

PREPARATION, PROPERTIES AND STRUCTURE
OF SOME INTERMEDIATE *nido*- AND *arachno*-MONOCARBABORANES

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The 6-N(CH₃)₃-6-CB₉H₁₁ carborane reacts with sodium in liquid ammonia with the formation of 6-CB₉H₁₂⁻ which was used as a starting compound for preparing the 4-CB₈H₁₄, 9-L-6-CB₉H₁₃ (L = (CH₃)₂S, CH₃CN and P(C₆H₅)₃), 1-(η⁵-C₅H₅)-1,2-FeCB₉H₁₀⁻, and 2,3-(η⁵-C₅H₅)₂-2,3,1-CO₂CB₉H₁₀⁻ carboranes. The 4-CB₈H₁₄ compound was dehydrogenated at 623 K to give 4-(7)-CB₈H₁₂ carborane. Base degradation of 6-N(CH₃)₃-6-CB₉H₁₁ in methanol resulted in the formation of 3,4-μ-N(CH₃)₃CH—B₅H₁₀. The structure of all compounds was proposed on the basis of their ¹¹B and ¹H-NMR spectra and X-ray diffraction was used in the case of the transition metal complexes.

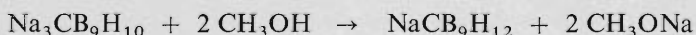
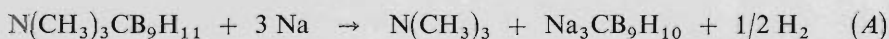
To a larger extent, eleven and twelve-vertex monocarbaboranes and their derivatives whose synthesis starts from a relatively available decaborane(14) have been studied. Onak and coworkers^{1,2} and Dunks and Hawthorne³ reported the synthesis of 1-CB₅H₇ and 2-CB₅H₉ representing monocarbaboranes with the lowest number of skeletal atoms. In the area of intermediate 7–10 atom monocarbaboranes, only *closo*-1-CB₉H₁₀⁻, *nido*-6-N(CH₃)₃-6-CB₉H₁₁ (ref.^{4,5}) and recently isolated *closo*-1-N(CH₃)₃-1-CB₉H₉ (ref.⁶) have been prepared and characterized. We wish to report in this article the preparation and characterization of monocarba derivatives of the polyhedral fragment ions B₉H₁₂⁻, B₉H₁₄⁻, B₁₀H₁₂²⁻ and B₁₀H₁₄²⁻, which not only enlarge the spectrum of intermediate carboranes but also extend the area of closed metal carborane polyhedra to 11- and 12-atom systems derived from CB₉H₁₀³⁻.

As the basic compound for preparing new intermediate carboranes, 6-N(CH₃)₃-6-CB₉H₁₁ (*I*) was used which was obtained by methylating the 7-NH₃-7-CB₁₀H₁₂ (*II*) and 6-NH₃-6-CB₉H₁₁ (*III*) mixture arising from acidification of the 6-NCB₁₀H₁₃²⁻ anion with concentrated hydrochloric acid. According to the original paper⁴, *II* and *III* are formed under these conditions in a ratio of about 3 : 7. Reproducing this reaction we have found, however, the reverse proportion of the products formed. We have therefore searched for optimum conditions for preparing *I* and found that using dilute aqueous HCl (2 : 1) a mixture of compounds *II* and *III* has been formed in a ratio of 2 : 1.

The reaction of *I* with sodium in boiling tetrahydrofuran lead to the *closo*-1- $\text{CB}_9\text{H}_{10}^-$ anion⁴. However, when we performed this reaction in liquid ammonia we obtained⁷, upon subsequent methanolysis of the intermediate formed, the *nido*-6- $\text{CB}_9\text{H}_{12}^-$ anion *IV* as tetramethylammonium salt in high yield. Regarding the reaction conditions and a considerable similarity of the ^{11}B -NMR spectra of *IV* and *I*, the same arrangement of skeletal atoms in both compounds should be assumed. The signal of the skeletal CH group in the $\{^{11}\text{B}\}^1\text{H}$ -NMR spectrum of *IV* is split into a quartet, probably due to a coupling with hydrogen atoms of three adjacent BH groups.

In contrast to the structure *I* suggested by Knoth⁴, we prefer an alternative structure having the bridging hydrogens between the $\text{B}_{(8)}-\text{B}_{(9)}$ and $\text{B}_{(9)}-\text{B}_{(10)}$ atoms for the ^{11}B -NMR spectrum of both compounds involves an upfield signal (intensity 1) assigned to the $\text{B}_{(4)}$ atom. The same arrangement of hydrogen bridges was suggested⁸ even for the isoelectronic 6- SB_9H_{11} . Regarding the earlier formulated rules⁹, an upfield signal (intensity 2) should be present in the spectra of compounds *I* and *IV* if the earlier suggested arrangement were considered. Beside this, Knoth's structure involves a four coordinate $\text{B}_{(9)}$ atom, *i.e.* the structural feature which has not been observed in any borane compound so far prepared.

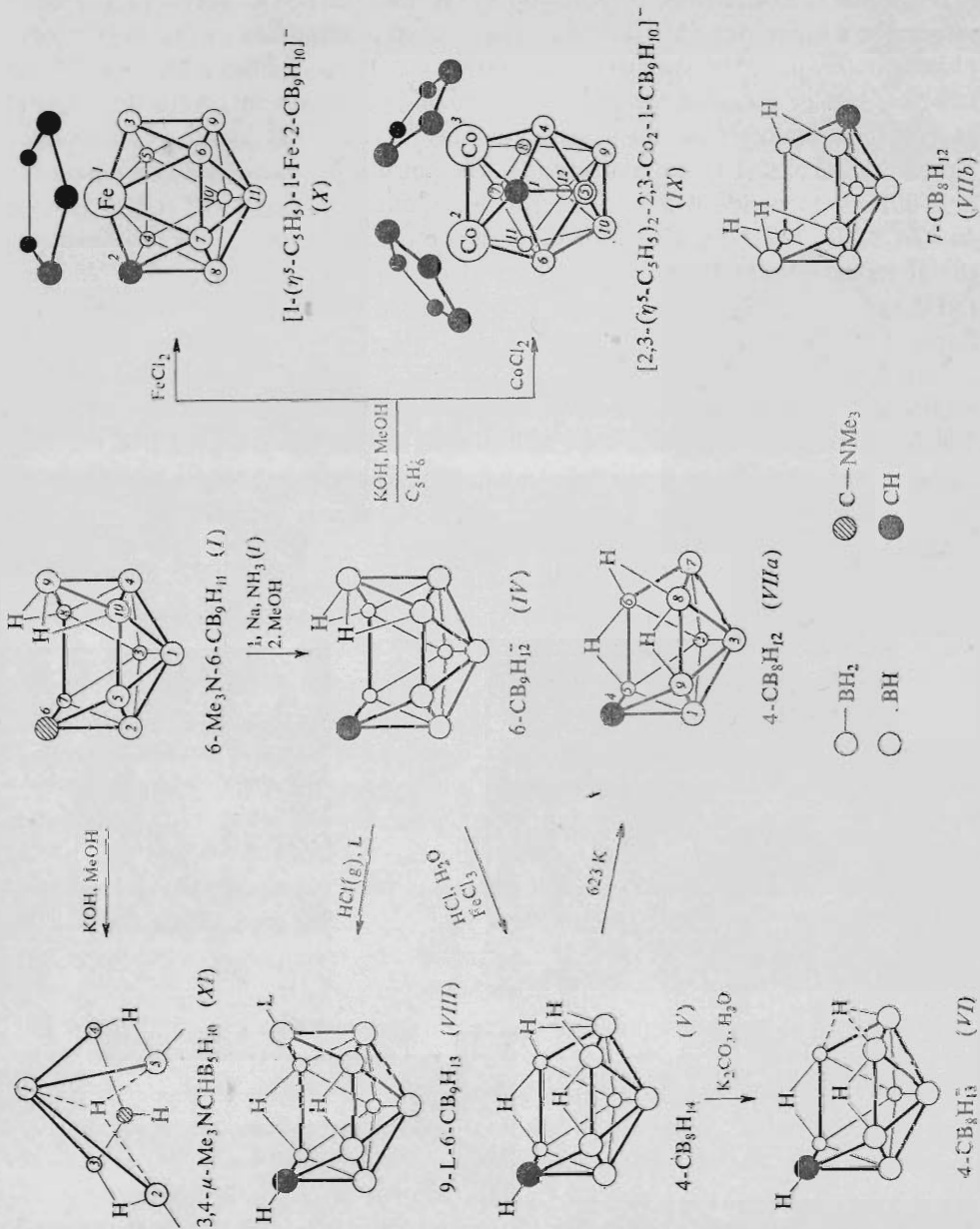
The formation of the anion *IV* can be explained by the formation of an intermediate 6- $\text{CB}_9\text{H}_{10}^{3-}$ anion which yields *IV* by methanolysis.



Anion *IV* proved to be a useful starting compound for preparing further carboranes. When *IV* is treated with ferric chloride in acidic medium⁷, an oxidative-hydrolytic degradation of the $\text{B}_{(9)}$ atom occurs to produce a neutral 4-carba-*arachno*-nonaborane(14), 4- CB_8H_{14} (*V*), which is isoelectronic to $\text{B}_9\text{H}_{14}^-$. Both ^1H and ^{11}B -NMR spectra of *V* are consistent with a structure containing two pairs of equivalent hydrogen bridges and one CH_2 group occupying the lowest coordinate position of the nonaborane framework. Such an arrangement disobeys the Lipscomb's rules¹⁰ in having the $\text{B}_{(7)}$ atom of connectivity 4 bonded to other two boron atoms by hydrogen bridges.

By treatment of carborane *V* with aqueous K_2CO_3 the abstraction of one bridging proton takes place to form the 4- $\text{C}_1\text{B}_8\text{H}_{13}^-$ (*VI*) anion the symmetrical structure of which, with two kinds of hydrogen bridges of relative intensity 2 : 1, follows from NMR spectra. The most probable arrangement seems to be that shown in Fig. 1, involving the hydrogen bridge shared by the $\text{B}_{(6,7,8)}$ atoms.

Carborane *V* undergoes a thermal dehydrogenation¹¹ when sublimed through a ceramic packing at 623 K/1.3 Pa to give a new carba-*nido*-nonaborane(12), CB_8H_{12}



(VII), which is isoelectronic to $B_9H_{12}^-$. The 1H and ^{11}B -NMR spectra of VII correspond to a ninevertex *nido*-skeleton with the open pentagonal face and the C atom placed in the plane of symmetry intersecting the $B_{(1,4,7)}$ atoms. The $1-CB_8H_{12}$ structure can be excluded for the C atom in this position would have the highest coordination number¹² and the formation of this isomer would require a complicated reorganization of skeletal atoms during the reaction. On the basis of the data obtained, it is difficult to decide which of the two remaining alternatives, $4-CB_8H_{12}$ (VIIa) and $7-CB_8H_{12}$ (VIIb), is actual for the formation of both isomers is possible under the given experimental conditions. Simple dehydrogenation would yield VIIa and the dehydrogenation connected with a 60° rotation of the $B_{(1,2,3)}$ triangle in the framework of V would lead to VIIb. The VIIa structure should be favoured due to the uncomplicated formation and the presence of the C atom at the lowest coordinate position. It is, however, in disharmony with the found sequence of signals in the ^{11}B -NMR spectrum involving a downfield signal of intensity 1 instead of the expected signal of intensity 2 attributed to the $B_{(2,3)}$ atoms in the position opposite to hydrogen bridges⁹ between the $B_{(5,6)}$ and $B_{(8,9)}$ atoms. On the other hand, the character of the ^{11}B -NMR spectrum is in agreement with the structure VIIb but the $C_{(7)}$ atom has a higher coordination number in this case.

In contrast to the formation of $4-CB_8H_{14}$ in the reaction of IV with dilute hydrochloric acid, the anion IV reacts with anhydrous HCl in the presence of some Lewis bases¹³ to give the *arachno*-9-L-6- CB_9H_{13} (VIII) compounds, where L = $(CH_3)_2S$ (VIIIa), CH_3CN (VIIIb), and $(C_6H_5)_3P$ (VIIIc). The reaction can be interpreted as an addition of proton to the anion IV followed by the attack of base at position 9 combined with the rearrangement of hydrogen bridges without a significant movement of skeletal atoms. The structure of compounds VIII, which are isoelectronic with *arachno*- $B_{10}H_{14}^{2-}$, has been suggested on the basis of the 1H and ^{11}B -NMR spectra. The 1H -NMR spectra exhibit signals of two equivalent hydrogen bridges and two signals attributable to the axial and equatorial protons of the skeletal CH_2 group¹³. In the $\{^{11}B\}^1H$ -NMR spectra of VIII, the signals of the axial CH group are split into a heptet, which is probably due to its interaction with the equatorial hydrogen of the same group and three hydrogen atoms of the adjacent BH groups. The ^{11}B -NMR spectra correspond to the proposed symmetry of the molecule and contain the expected signal of intensity 1 attributable to the BH_2 group substituted by ligand at position 9. The mass spectra of VIII exhibit, beside the corresponding molecular cut-off, intensive peaks of $^{12}C^{11}B_9^+H_{13}^+$ (m/z 124) along with the peaks of L^+ , thus indicating the fragmentation of the molecule under the conditions of the mass spectral experiment. All attempts to prepare CB_9H_{13} by the thermal decomposition of VIIIa were, however, unsuccessful.

Another interesting property of the anion IV is the formation of mixed metallo-carbaborane sandwich complexes in its reaction with transition metal halides and cyclopentadiene in strongly alkaline methanolic solutions¹⁴. In the reaction of IV

with $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$, the $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2\text{CB}_9\text{H}_{10}^-$ anion (*IX*) is produced while a similar reaction with $\text{FeCl}_2 \cdot 4 \text{O}_2$ gives $\eta^5\text{-C}_5\text{H}_5\text{FeCB}_9\text{H}_{10}^-$ (*X*). Both anions were characterized as tetramethylammonium salts. The NMR data of *IX*, allowing several possibilities as to the symmetry, lead to the suggestion of the incorrect structure for this compound¹⁴. Complex *X*, containing the Fe^{3+} ion with the d^5 electron shell, is paramagnetic and its NMR spectrum cannot be interpreted in a usual way. The structures of both *IX* and *X* were therefore solved by X-ray diffraction^{15,16}. The found structure of *IX* is consistent with a symmetrical *closo*-2,3- $(\eta^5\text{-C}_5\text{H}_5)_2$ -2,3,1- Co_2 . $\text{CB}_9\text{H}_{10}^-$ anion involving two adjacent $(\text{C}_5\text{H}_5\text{Co})^{2+}$ groups. The latter anion is isomeric with 2,11- $(\eta^5\text{-C}_5\text{H}_5)_2$ -2,11,1- $\text{Co}_2\text{CB}_9\text{H}_{10}^-$ obtained by Hawthorne and co-workers¹⁷ by polyhedral expansion of 1- $\text{CB}_9\text{H}_{10}^-$. The formation of both complexes, *IX* and *X*, can be explained in terms of insertion of one or two metal atoms into the open hexagonal face of the 6- $\text{CB}_9\text{H}_{10}^{3-}$ anion formed by abstracting two bridging protons of *IV* in strongly alkaline medium.

A very unusual type of reaction is the solvolysis of *I* performed in concentrated methanolic KOH and resulting in stepwise degradation of four $\text{B}_{(4,8,9,10)}$ atoms¹⁸ to give 3,4- $\mu\text{-N}(\text{CH}_3)_3\text{CH-B}_5\text{H}_{10}$ (*XI*). Melting point and IR spectrum of *XI* are very similar to those of the product A isolated by Knoth⁴ as an unidentified side product in the preparation of 1- $\text{CB}_9\text{H}_{10}^-$. Triplet of intensity 2 found in the ^{11}B -NMR spectrum of *XI*, collapsing to a singlet in the $\{^1\text{H}\}$ -NMR spectrum, establishes the presence of two equivalent BH_2 groups. Two signals of hydrogen bridges of area 2 : 1 were found in the ^1H -NMR spectrum. These data are consistent with the structure similar to that found in *arachno*- B_5H_{11} in which one hydrogen bridge has been replaced by the $(\text{CH}_3)_3\text{NCH}^{(+)}$ group. The ^1H -NMR spectra also indicate the presence of a special hydrogen bridge which, similarly as it was found by Schaeffer and co-workers¹⁹ in B_5H_{11} , belongs simultaneously to the $\text{B}_{(1,2,5)}$ atoms. If the bridging C atom of the $(\text{CH}_3)_3\text{NCH}^{(+)}$ group is considered to be a skeletal atom, compound *IX* is then isoelectronic to *hypho*- $\text{B}_6\text{H}_{12}^{2-}$; in the opposite case, *IX* will be a bridge substituted derivative of the *arachno*- $\text{B}_5\text{H}_{10}^-$ anion.

EXPERIMENTAL

All reactions were performed under nitrogen and modified vacuum line techniques were used for isolating the compounds, unless stated otherwise. TLC was carried out on Sulfolip plates (Kavalier, Votice, Czechoslovakia); detection by I_2 vapours followed by AgNO_3 spray. The 32.1 MHz ^{11}B and 100 MHz ^1H -NMR spectra were measured on a Varian XL-100 instrument, mass spectra were obtained using LKB-9000 and IR spectra were recorded on a Beckman IR 20A instrument. The ^1H and ^{11}B -NMR chemical shifts are given in δ (ppm, relative to tetramethylsilane and BF_3 etherate, respectively); the coupling constants are given in Hz.

6-Trimethylamine-6-carba-*nido*-decaborane(11) (I)

The mixture of $B_{10}H_{14}$ (18.6 g; 0.15 mol), NaCN (22.1 g; 0.45 mol), water (200 ml) and hexane (50 ml) was stirred for 4 h at room temperature until all $B_{10}H_{14}$ had disappeared from the hexane layer. Further work up of the mixture was performed in the following two ways: *a*) A saturated solution of CsCl (50 g) in water was added, the suspension formed was cooled to 278 K and $Cs_2B_{10}H_{13}CN$ was filtered off and rinsed several times with cold water (278 K). The isolated Cs^+ salt was further treated as in the next case. *b*) The mixture was poured in several portions under stirring to dilute (2 : 1) hydrochloric acid (300 ml). After the gas evolution had ceased, dioxane (100 ml) was added and the suspension of dioxanates was filtered off after cooling to 278 K. The precipitate was rinsed several times with 278 K cold water and dried at 298 K *in vacuo*. The mixture of dioxanates was dissolved in a 20% aqueous KOH (250 ml) and dimethyl sulphate (50 ml) was added under stirring to precipitate *I* and the N-trimethyl derivative of *II*. This mixture was enriched in *I* by a continuous extraction with boiling dichloromethane. The dichloromethane soluble portion was separated using dry column chromatography on silica gel in dichloromethane to give 9.2 g (34% based on $B_{10}H_{14}$ consumed) of *I*. ^{11}B -NMR spectrum* (hexadeuterioacetone): 1.0 (1B); -1.7 (2B); -5.9 (2B)8 -12.1 (2B); -29.9 (1B); -38.0 (1B, $B_{(4)}$).

Tetramethylammonium-dodecahydro-6-carba-*nido*-decaborane(-1) (IV)

To the compound *I* (4.5 g; 0.025 mol) liquid ammonia (50 ml) was condensed. To the stirred mixture, sodium (1.8 g; 0.078 mol) was added in several portions at reflux and the solution formed was stirred for additional 30 min and then treated with methanol (40 ml). Ammonia was distilled off through a column packed with solid KOH and the residual ammonia was evaporated *in vacuo* (water pump). To the resulting methanolic solution, water (40 ml) was added and, after stripping off the methanol *in vacuo*, the water solution was filtered and precipitated with an excess of tetramethylammonium chloride. The product was filtered off, washed with water and dried at 298 K/1.3 Pa to obtain 3.9 g (80% based on *I* consumed) of *IV*. For $N(CH_3)_4CB_9H_{12}$ (195.6) calculated: 30.70% C, 12.37% H, 49.78% B, 7.16% N, found: 30.32% C, 12.05% H, 50.24% B, 7.21% N. 1H -NMR spectrum (hexadeuterioacetone): 5.4 (1 H, $CH_{(s)}$); 3.4 (12 H, CH_3 protons); -3.7 (2 H, $H_{(b)}$). ^{11}B -NMR spectrum (acetone- d_6): 1.7 (2 B); -2.6 (1 B); -4.3 (2 B); -12.6 (2 B); -40.7 (1 B); -38.6 (1 N, $B_{(4)}$).

3-Carba-*arachno*-nonaborane(14) (V)

To the water solution of $NaCB_9H_{12}$ from the previous preparation, hexane (50 ml) was added and then dropwise a solution of $FeCl_3 \cdot 6 H_2O$ (33.0 g; 0.12 mol) in water (100 ml) and concentrated hydrochloric acid (45 ml) (exothermic reaction, gas evolution). After cooling to room temperature the hexane layer was separated, dried with $MgSO_4$ and filtered. The residue, remaining after distilling off the hexane on a rotatory evaporator *in vacuo*, was sublimed at 323 K/1.3 Pa to obtain 2.5 g (80% based on *I* consumed) of *V*, m.p. 318–319 K, R_F (ben-

* The NMR data are given as follows: ^{11}B -NMR spectrum (solvent); δ (intensity, interpretation) $J(^{11}B-^1H)/J(^{11}B-^1H)$; 1H -NMR spectrum (solvent): δ (intensity, interpretation). The following abbreviations are used to characterize the signals: $H_{(b)}$ hydrogen bridge, $CH_{(s)}$ skeletal CH group, $CH_{(ax)}$ and $CH_{(e)}$ axial and equatorial hydrogens of the skeletal CH_2 group.

zene-hexane 1 : 2) 0.3, and m/z 112 (corresponding to $^{12}\text{C}^{11}\text{B}_8^1\text{H}_{12}^+$). $^1\text{H-NMR}$ spectrum (hexadeuteriobenzene): 0.1 (1 H, $\text{CH}_{(\text{eq})}$); -0.45 (2 H, $\text{H}_{(\text{b}1)}$); -1.75 (1 H, $\text{CH}_{(\text{ax})}$); -3.52 (2 H, $\text{H}_{(\text{b}2)}$). $^{11}\text{B-NMR}$ spectrum (hexadeuteriobenzene): 17.0 (1 B, $\text{B}_{(7)}$) (160); -3.7 (1 B, $\text{B}_{(1)}$) (170); -6.3 (2 B, $\text{B}_{(5,9)}$) (160/35); -34.9 (2 B, $\text{B}_{(6,8)}$) (155/55); -41.1 (2 B, $\text{B}_{(2,3)}$) (155).

Tetramethylammonium tridecahydro-4-carba-*arachno*-nonaborane(-1) (VI)

A solution of K_2CO_3 (2 g; 0.015 mol) in water (30 ml) was shaken with *V* (1 g; 0.009 mol) for 15 min. The mixture was filtered into the excess of concentrated water solution of $\text{N}(\text{CH}_3)_4\cdot\text{Cl}$, filtered, rinsed several times with water and dried at 293 K/1.3 Pa. 1 g of *VI* (61.0% based on *V* consumed) was obtained which was crystallized from acetone-water mixture by slow evaporation of acetone at room temperature. For $\text{N}(\text{CH}_3)_4\text{CB}_8\text{H}_{13}$ (185.8) calculated: 32.32% C, 13.56% H, 46.58% B, 7.54% N; found: 31.98% C, 13.70% H, 46.35% B, 7.60% N. $^1\text{H-NMR}$ spectrum (hexadeuterioacetone): 4.35 (1 H, $\text{CH}_{(\text{eq})}$); 3.42 (12 H, CH_3 protons); -0.5 (1 H, $\text{CH}_{(\text{ax})}$); -1.87 (2 H, $\text{H}_{(\text{b}1)}$); -2.75 (1 H, $\text{H}_{(\text{b}2)}$). $^{11}\text{B-NMR}$ spectrum (hexadeuterioacetone): 1.6 (2 B) (140); -6.5 (1 B) (140); -24.0 (1 B) (150); -32.8 (2 B); -37.2 (2 B).

4-(7-) Carba-*nido*-nonaborane(12) (VII)

A quartz hot tube, equipped with ceramic packing, heating jacket and cold finger, was charged with a solution of *V* (0.7 g; 0.009 mol) in pentane (50 ml). The solvent was distilled off *in vacuo*, the lower part of the apparatus was cooled to 195 K and the ceramic packing was heated up to 623 K. Carbaborane *V* was slowly sublimed through the hot zone onto a 195 K cold finger at 323 K (bath)/1.3 Pa to give 0.6 g (88% based on *V* consumed) of *VII*, m.p. 321 to 322 K, m/e 112 (corresponding to $^{12}\text{C}^{11}\text{B}_8^1\text{H}_{12}^+$). $^1\text{H-NMR}$ spectrum (hexadeuteriobenzene): 3.6 (1 H, $\text{CH}_{(\text{s})}$); -3.1 (2 H, $\text{H}_{(\text{b}1)}$); -5.5 (1 H, $\text{H}_{(\text{b}2)}$). $^{11}\text{B-NMR}$ spectrum (hexadeuteriobenzene): 3.0 (1 B) (165); -8.2 (2 B) (160); -16.0 (2 B) (150/35); -31.2 (2 B) (170/40); -57.9 (150).

9-Dimethylsulphide-6-carba-*arachno*-decaborane(13) (VIIIa)

Gaseous HCl was slowly passed through a solution of *IV* (4 g; 0.024 mol) in dimethyl sulphide (60 ml) for 2 h at room temperature. The dimethyl sulphide was then evaporated *in vacuo* and the solid residue was extracted with benzene. Benzene solution was then placed atop a silica gel dry column and eluted with benzene. The combined fractions of R_F 0.32 (benzene) were evaporated *in vacuo* to give 3.4 g (90% based on *IV* consumed) of *VIIIa*. Analytical product obtained by crystallization from benzene-hexane mixture had m.p. 385–386 K (decomp.) and m/z 186 (corresponding to $^{23}\text{S}^{12}\text{C}_3^{11}\text{B}_9^1\text{H}_9^+$). $^1\text{H-NMR}$ spectrum (hexadeuterioacetone): 2.57 (6 H, CH_3 protons); 0.27 (1 H, $\text{CH}_{(\text{eq})}$); -1.6 (1 H, $\text{CH}_{(\text{ax})}$); -3.85 (2 H, $\text{H}_{(\text{b})}$). $^{11}\text{B-NMR}$ spectrum (hexadeuterioacetone): -0.27 (1 B, $\text{B}_{(2\text{ or }4)}$), (140); -6.0 (1 B, $\text{B}_{(2\text{ or }4)}$); -11.9 (2 B, $\text{B}_{(5,7)}$); -16.0 (2 B, $\text{B}_{(8,10)}$); -20.2 (1 B, $\text{B}_{(9)}$); -38.6 (2 B, $\text{B}_{(1,3)}$) (145).

9-Acetonitrile-6-carba-*arachno*-decaborane(13) (VIIIb)

Gaseous HCl was passed for 2 g at room temperature through a solution of *IV* (2 g; 0.01 mol) in acetonitrile (40 ml). The solvent was evaporated *in vacuo* and the isolation was performed as in the previous experiment to give 0.4 g (24% based on *IV* used) of *VIIIb*, m.p. 455–456 K (decomp.), R_F 0.22 (benzene) and m/e 165 (corresponding to $^{14}\text{N}^{12}\text{C}_3^{11}\text{B}_9^1\text{H}_6^+$). $^1\text{H-NMR}$

spectrum (hexadeuterioacetone): 2.3 (3 H, CH₃ protons); 0.12 (1 H, CH_(eq)); -1.65 (1 H, CH_(ax)); -3.65 (2 H, H_(b)). ¹¹N-NMR spectrum (hexadeuterioacetone): 0.7 (1 B, B_(2 or 4)) (140); -8.4 (1 B, B_(2 or 4)); -13.5 (2 B, B_(5,7)); -26.1 (1 B, B₍₉₎); -26.1 (2 B, B_(8,10)); -40.6 (2 B, B_(1,3)) (150).

9-Triphenylphosphine-6-carba-*arachno*-decaborane(13) (*VIIIc*)

To a suspension of *IV* (2 g; 0.01 mol) and triphenylphosphine (2.7 g; 0.01 mol) in benzene-diethyl ether (1 : 4) (50 ml), gaseous HCl was introduced over 2 h at room temperature. After working up as in the previous experiment, 0.8 g (20.3% based on *IV* used) of *VIIIc* was obtained, m.p. 493–494 K, *R_F* 0.60 (benzene) and *m/z* 386 (corresponding to ³¹P¹²C₁₉.¹H₂₈⁺). ¹H-NMR spectrum (hexadeuterioacetone): 7.75–8.35 (15 H, C₆H₅ protons); 0.4 (1 H, CH_(eq)); -0.95 (1 H, CH_(ax)); -3.37 (2 H, H_(b)). ¹¹B-NMR spectrum (hexadeuterioacetone): 1.6 (1 B, B_(2 or 4)); -3.9 (1 B, B_(2 or 4)); -11.8 (2 B, B_(5,7)) (145); -24.6 (2 B, B_(8,10)); -30.6 (1 B, B₍₉₎) (*J*¹¹B³¹P = 120); -38.0 (2 B, B_(1,3)) (155).

Tetramethylammonium-decahydro-bis-2,3-(η⁵-cyclopentadienyl)-
-2,3-cobalta-1-carba-*closo*-dodecaborane(-1) (*IX*)

To a solution of KOH (60 g) in methanol (120 ml), cyclopentadiene (3.3 g; 0.05 mol), *IV* (1.37 g; 0.007 mol) and the solution of CoCl₂.6 H₂O (2.5 g; 0.01 mol) in methanol (50 ml) were added. The mixture was stirred for 5 h at 343 K. After cooling to room temperature, water (500 ml) was added and the mixture was neutralized with solid CO₂ and filtered. An excess of concentrated water solution of N(CH₃)₄Cl was added to precipitate the product which was filtered off, washed with water and benzene and recrystallized from water-acetone to give 1.2 g (38% based on *IV* used) of green *IX* (X-ray diffraction, see¹⁵). ¹H-NMR spectrum (hexadeuteriodimethyl sulphoxide): 5.06 (10 H, C₅H₅ protons); 3.6 (1 H, CH_(s)); 3.12 (12 H, CH₃ protons). ¹¹B-NMR spectrum (hexadeuteriodimethyl sulphoxide): 21.4 (1 B) (135); 2.35 (2 + 2 B); -10.7 (2 + 1 B); -20.0 (1 B) (145).

Tetramethylammonium decahydro-1-(η⁵-cyclopentadienyl)
-1-ferra-2-carba-*closo*-undecaborane(-1) (*X*)

To a solution of KOH (60 g) in methanol (120 ml), cyclopentadiene (3.3 g; 0.05 mol), *IV* (2 g; 0.01 mol) and FeCl₂.4 H₂O (3 g; 0.015 mol) were added. The mixture was stirred for 6 h at 333–343 K and the product was isolated as in the previous experiment to obtain 1.9 g (60% based on *IV* used) of violet *X* (X-ray diffraction, see¹⁶). ¹H-NMR spectrum (hexadeuterioacetone): 3.17 (CH₃ protons).

3,4-μ-Trimethylammonium-carba-*arachno*-pentaborane(10) (*XI*)

To a solution of KOH (60 g) in methanol (100 ml), *I* (3.6 g; 0.02 mol) was added and the mixture was heated over 1.5 h at 333 K. After cooling to room temperature the solution was diluted with water (100 ml) and neutralized with solid CO₂. The precipitate was filtered off, washed with water (50 ml), dried at 293 K/1.3 Pa and its dichloromethane solution was mounted onto the silica gel column. Dichloromethane eluted the main fraction of *R_F* 0.46 and, on stripping off the solvent, 2.05 g (75% based on *I* used) of *XI* were isolated. Analytical product, m.p. 412–413 K, *m/e* 137 (¹⁴N¹²H₄¹¹B₅¹H₂₀⁺) as obtained by recrystallization from dichloromethane-hexane. ¹H-NMR spectrum (hexadeuterioacetone): 3.15 (9 H, CH₃ protons);

1.32 (1 H, $\text{CH}_{(b)}$); 0.55 (1 H, $\text{H}_{(b1)}$); -1.87 (2 H, $\text{H}_{(b2)}$). ^{11}B -NMR spectrum (hexadeuterioacetone): -12.4 (2 B, $\text{B}_{2,5}$) (115) triplet; -23.2 (2 B, $\text{B}_{(3,4)}$) (120/30); -60.2 (1 B, $\text{B}_{(1)}$) (140/55).

The NMR spectra were measured by Mr P. Pech and Dr P. Trška and the mass spectra by Dr V. Kubelka, Prague Institute of Chemical Technology. Analyses were performed by Mr J. Skalický and Mr P. Filip, the IR spectra were recorded by Dr F. Hanousek and Dr M. Haruda, Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, Prague. We would like to thank these colleagues for their assistance and Dr S. Heřmánek for his help in interpreting the NMR results.

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