B<sub>10</sub>H<sub>14</sub> (6.2 g, 0.051 mol; 50 ml). The mixture was stirred for 5 h at 313 K. The residue after the removal of tetrahydrofuran by distillation was covered with 50 ml of hexane and the concentrated H<sub>2</sub>SO<sub>4</sub> was added dropwise similarly as in the preparation of VII. The hexane layer was then separated and dimethyl sulfide (2.88 g, 0.047 mol) was added dropwise during 15 min. The resulting mixture was stirred for another 10 min, the pre-



precipitate was filtered off, extracted with three 10 ml portions of hexane and dried, yielding 3.4 g (36% related to *I*) of compound *IXa*; m.p. 344–346 K (dec.).

9-Acetonitrile-6-aza-*arachno*-decaborane(12), 9-CH<sub>3</sub>CN-6-NB<sub>9</sub>H<sub>12</sub> (*IXb*)

*a*) Acetonitrile (1.8 g, 0.044 mol) was added dropwise within 15 min under stirring to the hexane solution of compound *VII* (see preparation of *IXa*) and the resulting mixture was stirred for another 10 min. The precipitate was filtered, extracted with 3 × 10 ml of hexane and dried yielding 3.25 g (39% calculated on *I*) of the compound *IXb*; m.p. 358–361 K (dec.).

*b*) To the solution of compound *VII* (0.8 g, 0.0065 mol) in 20 ml of hexane was added acetonitrile (0.266 g, 0.0065 mol) under stirring. The mixture was agitated for 10 min, the precipitate was filtered, washed with three 10 ml portions of hexane and dried to yield 1.0 g (93% related to *VII*) of compound *IXb*.

9-Triphenylphosphine-6-aza-*arachno*-decaborane(12), 9-(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P-6-NB<sub>9</sub>H<sub>12</sub> (*IXc*)

A benzene solution of triphenyl phosphine (12.0 g, 0.046 mol; 20 ml) was added dropwise within 15 min under stirring to the hexane solution of compound *VII* (see preparation of *IXa*). The mixture was stirred for further 10 min. The yellow precipitate was filtered off, washed three times with 10 ml of hexane and dried yielding 14.2 g (80% related to *I*) of compound *IXc*; m.p. 432–434 K.

Tridecahydro-6-aza-*arachno*-decaborate[1-], 6-NB<sub>9</sub>H<sub>13</sub><sup>-</sup> (*X*)

A solution of compound *IXb* (1.0 g, 0.0061 mol) in tetrahydrofuran (10 ml) was added dropwise under stirring to the suspension of 1.5 g (0.0395 mol) LiAlH<sub>4</sub> in 20 ml of tetrahydrofuran (exothermic reaction, gas evolution). The mixture was then refluxed for 40 min and after cooling down to the ambient temperature the tetrahydrofuran was distilled off. The residue was successively decomposed with the total amount of 30 ml of ethanol (exothermic reaction, gas evolution), after which 20 ml of water was added. The mixture was filtered, ethanol was removed by distillation and the remaining aqueous solution was precipitated with (CH<sub>3</sub>)<sub>4</sub>N<sup>+</sup>Cl<sup>-</sup> (excess). The precipitate was filtered off, washed with 10 ml of water and dried *in vacuo* yielding 1.1 g (91.1% related to *IXb*) of compound *X* in the form of the tetramethyl ammonium salt. The characteristic constants are in accord with literature data<sup>1</sup>.

6-Thia-*nido*-decaborane(11), 6-SB<sub>9</sub>H<sub>11</sub> (*XII*)

A mixture of B<sub>10</sub>H<sub>14</sub> (6.2 g, 0.051 mol), K<sub>2</sub>S<sub>2</sub>O<sub>5</sub> (11.1 g, 0.051 mol), 100 ml of water and 50 ml of hexane was stirred for 48 h at the ambient temperature. When B<sub>10</sub>H<sub>14</sub> disappeared from the hexane layer, hexane was distilled off *in vacuo*, the solution was filtered and the filtrate was precipitated with the (CH<sub>3</sub>)<sub>4</sub>N<sup>+</sup>Cl<sup>-</sup> solution (11.5 g, 0.105 mol). The precipitate was filtered, washed with ether (80 ml) and dried *in vacuo*. The dry intermediate was covered with hexane (50 ml) and concentrated H<sub>2</sub>SO<sub>4</sub> was added dropwise under stirring within 3 h (exothermic reaction, gas evolution). After cooling down to the ambient temperature the hexane layer was separated, hexane removed *in vacuo* and the crude product was sublimed at 343 K/1.3 Pa yielding 1.5 g (20.8% related to *I*) of compound *XII*, physical constant of which are identical with those published earlier<sup>1,18</sup>.

4-Thia-*arachno*-nonaborane(12), 4-SB<sub>8</sub>H<sub>12</sub> (XIII)

Decaborane(14) was treated with K<sub>2</sub>S<sub>2</sub>O<sub>5</sub> in the same manner as in the previous experiment. When B<sub>10</sub>H<sub>14</sub> disappeared from the hexane layer, 4M-HCl (100 ml) was added under stirring (exothermic reaction, gas evolution). After cooling down to the ambient temperature the hexane layer was separated, dried with MgSO<sub>4</sub>, the solution was reduced to the volume of 20 ml and the product mixture was separated by means of hexane on a short dry column of silica gel. Hexane was removed by distillation and the crude product was sublimed at 313 K/1.3 Pa affording 0.9 g (14.1% related to I) of yellowish compound XIII which decomposes by heating; R<sub>f</sub> (benzene-hexane 1 : 1) 0.59. The IR spectral data of XIII are identical with those published in<sup>18</sup>. <sup>1</sup>H NMR spectrum (100 MHz, hexadeuterobenzene): δ -1.35 (2 H, H<sub>(b1)</sub>); -2.40 (2 H, H<sub>(b2)</sub>). <sup>11</sup>B NMR spectrum (32.1 MHz, hexadeuterobenzene): δ 13.8 (1 B, B<sub>(7)</sub>); -3.82 (2 B, B<sub>(5,9)</sub>); -12.3 (1 B, B<sub>(1)</sub>); -41.8 ppm (4 B, B<sub>(2,3,6,8)</sub>).

7,8-Diselena-*nido*-undecaborane(9), 7,8-Se<sub>2</sub>B<sub>9</sub>H<sub>9</sub> (XIV)

To the solution of B<sub>10</sub>H<sub>14</sub> (6.2 g, 0.051 mol) in 50 ml of tetrahydrofuran, 26.3 g (0.10 mol) of Na<sub>2</sub>SeO<sub>3</sub>·5 H<sub>2</sub>O was added and the mixture was stirred for 24 h at the ambient temperature (slightly exothermic reaction, gas evolution, a change of the color of the solution to red). Tetrahydrofuran was then distilled off *in vacuo*. The residue was covered with 50 ml of hexane and 100 ml of 4M-HCl was added in portions under stirring (exothermic reaction, gas evolution). When the reaction ceased, the hexane layer was separated, dried with MgSO<sub>4</sub>, the volume reduced to 20 ml and the product mixture was separated chromatographically (silica gel, hexane). After removing hexane by distillation, the crude product was purified by sublimation at 353 K/1.3 Pa to yield 2.0 g (15% related to I) of compound XIV which does not melt to 523 K and which shows *m/z* 270 corresponding to <sup>80</sup>Se<sup>82</sup>Se<sup>11</sup>B<sub>9</sub><sup>1</sup>H<sub>9</sub><sup>+</sup>. IR spectrum (dichloromethane): 828 w, 862 w, 890 m, sh, 905 m, sh, 912 m, 983 s, 1 008 s, 2 575 vs, 2 610 vs cm<sup>-1</sup>. <sup>1</sup>H NMR spectrum (100 MHz, hexadeuterobenzene): overlapped signals in the region δ 0.5 to -7.5 ppm (9 H, H<sub>(1)</sub>). <sup>11</sup>B NMR spectrum (32.1 MHz, hexadeuterobenzene): δ -0.2 (3 B); -2.4 (4 B); -10.2 (1 B); -36.4 (1 B).

The NMR spectra were measured by Mr P. Pech and Dr P. Trška from the Prague Institute of Chemical Technology, Prague, by Dr A. Lyčka from the Research Institute of Organic Syntheses, Pardubice-Rybitví and by Dr S. Heřmánek from the Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences. The IR and UV spectra were recorded by Drs F. Hanousek and F. Haruda, the Raman spectra were obtained by Dr F. Hanousek, Institute of Inorganic Chemistry ČSAV, Řež near Prague. The mass spectra were measured by Dr V. Kubelka from the Prague Institute of Chemical Technology, Prague, and by Dr Z. Weidenhoffer, Stavební geologie, Prague. The author thanks all these colleagues for their assistance. Special thanks are due to Dr S. Heřmánek for his help in the interpretation of NMR spectra and to Dr F. Hanousek for his assistance in interpreting the IR and UV spectra.

## REFERENCES

- Hertler W. R., Klanberg F., Muettterties E. L.: *Inorg. Chem.* **6**, 1696 (1967).
- Friesen G. D., Barriola A., Todd L. J.: *Chem. Ind. (London)* 1978, 631.
- Friesen G. D., Kump R. L., Todd L. J.: *Inorg. Chem.* **19**, 1485 (1980).
- Little J. L., Friesen G. D., Todd L. J.: *Inorg. Chem.* **16**, 869 (1977).
- Little J. L., Wong A. C.: *J. Amer. Chem. Soc.* **93**, 522 (1971).
- Little J. L., Pao S. S., Sugathan K. K.: *Inorg. Chem.* **13**, 1752 (1974).
- Knoth W. H.: *J. Amer. Chem. Soc.* **89**, 1274 (1967).

8. Knoth W. H.: *Inorg. Chem.* **10**, 598 (1971).
9. Muetterties E. L., Ford C.: U.S. 3 050 361 (1962).
10. Plešek J., Štíbr B., Heřmánek S.: *Chem. Ind. (London)* **1974**, 622.
11. Bratsev V. A., Knyazev S. P., Danilova G. M., Stanko V. I.: *Zh. Obshch. Khim.* **45**, 1393 (1975).
12. Plešek J., Heřmánek S., Janoušek Z.: *This Journal* **42**, 785 (1977).
13. Baše K., Štíbr B., Dolanský J., Duben J.: *This Journal* **46**, 2345 (1981).
14. Aftandilian V. D., Miller H. C., Muetterties E. L.: *J. Amer. Chem. Soc.* **83**, 2471 (1961).
15. Hough W. V., Edwards L. J.: National Meeting of the American Chemical Society, San Francisco, California, April 1958.
16. Lipscomb W. N.: *Boron Hydrides*, p. 49. Benjamin, New York, Amsterdam 1963.
17. Baše K., Hanousek F., Plešek J., Štíbr B., Lyčka A.: *J. Chem. Soc., Chem. Commun.* **1981**, 1162.
18. Pretzer W. R., Rudolph R. W.: *J. Amer. Chem. Soc.* **98**, 1441 (1976).
19. Baše K., Heřmánek S., Plešek J., Huffman J., Ragatz P., Schaeffer R.: *J. Chem. Soc., Chem. Commun.* **1975**, 934.
20. Benjamin L. E., Stafiej S. F., Takacs E. A.: *J. Amer. Chem. Soc.* **85**, 2674 (1963).
21. Bicerano J., Lipscomb W. N.: *Inorg. Chem.* **19**, 1825 (1980).
22. Dolanský J., Heřmánek S., Zahradník R.: *This Journal* **46**, 2479 (1981).
23. Baše K.: *Thesis*. Czechoslovak Academy of Sciences, Prague 1979.
24. Baše K., Heřmánek S., Gregor V.: *Chem. Ind. (London)* **1979**, 743.
25. Baše K., Štíbr B., Zakharova I. A.: *Synth. React. Inorg. Metal.-Org. Chem.* **10**, 509 (1980).
26. Baše K.: Proceedings of the Conference on Advances in Elementoorganic Chemistry, May 23–25, 1977, Liblice, Czechoslovakia, Abstr. C–1.
27. Baše K., Štíbr B.: *Chem. Ind. (London)* **1977**, 951.

Translated by S. Heřmánek.