

THE INTERMEDIATE DICARBA-*NIDO*-BORANES

J. PLEŠEK and S. HEŘMÁNEK

*Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences,
Řež near Prague, Czechoslovakia*

ABSTRACT

The formation of several *nido*-carboranes, their structures, chemistry, some comparisons with *nido*-boranes and general stability rules are briefly reviewed.

Oxidation of the $7,8\text{-C}_2\text{B}_9\text{H}_{12}^-$ anion was found to afford selectively various new *nido*-carboranes, namely, $5,6\text{-C}_2\text{B}_8\text{H}_{12}$, $n\text{-C}_4\text{B}_{18}\text{H}_{22}$, $\text{iso-C}_4\text{B}_{18}\text{H}_{22}$ and the $\text{C}_4\text{B}_{18}\text{H}_{23}^-$ anion. The $5,6\text{-C}_2\text{B}_8\text{H}_{12}$ was used as the starting material in syntheses of further new or known compounds, e.g. $1,2\text{-C}_2\text{B}_8\text{H}_{10}$, $1,10\text{-C}_2\text{B}_8\text{H}_{10}$, $6,9\text{-C}_2\text{B}_8\text{H}_{14}$, $5\text{-Cl-}6,9\text{-C}_2\text{B}_8\text{H}_{13}$, $1,3\text{-C}_2\text{B}_7\text{H}_{13}$ etc. Analogous oxidations of substituted (Br , C_6H_5) $\text{C}_2\text{B}_9\text{H}_{12}^-$ ions and the direct bromination and deuteration of the parent carborane in bridge-positions resulted in derivatives which made it possible to elucidate the ^{11}B n.m.r. spectrum of $5,6\text{-C}_2\text{B}_8\text{H}_{12}$.

The $n\text{-C}_4\text{B}_{18}\text{H}_{22}$ is a new carborane type, consisting of two $\text{C}_2\text{B}_9\text{H}_{11}$ units, bonded by two three-centre exo-bonds. The structure was solved by combination of selected reactions [BH_3 -insertion, splitting with Lewis bases, reduction of the $\text{C}_4\text{B}_{18}\text{H}_{20}^{2-}$ salt] and elucidation of structures of the compounds formed. The accompanying $\text{iso-C}_4\text{B}_{18}\text{H}_{22}$ is, according to its n.m.r. spectra, composed of the $5,6\text{-C}_2\text{B}_8\text{H}_{11}$ and *o*-carborane fragments attached by means of a B—B bond probably in position 8 of the former compound and 3 of the latter framework. The $\text{C}_4\text{B}_{18}\text{H}_{23}^-$ anion was revealed as a $\text{C}_2\text{B}_9\text{H}_{11}\text{-H-C}_2\text{B}_9\text{H}_{11}$ system with a hydrogen bridge bound to B[9] of each unit.

The reaction of the $7,8\text{-C}_2\text{B}_9\text{H}_{12}^-$ anion with nitrous acid results in degradative insertion with the formation of novel $10\text{-N-}7,8\text{-C}_2\text{B}_8\text{H}_{11}$ and $8,9\text{-NH}_2\text{-}5,6\text{-C}_2\text{B}_8\text{H}_{11}$ *nido* species.

Under forced conditions, the *p*-carborane was degraded to a new $2,9\text{-C}_2\text{B}_9\text{H}_{12}^-$ anion, the acidification of which led to the relatively stable $2,9\text{-C}_2\text{B}_9\text{H}_{13}$ *nido*-carborane.

On the basis of an intercomparison of various *nido*-carboranes with other members of this family and with *nido*-boranes, general stability rules for *nido*-carboranes are proposed.

INTRODUCTION

While the *nido*-boranes represent the oldest class, the analogous *nido*-carboranes are relatively the youngest and least investigated group of the borane family¹. This article deals with the intermediate dicarba-*nido*-boranes of the C_2B_7 to C_2B_9 series.

As the first representative of this dicarba-*nido*-borane group, $7,8\text{-dicarba-nido-undecaborane(13)}$ was discovered by Wiesboeck and Hawthorne².

This compound was obtained by alkaline degradation of 1,2-dicarbaborane-*closo*-dodecaborane(12) followed by acidification of the fairly stable *nido*-anion $7,8\text{-C}_2\text{B}_9\text{H}_{12}^-$.

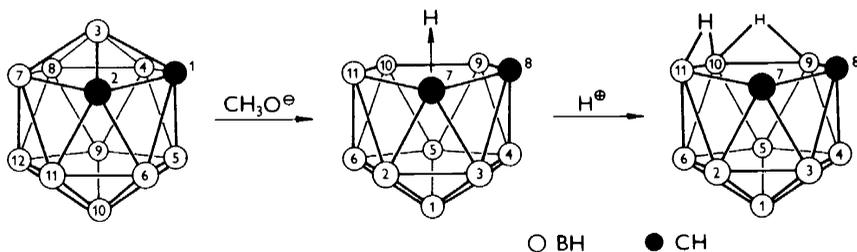


Figure 1. Formation of $7,8\text{-C}_2\text{B}_9\text{H}_{13}$ from *o*-carborane²

Another important compound of this series, the *nido*-carborane $1,3\text{-C}_2\text{B}_7\text{H}_{13}$ was observed by Hawthorne *et al.*³ as the main product in the oxidation of the $7,9\text{-C}_2\text{B}_9\text{H}_{12}^-$ ion.

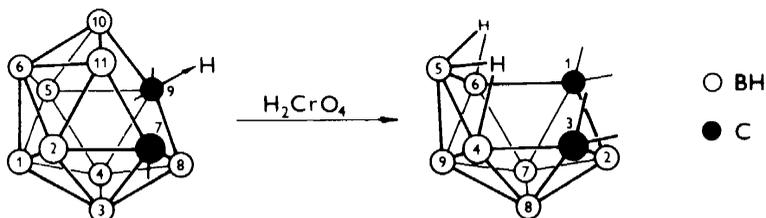


Figure 2. Oxidation of the $7,9\text{-C}_2\text{B}_9\text{H}_{12}^-$ anion to $1,3\text{-C}_2\text{B}_7\text{H}_{13}$ ³

The $1,3\text{-C}_2\text{B}_7\text{H}_{13}$ carborane was used as the starting material in the synthesis of a further member, the $5,7\text{-C}_2\text{B}_8\text{H}_{12}$ carborane⁴.

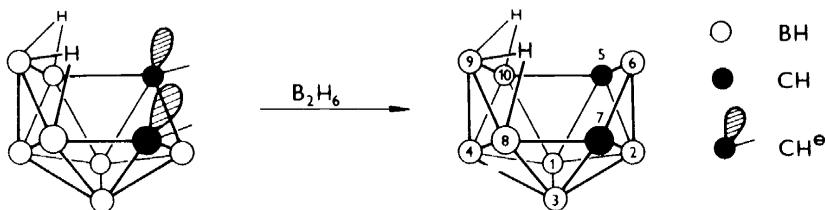
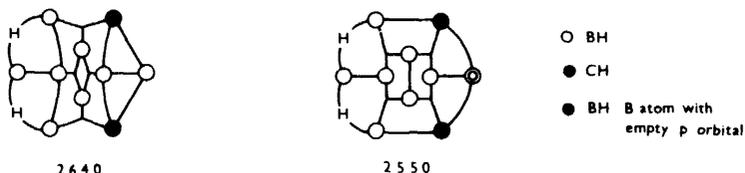


Figure 3. Formation of $5,7\text{-C}_2\text{B}_8\text{H}_{12}$ by insertion of the BH_3 group into the $1,3\text{-C}_2\text{B}_7\text{H}_{13}^-$ anion⁴

The topological representation of the latter compound is unique. It can be expressed by the 2640 styx description but the ^{11}B n.m.r. spectrum is more in accordance with the 2550 structure where one B atom is sp^2 hybridized and bears an empty orbital. This bond arrangement is also in good agreement with the chemical behaviour, i.e. the addition of trimethylamine and reaction with hydrogen chloride with the formation of $6\text{-Cl-}5,7\text{-C}_2\text{B}_8\text{H}_{11}$ and with a low stability of the compound⁴.

THE INTERMEDIATE DICARBA-NIDO-BORANES



Scheme 1

Three other types of *nido*-carboranes were discovered by Schaeffer and Rietz in the reaction of octaborane(12) with acetylene or dimethylacetylene⁵⁻⁷. The main product of these reactions is either 5,6-C₂B₈H₁₂ or 5,6-(CH₃)₂-5,6-C₂B₈H₁₀, depending on whether acetylene or dimethylacetylene is added to the B₈ skeleton.

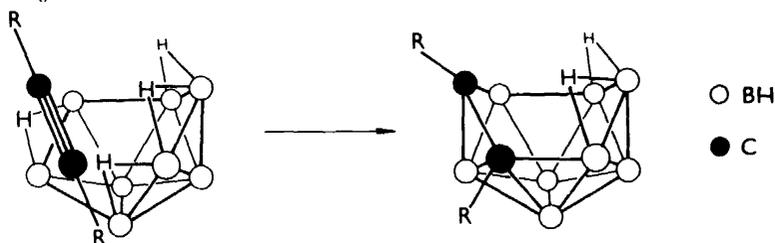


Figure 4. Insertion of acetylene into the B₈H₁₂ borane⁵⁻⁷

The reaction is always accompanied by a degradation product, namely, a *nido*-carborane of the C₂B₇ framework, the structure of which depends on the character of the acetylenic compound^{7, 8}.

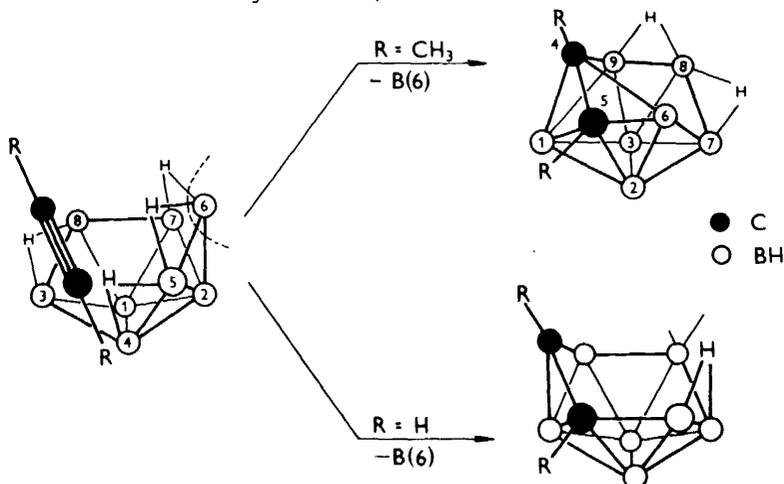


Figure 5. Structure of the 4,5-(CH₃)₂-4,5-C₂B₇H₉ carborane and proposed structure of the C₂B₇H₁₁ carborane† formed as byproducts in the reaction of B₈H₁₂ with (a) dimethylacetylene, (b) acetylene^{6, 7}

† The later structure is more likely to be the analogue of the first one with C-atoms in positions 4 and 9, *8-BH₂ group and hydrogen bridge between 6-7 positions. This arrangement has no H-tautomerism and is in agreement with the presence of BH₂ triplet in the ¹¹B n.m.r. spectrum. This triplet is improbable in the case of the later structure, where the H-tautomerism 6-7μH, 8-BH₂ ⇌ 6-BH₂, 7-8μH ⇌ 6-7μH, 8-9μH and therefore no BH₂ triplet may be expected (see our rule 2 on p. 451).

The schemes of the preparation of the known intermediate dicarba-*nido*-boranes also show the structures and availability which is satisfactory in the case of 7,8-C₂B₉H₁₃ or 1,3-C₂B₇H₁₃ carboranes but insufficient with the remaining compounds. Owing to the difficult availability, many species of this group have been only poorly investigated.

The interest in a detailed intercomparison of various *nido*-carboranes and *nido*-boranes led us to the search for efficient routes in the preparation of some key *nido*-carboranes. As the most significant of these substances, they have been considered the C₂B₈-*nido* compounds since their structures, electron densities and chemical characteristics are comparable with those of substances of the extensively studied decaborane family.

NIDO-CARBORANES FROM THE OXIDATION OF THE 7,8-C₂B₉H₁₂⁻ ION

The most readily available *nido*-carborane derivative is the 7,8-C₂B₉H₁₂⁻ anion², the degradation of which represents the most promising route in the preparation of further *nido*-carboranes. Concerning the oxidative degradation of this anion we have observed that the result depends dramatically on the oxidant and the reaction conditions. A series of new *nido*-carboranes was formed from the above precursor as will be shown in detail in the following text.

Preparation and chemistry of 5,6-dicarba-*nido*-decaborane(12)

Oxidation of the 7,8-C₂B₉H₁₂⁻ anion with aqueous ferric chloride affords about 50 per cent of 5,6-C₂B₈H₁₂ and ten per cent of at least four additional volatile compounds^{9,10}. It may be inferred from the two structural formulae in *Figure 6* that the 5,6-dicarba-*nido*-decaborane(12) is formed by an oxidative displacement of the B(9) atom from the 7,8-C₂B₉H₁₂⁻ anion.

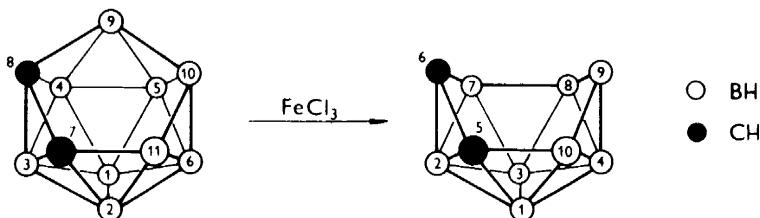


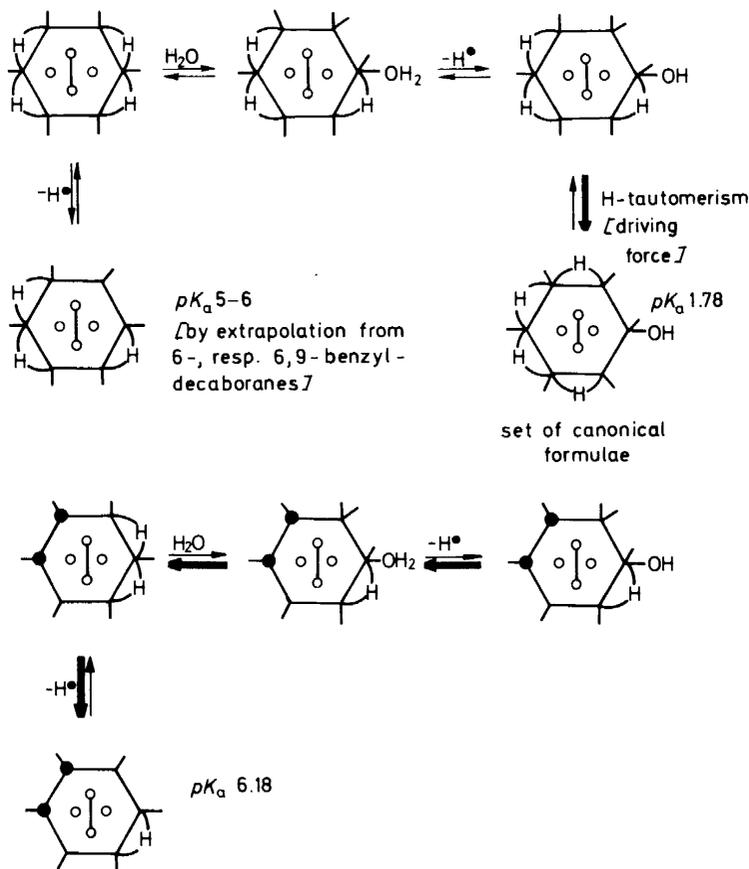
Figure 6. Formation of 5,6-C₂B₈H₁₂ from the 7,8-C₂B₉H₁₂⁻ ion^{9,10}

The compound has no element of symmetry, in agreement with the ¹¹B n.m.r. spectrum exhibiting eight distinct doublets [*Figure 7* (i)] and the ¹H n.m.r. spectrum containing two different CH signals of relative intensities 1, and δ values 6.48 and 4.98 p.p.m. (relative to tetramethylsilane).

5,6-Dicarba-*nido*-decaborane(12) is isoelectronic with the known B₁₀H₁₂²⁻ anion¹¹ and the principal part of the molecule resembles the decaborane(14). In addition to this structural relationship, the presence of two carbon atoms brings about new qualities which strongly affect the behaviour of the 5,6-dicarba-*nido*-decaborane(12). In addition to changes in dislocation of

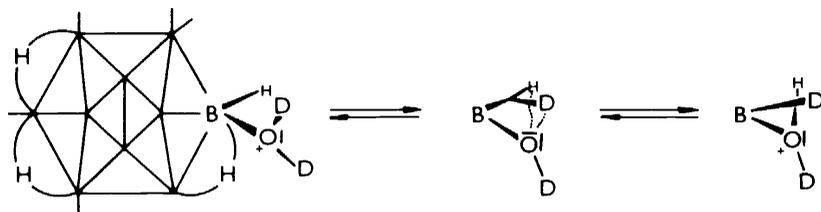
THE INTERMEDIATE DICARBA-NIDO-BORANES

chemical bonds and electron densities, the most important new quality consists of the restricted possibility of H-tautomerism. For instance, this effect is probably the reason for different acidity in the two compounds. While decaborane(14) reacts on titration in aqueous ethanol as a Lewis acid, forming the strongly acidic $B_{10}H_{14}\text{-OH}_2$ adduct of pK_a 1.78 (refs. 12, 13) which is immediately converted to the $B_{10}H_{14}OH^-$ anion of a $B_{10}H_{15}$ -like structure^{12, 13}, the 5,6- $C_2B_8H_{12}$ carborane reacts under similar conditions exclusively as Brønsted acid of pK_a 6.18 (refs. 12, 13).



Scheme 2. Explanation of different acidic characters of $B_{10}H_{14}$ and 5,6- $C_2B_8H_{12}$

This scheme is supported by the observation that both the compounds exchange μH by μD in the presence of D_2O but that in decaborane(14), the terminal hydrogens on B(6) and B(9) atoms are also rapidly exchanged, probably according to the following scheme:



Scheme 3. Possible course of an exchange of B-H, by D₂O at positions 6 and 9 in decaborane (4)

Introduction of deuterium into positions 6 and 9 of decaborane(14) and practical absence of this exchange in the case of 5,6-C₂B₈H₁₂ carborane indicates that the opening of the hydrogen bridge is more favoured in the former compound.

The presence of two carbon atoms in the skeleton brings about a change in electron densities on particular boron atoms as shown by bromination in the presence of AlBr₃. This reaction leads to 3-Br-5,6-C₂B₈H₁₁ [Figure 7(iii)] and not to the expected 4-bromo derivative which was prepared by the direct oxidation of the 5-Br-7,8-C₂B₉H₁₁⁻ anion¹⁴ [Figure 7(iv)].

Similarly, the oxidation of the 3-C₆H₅-7,8-C₂B₉H₁₁⁻ anion affords a mixture in which the 2-C₆H₅-5,6-C₂B₈H₁₁ derivative predominates. The above-mentioned compounds made it possible to assign three of the eight signals, i.e. the doublet at 38.3 p.p.m. to B(4), 26.1 to B(2), and -7.6 or -6.0 to B(3). The further signal, a doublet at 9.2 p.p.m., shows a distinct hydrogen bridge coupling of $J_{B-\mu H}$ 45 Hz. Such an outstanding μH bridge splitting is usually caused by the presence of the C—B— μH arrangement and consequently we assign this signal to the B(10) atom. For the assignment of two more signals, a simple method has been developed which is based on the fact that μ -deuteration removes the $J_{B-\mu H}$ coupling, i.e. it narrows the signals belonging to boron atoms bonded to the hydrogen bridge and deepens the doublet valley¹⁵. Comparison of the ¹¹B n.m.r. spectra of 5,6-C₂B₈H₁₂ and μ -D₂-5,6-C₂B₈H₁₀ shows a distinct narrowing and deepening of the three signals at -4.6, 3.0 and 8.3 p.p.m. [Figure 7(ii)]. Consequently, the first two doublets belong to the B(8) and B(9) atoms and implicitly, the remaining two signals at -7.9 and -6.2 may be assigned to the B(1) and B(3) atoms.

The 5,6-C₂B₈H₁₂ carborane proved to be a very useful starting material for the preparation of further carboranes. Thus the pyrolytic dehydrogenation at about 240°C affords the new 1,2-dicarba-*closo*-decaborane(10) contaminated by the 1,6-C₂B₈H₁₀ isomer. In the presence of *N*-ethylpiperidine-borane(3), the dehydrogenation temperature is markedly lower; the 1,2-C₂B₈H₁₀ species⁹ is obtained as the predominant product which is accompanied by about ten per cent of the 7,8-C₂B₉H₁₂ anion originated by insertion of the boron atom¹⁰ [Figure 8].

The ¹¹B n.m.r. spectrum of 1,2-dicarba-*closo*-decaborane(10) (Figure 9) with four doublets of relative intensities 1:1:2:4 as well as the ¹H n.m.r. spectrum with two signals at δ 5.60 and 3.41 p.p.m. is consistent with the structure proposed.

THE INTERMEDIATE DICARBA-NIDO-BORANES

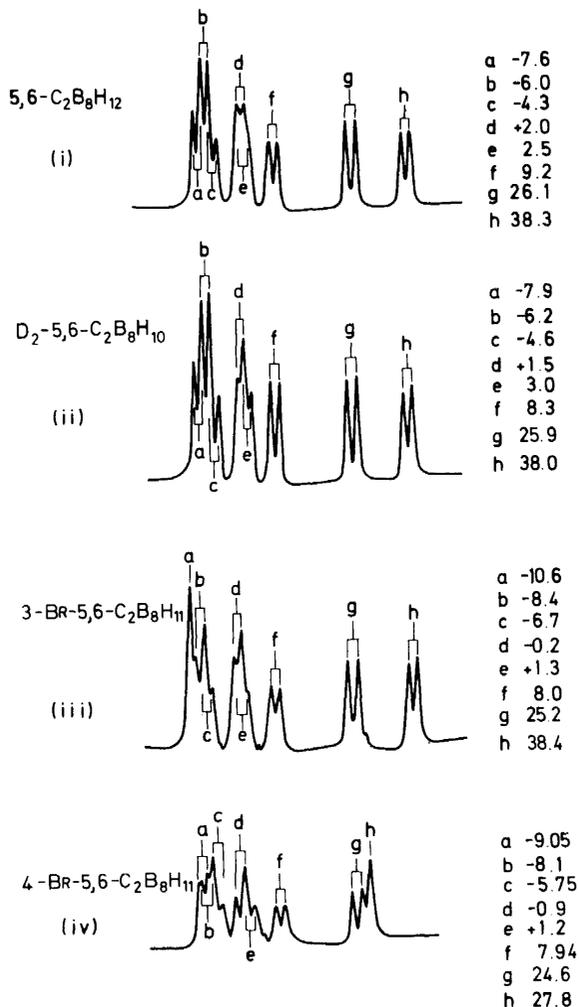


Figure 7. The ¹¹B n.m.r. spectra at 80.5 MHz [relative to BF₃·O(C₂H₅)₂] of 5,6-C₂B₈H₁₂ (i), μD₂-5,6-C₂B₈H₁₀ (ii), 3-Br-5,6-C₂B₈H₁₁ (iii) and 4-Br-5,6-C₂B₈H₁₁ (iv)

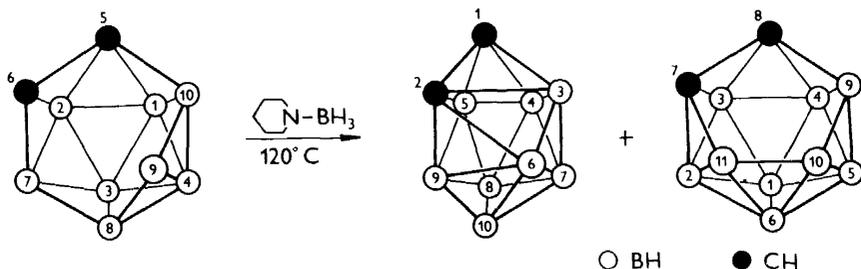
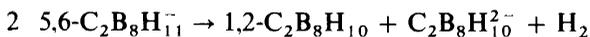


Figure 8. Formation of the 1,2-C₂B₈H₁₀ and 7,8-C₂B₈H₁₂⁻ ion in dehydrogenation of 5,6-C₂B₈H₁₂ catalysed by piperidineborane(3)¹⁰

The easiest approach to the preparation of a quite pure 1,2- $C_2B_8H_{10}$ is the thermolysis of the solvent-free 5,6- $C_2B_8H_{11}^-$ anion, prepared by the action of sodium hydride in diethyl ether¹⁶. In this reaction, a disproportionation occurs with the simultaneous formation of a $C_2B_8H_{10}^{2-}$ ion, the structure of which remains obscure.



The $C_2B_8H_{10}^{2-}$ anion is very interesting from the standpoint of further transformations (Figure 10). Thus, depending on the medium, either 1,3-

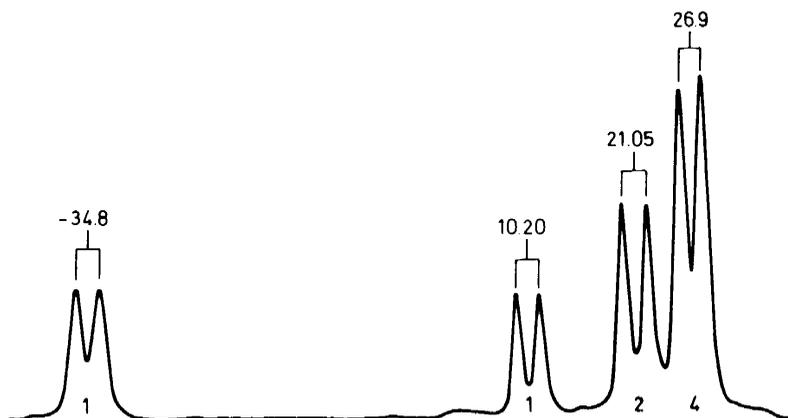


Figure 9. ^{11}B n.m.r. spectrum of 1,2- $C_2B_8H_{10}$ at 70.6 MHz

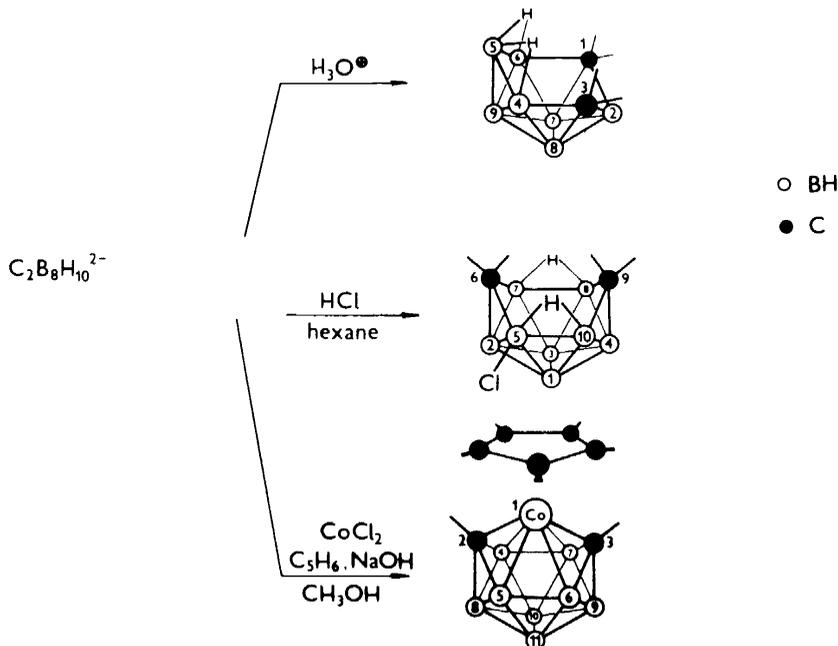


Figure 10. Compounds formed from the $C_2B_8H_{10}^{2-}$ ion (unknown constitution)

THE INTERMEDIATE DICARBA-NIDO-BORANES

$C_2B_7H_{13}$ (ref. 16) or a new 5-Cl-6,9- $C_2B_8H_{13}$ carborane derivative¹⁷ is formed by the action of hydrogen chloride. On treatment with cobaltous chloride and cyclopentadiene, there is obtained (π -cyclopentadienyl)-2,3-dicarba-1-cobalta-undecaborane(11) (ref. 14), prepared recently by Hawthorne *et al.* by the polyhedral expansion of 1,6- $C_2B_8H_{10}$ (ref. 18) or 1,10- $C_2B_8H_{10}$ (ref. 19) carboranes.

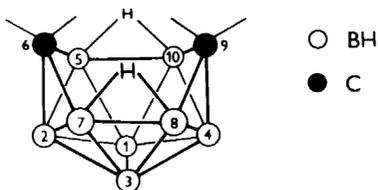


Figure 11. Simplified drawing of 6,9- $C_2B_8H_{14}$

One of the most interesting compounds of the C_2B_8 group is the 6,9- $C_2B_8H_{14}$ arachno-carborane (Figure 11). This compound is obtained in a low yield on alkaline ethanolysis of 5,6-dicarba-nido-decaborane(12) (ref. 20).

Improved yields (10–30 per cent) were obtained in the reaction of 5,6- $C_2B_8H_{12}$ with sodium amalgam in hot ethanol²¹. This result is in accordance with our idea that the separation of the carbon atoms proceeds in the stage of a doubly charged anion with interruption of the C(5)—C(6) and C(6)—B(2) bonds and shift of the C(6) atom into the neighbourhood of B(8) and B(9) atoms in the skeleton I (Figure 12).

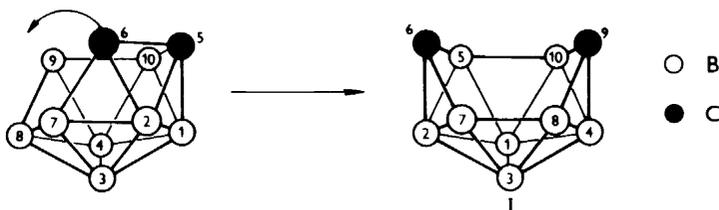


Figure 12. Probable transformation of 5,6- C_2B_8 to the 6,9- C_2B_8 skeleton I

The 6,9- $C_2B_8H_{14}$ carborane is isoelectronic and isostructural with the $B_{10}H_{14}^{2-}$ anion and belongs therefore to the arachno series^{22, 23}. The presence of the two CH_2 groups may be inferred from the 1H n.m.r. spectrum where two different CH signals are present at δ 0.81 and -0.70 p.p.m., attributable to the equatorial and axial H atoms. The presence of hydrogen bridges between the 5–10 and 7–8 boron atoms is supported by splitting of the doublet of intensity 4 in the ^{11}B n.m.r. spectrum [Figure 13(a)].

In contrast to other known *nido*-carboranes, the 6,9- $C_2B_8H_{14}$ member is highly thermally stable and does not undergo dehydrogenation or rearrangement up to 350°C.

In the reaction of deuterium oxide with 6,9-dicarba-*nido*-borane(14), both the two CH axial and the two bridging hydrogen atoms are exchanged as

indicated by the disappearance of the signal at $\delta -0.70$ p.p.m. in the ^1H n.m.r. spectrum and disappearance of $J_{\text{B}-\mu\text{H}}$ coupling in the ^{11}B n.m.r. spectrum [Figure 13(b)]. This observation indicates that both the carbon atoms are sites of a distinct positive charge in the neutral carborane molecule and impart an acidic character not only to hydrogens attached to the carbon atoms but also to both the bridging hydrogen atoms. This effect has not been observed in related $\text{L}_2\text{B}_{10}\text{H}_{12}$ derivatives²⁴.

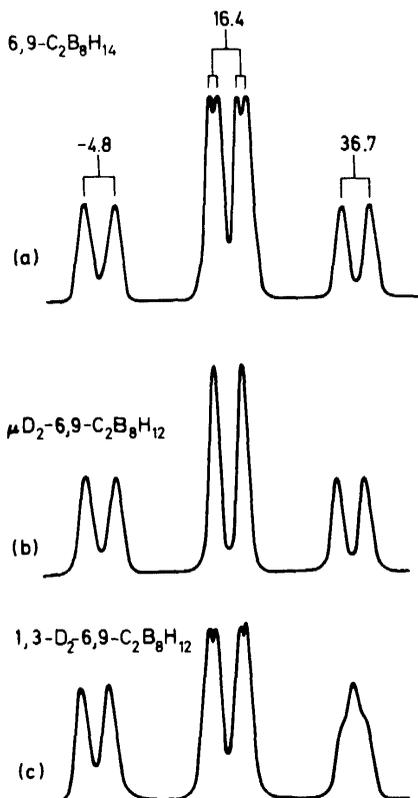


Figure 13. ^{11}B n.m.r. spectra at 25 MHz (a) $6,9\text{-C}_2\text{B}_8\text{H}_{14}$, (b) $\mu\text{D}_2\text{-}6,9\text{-C}_2\text{B}_8\text{H}_{12}$, (c) $1,3\text{-D}_2\text{-}6,9\text{-C}_2\text{B}_8\text{H}_{12}$

According to our empirical rules^{15, 25}, the low-field doublet was assigned to the B(2, 4) atoms and the high-field doublet to the B(1, 3) atoms²⁰. According to this assignment, deuterium chloride in the presence of aluminium chloride brings about exchange of hydrogen atoms on B(1, 3), i.e. at positions most distant from the $\delta+$ charged carbon atoms [Figure 13(c)]. This idea is also in agreement with the highest electron density attributed to these atoms in the isostructural and isoelectronic $\text{B}_{10}\text{H}_{14}^{2-}$ skeleton²⁶.

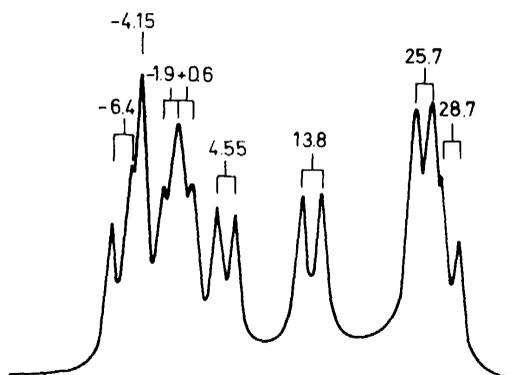


Figure 15. ^{11}B n.m.r. spectrum of $n\text{-C}_4\text{B}_{18}\text{H}_{22}$

indicate the presence of eight BH and two CH groups, i.e. ten terminal H atoms. The presence of one singlet in the ^{11}B n.m.r. spectrum is consistent with the absence of the terminal hydrogen on the B(9) atom. The remaining eleventh H atom of each moiety should therefore occupy a unique position above the open pentagonal face of the $\text{C}_2\text{B}_9\text{H}_{11}$ framework. In accordance with this suggestion, $n\text{-C}_4\text{B}_{18}\text{H}_{22}$ behaves as a dibasic acid of identical pK_a^I and pK_a^{II} values equal to 2.4.

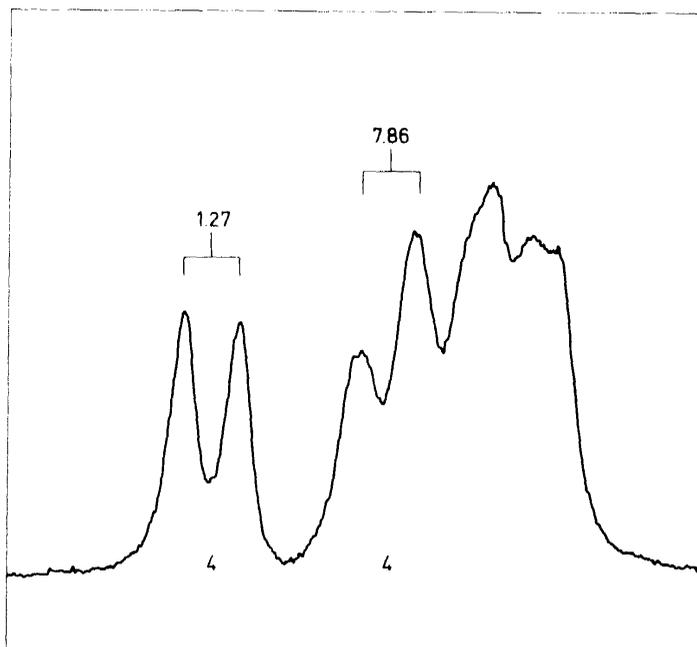


Figure 16. ^{11}B n.m.r. spectrum of 4,4'-bis(o-carboranyl) at 70.6 MHz

The existing proximity of the two carbon atoms in each fragment was confirmed by insertion of diborane (under pressure) into the $C_4B_{18}H_{22}$ carborane, leading to *o*-carborane and bis(*o*-carboranyl). The latter compound (m.pt 230°C) differs from the known 1,1'-bis(*o*-carboranyl)²⁹ (m.pt 309–310°C); connection through the B(9) atoms is excluded by the ¹¹B n.m.r. spectrum (Figure 16).

The complete elucidation of the $n-C_4B_{18}H_{22}$ structure made it possible to assign retrospectively to the dimer the constitution of 4,4'-bis(*o*-carboranyl)^{28, 30}, the formation of which is shown in Figure 17.

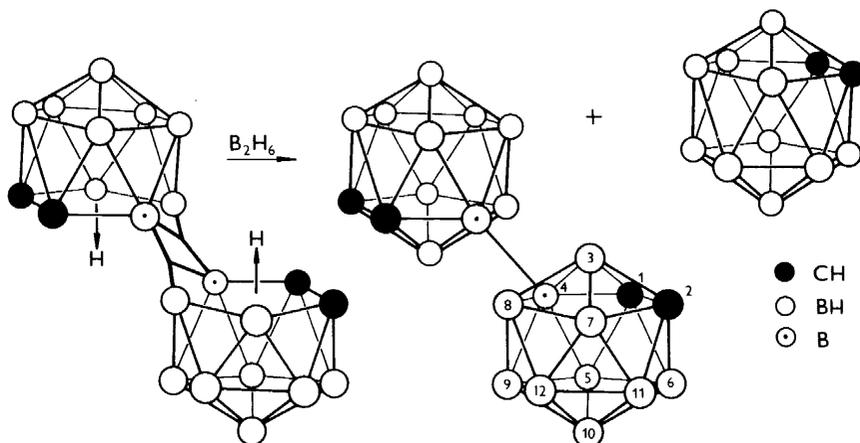
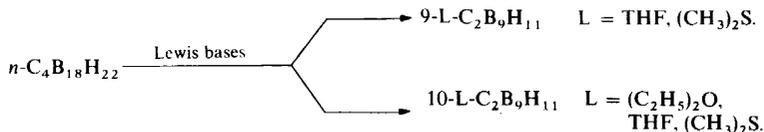


Figure 17. Formation of 4,4'-(1,2- $C_2B_{10}H_{11}$)₂ and *o*-carborane by BH_3 -insertion into $n-C_4B_{18}H_{22}$

Lewis bases split the $n-C_4B_{18}H_{22}$ carborane to their 9- and/or 10- $L-C_2B_9H_{11}$ derivatives [$L = THF, (C_2H_5)_2O, (CH_3)_2S$]; the tetrahydrofuran derivatives, obtained otherwise have been reported earlier by Hawthorne *et al.*³¹. The result of this splitting also confirmed the neighbourhood of



carbon atoms and their location in the open pentagonal face of the $C_2B_9H_{11}$ fragment.

Analogously to the $B_{20}H_{18}^{2-}$ anion which affords (by the action of sodium in liquid ammonia) a $B_{20}H_{18}^{4-}$ ion containing two $B_{10}H_{10}^{2-}$ polyhedra connected by means of a B—B bond³², the $Cs_2C_4B_{18}H_{20}$ salt is also reduced under similar conditions to a new $C_4B_{18}H_{22}^{2-}$ dianion (Figure 18).

The structure of the $C_4B_{18}H_{22}^{2-}$ anion as shown in Figure 18 was deduced from the ¹¹B n.m.r. spectrum (Figure 19) exhibiting features of the 9- $L-C_2B_9H_{11}$ derivatives [$L = THF, (CH_3)_2S$] as well as the characteristics of the $C_2B_9H_{12}^-$ anion substituted on the B(9) atom. In assigning the boron

signals shown in Figure 19, the reported data of the parent $C_2B_9H_{12}^-$ compound^{13,34} were used and combined with our empirical rules^{15,25}.

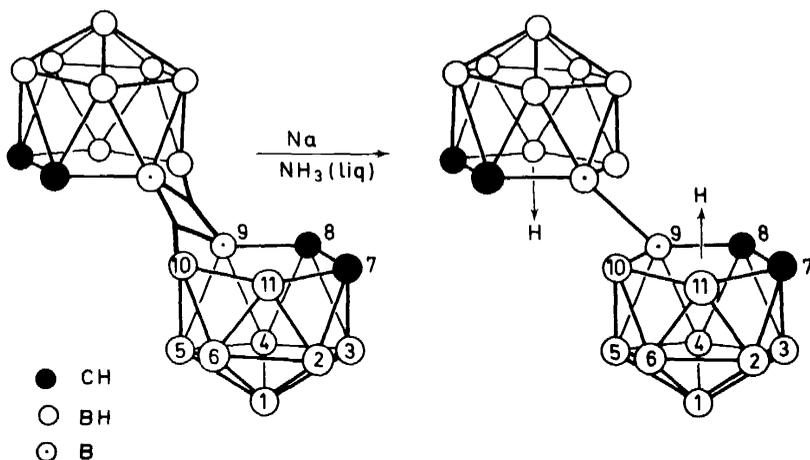


Figure 18. Reduction of the $n-C_4B_{18}H_{20}^-$ to the $9,9'-(7,8-C_2B_8H_{11})_2^-$ ion with sodium in liquid ammonia

The relation between the $n-C_4B_{18}H_{22}$ carborane and the $C_4B_{18}H_{22}^-$ anion of the above established structure is demonstrated in Figure 18 and makes it possible to propose retrospectively the probable constitution of the $n-C_4B_{18}H_{22}$ species. It is of interest that despite the existence of the highly stable 2,3- $C_2B_9H_{11}$ *closo*-carborane, neither this compound nor any isomers are formed by thermolysis of the formal dimer.

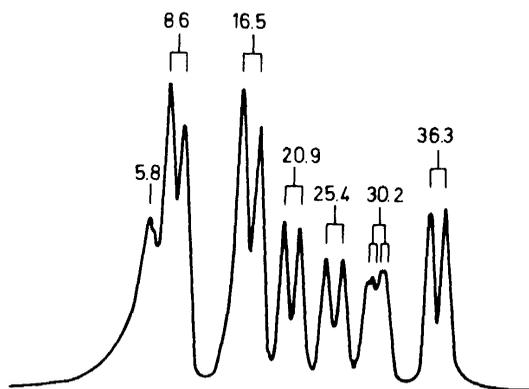


Figure 19. ^{11}B n.m.r. spectrum of the $C_4B_{18}H_{22}^-$ anion at 80.5 MHz

The $n-C_4B_{18}H_{22}$ carborane is the first example of a new structural type in which two *nido*-skeletons are connected by means of two three-centre exo-bonds. Since this type may be considered to be a general one, we may expect the potential existence of further species consisting of two identical or

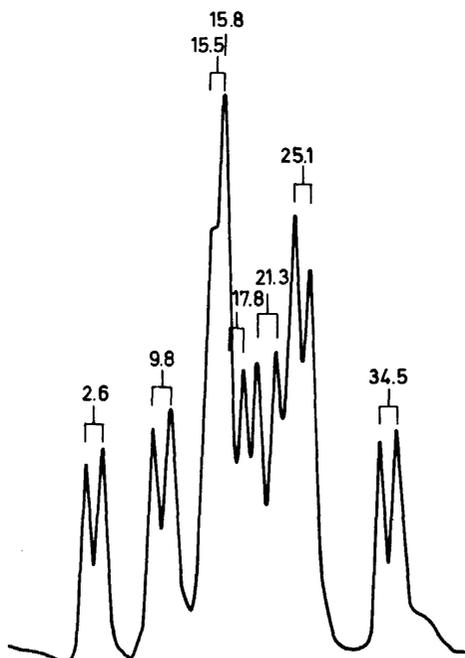


Figure 20. ^{11}B n.m.r. spectrum of the $\text{C}_4\text{B}_{18}\text{H}_{23}^-$ ion at 80.5 MHz

different *nido*-skeletons of various shapes, numbers of atoms or positions of carbon atoms. The necessary condition for the existence of such a di-*nido* species would probably be the possibility to locate the extra hydrogen atom into the open pentagonal face of each unit. This requirement could be the reason for the different course of chromic acid oxidation of the $7,9\text{-C}_2\text{B}_9\text{H}_{12}^-$ anion which is not coupled but degraded to the $1,3\text{-C}_2\text{B}_7\text{H}_{13}$ carborane³.

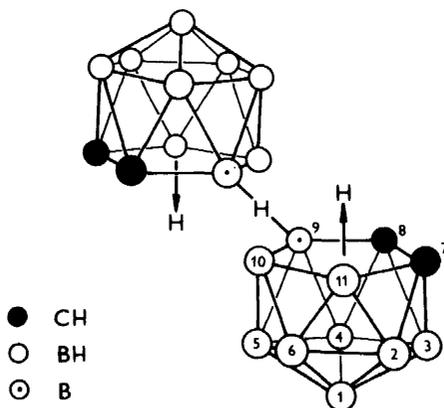


Figure 21. Proposed structure of the $\text{C}_4\text{B}_{18}\text{H}_{23}^-$ ion

The similarity between the oxidative coupling of the $B_{10}H_{10}^{2-}$ ion and the $7,8-C_2B_9H_{12}^-$ anion leads to the assumption that the $C_4B_{18}H_{23}^-$ anion is analogous to the $B_{20}H_{19}^{3-}$ anion³⁵, i.e. that it consists of two $C_2B_9H_{11}$ units connected by a hydrogen bridge²⁷ on the B(9) and B(9') atoms²⁸. This idea is in agreement with the ^{11}B n.m.r. spectrum (Figure 20) which exhibits eight doublets and one singlet, all of area 1, as the confirmation of a coupling of two identical fragments bonded through a hydrogen bridge extending to equivalent boron atoms located out of the plane of symmetry as presented in Figure 21.

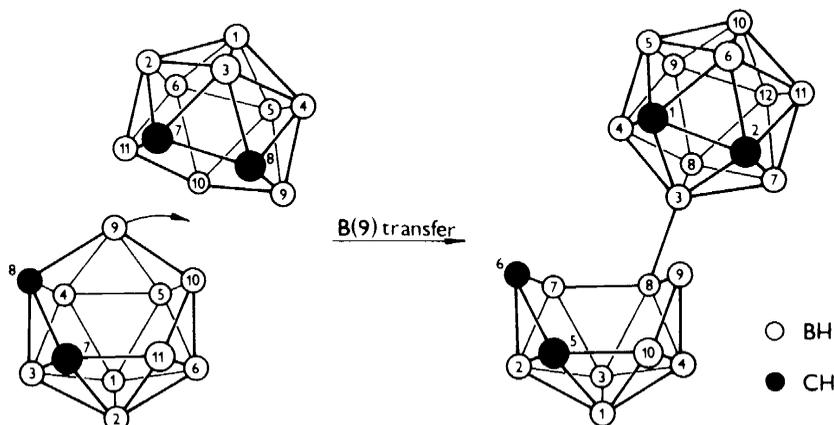


Figure 22. Proposed structure of $iso-C_4B_{18}H_{22}$ and probable formation

As mentioned above, chromic acid oxidation of the $7,8-C_2B_9H_{12}^-$ anion affords $n-C_4B_{18}H_{22}$ along with a trace of another carborane of the same empirical formula, namely, the $iso-C_4B_{18}H_{22}$, for which the structure of 8-(3-*o*-carboranyl)-5,6-dicarba-*nido*-decaborane(12) has been proposed³⁶ (Figure 22).

The connection of two different carborane frameworks may be inferred from the ^{11}B n.m.r. spectrum which shows three signals of relative intensities 1:1:2 and centred at δ 6.5, 5.05 and 3.56 p.p.m. The first two signals are very similar to those of 5,6- $C_2B_8H_{12}$ (δ 6.48 and 4.98) while the signal of intensity 2 is comparable to that of *o*-carborane (δ 3.50). This suggestion is also confirmed by the ^{11}B n.m.r. spectrum of $iso-C_4B_{18}H_{22}$ which consists of superimposed spectra of both the parent carboranes as shown in Figure 23.

Concerning the characteristics of $iso-C_4B_{18}H_{22}$ and the parent 5,6- $C_2B_8H_{12}$ *nido*-carborane (values in parentheses), there is a good agreement in the pK_a value 6.8 (6.18), ultra-violet absorption λ_{max} 276, ϵ 5350 (λ_{max} 278, ϵ 2775) as well as hydrogen bridge absorptions in the infra-red spectrum at 1865 w and 1552 $ms\ cm^{-1}$ (1875 w and 1555 $ms\ cm^{-1}$).

The $iso-C_4B_{18}H_{22}$ carborane thus represents the first known case of an uncharged combination of a *nido*- and *closo*-carborane. This iso-species is probably formed by boron transfer from one C_2B_9 skeleton to the missing vertex of the other C_2B_9 skeleton in some reaction intermediate. The trans-

THE INTERMEDIATE DICARBA-NIDO-BORANES

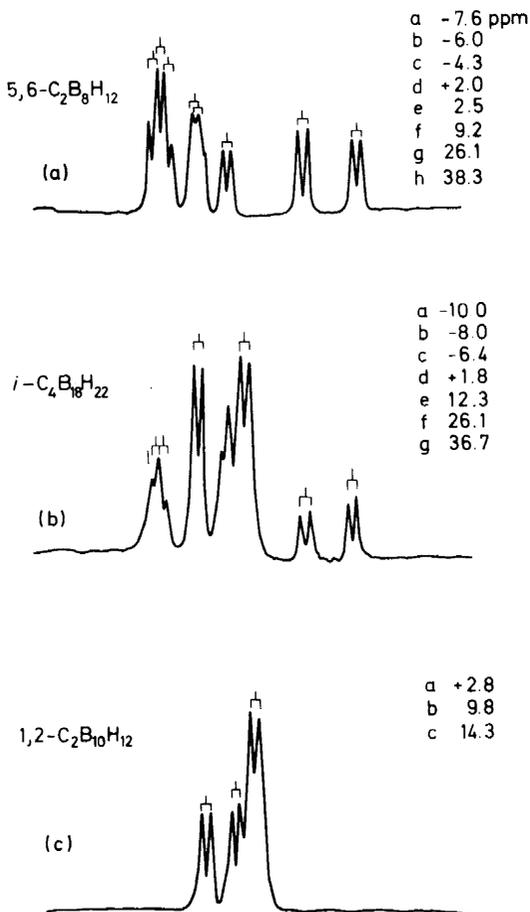


Figure 23. The 80.5 MHz ¹¹B n.m.r. spectra of 5,6-C₂B₈H₁₂ (a), iso-C₄B₁₈H₂₂ (b) and 1,2-C₂B₁₀H₁₂ (c)

ferred boron atom thus represents the B(3) atom of the *o*-carborane framework and remains simultaneously attached to one of the three boron atoms (B-7, B-8 or B-9) of the *nido* moiety. Once *n*-C₄B₁₈H₂₂ was formed we were unable to effect such a shift of a boron atom which would convert it to the iso-compound. Treatment of the ¹¹B n.m.r. spectrum of iso-C₄B₁₈H₂₂ carborane with a curve resolver indicates the presence of a B singlet at -10.0 p.p.m. and the disappearance of one of the three low-field doublets occurring in the ¹¹B n.m.r. spectrum of the original 5,6-C₂B₈H₁₂ species. As shown on p. 437, these three signals most probably belong to the B-1, B-3 and B-8 atoms. Consequently, the structure of 8-(3-*o*-carboranyl)-5,6-dicarba-*nido*-decaborane(12) has been suggested for the iso-C₄B₁₈H₂₂ species (see Figure 22).

Aza-*nido*-carboranes from the reaction of the 7,8-C₂B₉H₁₂-anion with nitrous acid

The attempted nitrosation of the 7,8-C₂B₉H₁₂⁻ anion in an acidic solution at 0°C resulted surprisingly in the formation of two new aza-carboranes³⁷, namely, NC₂B₈H₁₁ (15 per cent) and NC₂B₈H₁₃ (35 per cent). Since one BH₂⁻ group was formally replaced by a NH group in the former case and by a NH₃ group in the latter case, the reaction may be classed as a degradative insertion.

Compound NC₂B₈H₁₁ can be formulated as 10-aza-7,8-dicarba-*nido*-undecaborane(11). This structure may be inferred from a combination of the chemical formation and the spectral characteristics of this aza-carborane. The ¹H n.m.r. spectrum shows one CH signal of relative intensity 2 at δ 2.19 p.p.m. and the ¹¹B n.m.r. spectrum (Figure 24) displays five doublets of relative intensities 2† : 1† : 2 : 2 : 1 († superimposed signals). A single intensive NH stretching band was found in the infra-red spectrum at 3370 cm⁻¹. As clearly indicated by the above spectra, the molecule has a plane of symmetry and each of the C, B and N atoms bears one terminal hydrogen. The presence of the NH group was also confirmed by a methylation with CH₃I in the presence of K₂CO₃, yielding quantitatively the N-methyl derivative CH₃NC₂B₈H₁₀.

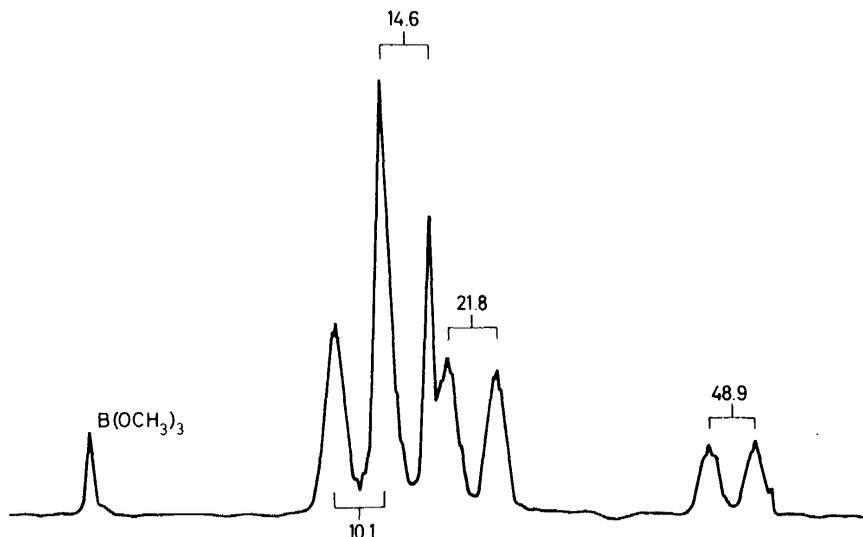


Figure 24. ¹¹B n.m.r. spectrum of 10-*N*-7,8-C₂B₈H₁₁ at 32.1 MHz

Despite the formal resemblance to the *closo*-type, a *nido* arrangement is preferred for the NC₂B₈H₁₁ species; in such a system, the NH group donates four electrons to the skeleton and is located in the open pentagonal face as shown in Figure 26. The NC₂B₈H₁₁ species is isoelectronic and isostructural with the dianion C₂B₉H₁₁²⁻ being thus formally a neutral ligand bearing six electrons in five orbitals. However, no sandwich-type complex of this

compound has been obtained so far. The above $\text{NC}_2\text{B}_8\text{H}_{11}$ species represents a unique example of an uncharged *nido* compound free of any extra hydrogen.

Compound $\text{NC}_2\text{B}_8\text{H}_{13}$ was identified as the hitherto unknown 8,9- μ -amino-5,6-dicarba-*nido*-decaborane(12). Its ^{11}B n.m.r. spectrum exhibits features similar to those of 5,6-dicarba-*nido*-decaborane(12)^{7,10}, suggesting thus a similar constitution of both the compounds. The presence of eight doublets in the ^{11}B n.m.r. spectrum and of two distinct C—H signals at δ 3.84 and 5.56 p.p.m. in the ^1H n.m.r. spectrum indicates that to each boron and carbon atom there is attached one terminal hydrogen. These findings exclude envisaging the NH_2 group (inferred from an intense doublet at 3341 and 3415 cm^{-1} in the infra-red spectrum) as terminal. The doublet centred at 25.51 p.p.m. in Figure 25 is distinctly split by the bridge hydrogen; this splitting indicates the presence of a C—B—H—B system, i.e. of a B(9)—H—B(10) bridge. Consequently, the existence of a B(9)— NH_2 —B(8) bridging NH_2 group would be the most probable explanation of the observations.

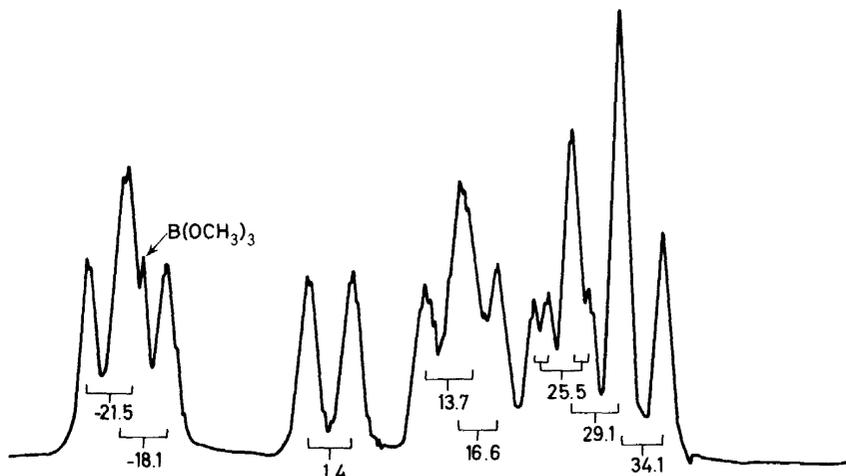


Figure 25. ^{11}B n.m.r. spectrum of 8,9- μNH_2 -5,6- $\text{C}_2\text{B}_8\text{H}_{11}$ at 32.1 MHz

The probable course of the degradative insertion explaining the formation of both the aza-carboranes is shown in Figure 26. The first step would consist of reduction of the NO^+ cation by the most hydridic B(10)—H group followed by transfer of the second hydrogen from the vicinal B(9) atom with the formation of a nitrogen bridge between the B(9) and B(10) atoms. The positive charges on the nitrogen atom as well as on both the carbon atoms activate both the B(10) and especially the B(9) positions for a nucleophilic attack by H_2O . According to the general scheme³⁸, the final result consists of the solvolytic removal of one boron atom and incorporation of the nitrogen atom into the missing vertex.

Preparation of 2,9- $\text{C}_2\text{B}_9\text{H}_{13}$ from *p*-carborane

In preceding sections, the 7,8- and 7,9- $\text{C}_2\text{B}_9\text{H}_{12}^-$ ions were treated as precursors of many members of the *nido*-carborane family. While these

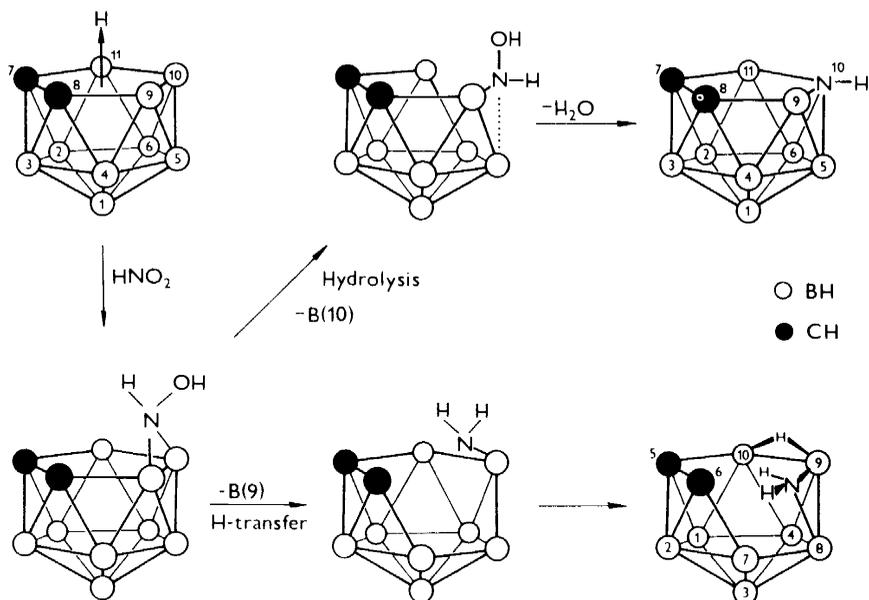


Figure 26. Proposed structures and course of formation of the $\text{NC}_2\text{B}_8\text{H}_{11}$ and $\text{NC}_2\text{B}_8\text{H}_{13}$ species

compounds are formed by alkaline solvolysis of ortho-² or *m*-carborane³⁹, the *p*-carborane was found resistant toward bases⁴⁰. The reason for this difference might reside in the double activation of the boron atom to be removed by the positively charged carbon atoms in the case of ortho- and *m*-carborane in contrast to the *p*-isomer. Despite the low activation of the latter compound, we have found that under forced conditions, i.e. by heating with 20 per cent potassium hydroxide in 1,2-propanediol at 170°C for 6 hours, 1,12-dicarba-*closo*-decaborane(12) is degraded to the 2,9-dicarba-*nido*-dodecahydroundecaborate(1⁻) anion, the acidification of which affords the 2,9- $\text{C}_2\text{B}_9\text{H}_{13}$ carborane in 15 per cent yield⁴¹ (Figure 27).

The 2,9-dicarba-*nido*-undecaborane(13) is a crystalline substance of m.pt 189–190°C, stable in water and air, and it may be sublimed without decomposition. Its structure (Figure 27) is consistent with the ¹¹B n.m.r.

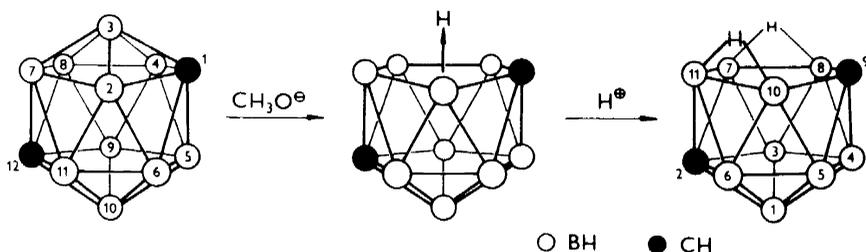


Figure 27. Formation of $2,9\text{-C}_2\text{B}_9\text{H}_{13}$ from *p*-carborane

spectrum exhibiting five doublets of relative intensities 2:2:1:2:2, and with the infra-red spectrum displaying the hydrogen bridge absorptions at 1800–2100 cm^{-1} . The hydrogen bridges are the reason for the acidic behaviour of 2,9- $\text{C}_2\text{B}_9\text{H}_{13}$ carborane (pK_a 3.15) which is similar to that of the related 7,8- $\text{C}_2\text{B}_9\text{H}_{13}$ carborane (pK_a 2.95)².

The relatively high stability of the 7,8- $\text{C}_2\text{B}_9\text{H}_{13}$ ² and 2,9- $\text{C}_2\text{B}_9\text{H}_{13}$ ⁴¹ carborane and the instability of the 7,9- $\text{C}_2\text{B}_9\text{H}_{13}$ isomer⁴¹ might be ascribed to the possibility or impossibility of locating both hydrogen bridges in the open pentagonal face of the corresponding molecule.

CONCLUSIONS

Prior to 1971, only two intermediate *nido*-carboranes were known. Now the number is nine and many interesting features of this class of compounds have been discovered. Thus, more reasonable predictions are now possible on further probable structural types and on conditions of stability in this series. Such predictions have been mentioned frequently in the past and seem to be valuable at least as a challenge for experimental chemists. A summary of the already published rules and their extensions based on the progress of the art is given below.

Skeletal types

Basic skeletal types of the *nido*-carboranes will not significantly differ from the existing boranes and their anions. For topological reasons, the 'open mouth' will be pentagonal for the $\text{C}_2\text{B}_7\text{H}_{11}$ and $\text{C}_2\text{B}_9\text{H}_{13}$ series and hexagonal for the $\text{C}_2\text{B}_8\text{H}_{12}$ series. Topology and steric factors will require only hexagonal opening for the $\text{C}_2\text{B}_n\text{H}_{n+6}$ class of carboranes of the $\text{C}_2\text{B}_7\text{H}_{13}$ and $\text{C}_2\text{B}_8\text{H}_{14}$ series. The $\text{C}_2\text{B}_9\text{H}_{15}$ series will probably not exist, because a hexagonal opening in the 11-vertex framework would not be possible without gross distortion of the skeleton. Openings larger than hexagonal or smaller than pentagonal are improbable in the intermediate series.

Numerous isomers could theoretically be expected because of many possible variations in mutual positions of the two carbon atoms in the basic framework. For instance in the $\text{C}_2\text{B}_7\text{H}_{13}$ series, 21 isomers would be possible, 16 isomers both in the $\text{C}_2\text{B}_8\text{H}_{12}$ and $\text{C}_2\text{B}_8\text{H}_{14}$ series and 9 isomers in the $\text{C}_2\text{B}_9\text{H}_{13}$ series.

However, the number of isomers may be strongly restricted due to various stability conditions as discussed later in this paper.

Polynuclear *nido*-carboranes will be very numerous because of the possibility of connecting several mononuclear units by two- and three-centre bonds or of sharing common atoms. Dicarba- as well as tetracarba-analogues of binuclear hydrides $\text{B}_{14}\text{H}_{18}$, $\text{B}_{16}\text{H}_{20}$ or $\text{B}_{18}\text{H}_{22}$ will without doubt be discovered soon.

General stability rules

1. It should be possible to draw appropriate topological formulae free of strains and extreme charge distributions. C—H—C and B—H—C bridges are not allowed.
2. Hydrogen atoms, exceeding the number of skeletal atoms, should be

consumed preferentially for the B—H—B bridges, followed by the CH₂ groups. The BH₂ groups are not likely to be favoured. Thus, topologies 2t40 for the C₂B_nH_{n+4} series and 2t32 for the C₂B_nH_{n+6} series are highly favoured.

3. The carbon atoms should occupy the sites with lowest possible coordination number (Williams's rule²²).

Although the hierarchy of these rules is still not entirely clear, they can be very useful for estimating the stability of non-existent isomers in all series. Such an estimation is demonstrated for the C₂B₈H₁₂ family with a hexagonal face.

Table 1. Possible isomers in the C₂B₈H₁₂ family with the decaborane(14) framework

Number	Position of C-atoms	Number	Position of C-atoms
1	1,2-	9	2,8-
2	1,3-	10	2,9-
3	1,5-	11	5,6-
4	1,6-	12	5,7-
5	1,7-	13	5,8-
6	2,4-	14	5,9-
7	2,5-	15	5,10-
8	2,6-	16	6,9-

Theoretically, 16 isomers would be possible (Table 1), but only two have been described so far. Table 2 shows favoured sites for carbon atoms in the framework of the decaborane type and allows us to divide the 16 isomers according to decreasing stability into six groups. Following our rules we see that the most plausible isomers 16 and 14 violate rules 1 and 2. Thus, the isomer 11 should be the most stable one of the whole series.

Table 2. Favoured and unfavoured sites for C-atoms in a decaborane framework according to rule 4

Coordination number of the C-atom			Number of the isomer
4	5	6	
2	—	—	16
1	1	—	11 14
1	—	1	4 8 10
—	2	—	12 13 15
—	1	1	3 5 7 9
—	—	2	1 2 6

In the next two triads, the sequences 10 > 8 > 4 and 13 > 15 > 12 may be expected. The existence of the remaining isomers 1, 2, 6; 3, 5, 7 and 9 are not favoured for gross violation of the rules 3 and 1 + 2, respectively.

Analogous estimation can be performed in the series C₂B₇H₁₁, C₂B₇H₁₃, C₂B₈H₁₄ and C₂B₉H₁₃, comprising theoretically 21, 21, 16 and 9 isomers, respectively.

Synthetic approach

Up to now, two general routes to *nido*-carboranes have been extensively used, namely, carbon insertion into *nido*-boranes on the one hand and the controlled degradation of higher *closo*- and *nido*-carboranes on the other. Although both these general schemes may remain important in the near future, the most promising approach seems to lie in the opening of *closo*-systems by addition of two electrons and protonation of the dianions obtained. This sequence is well known in the icosahedral series²⁻, where, however, only mono-anions have been isolated so far. But with the 1,2-C₂B₈H₁₀ compound, the same scheme led us to the 5,6-C₂B₈H₁₂ *nido* system in about 30 per cent yield. Other isomers of this compound may have been formed simultaneously, but we have not been able to isolate and identify them yet. This sequence could be of major importance for the preparation of whole isomeric families especially of the C₂B₈H₁₂ and C₂B₉H₁₃ types. The application of an analogous sequence to *nido*-carboranes of the C₂B_nH_{n+4} class could be useful in the synthesis of further representatives of the C₂B_nH_{n+6} class, as already demonstrated for C₂B₈H₁₄ carborane.

ACKNOWLEDGEMENT

We thank the Organizing Committee of International Meeting on Boron Compounds for the invitation to present this lecture. We acknowledge gratefully the work of all our co-workers mentioned in the references. Special thanks are due to Professor M. F. Hawthorne, Professor L. J. Todd and Professor F. A. L. Anet for permission and help in measuring ¹¹B n.m.r. spectra on a superconducting device and Drs R. J. Wiersema, A. O. Clouse and R. R. Rietz for making the measurements. Last but not least, we thank the Czechoslovak Academy of Sciences for support and finance of the whole research programme.

REFERENCES

- ¹ R. N. Grimes, *Carboranes*, Academic Press: New York (1970).
- ² R. A. Wiesboeck and M. F. Hawthorne, *J. Amer. Chem. Soc.* **86**, 1642 (1964).
- ³ F. N. Tebbe, P. M. Garrett and M. F. Hawthorne, *J. Amer. Chem. Soc.* **88**, 607 (1966).
- ⁴ P. M. Garrett, G. S. Ditta and M. F. Hawthorne, *J. Amer. Chem. Soc.* **93**, 1265 (1971).
- ⁵ R. R. Rietz and R. Schaeffer, *J. Amer. Chem. Soc.* **93**, 1263 (1971).
- ⁶ R. R. Rietz, *Thesis*, Indiana University: Bloomington, Indiana (1971).
- ⁷ R. R. Rietz and R. Schaeffer, *J. Amer. Chem. Soc.* **95**, 6254 (1973).
- ⁸ J. C. Huffman and W. E. Streib, *Chem. Commun.* 665 (1972).
- ⁹ J. Plešek and S. Heřmánek, *Chem. & Ind. (London)*, 1267 (1971).
- ¹⁰ J. Plešek and S. Heřmánek, *Coll. Czech. Chem. Commun.* **39**, 821 (1974).
- ¹¹ P. H. Wilks and J. C. Carter, *J. Amer. Chem. Soc.* **88**, 3441 (1966).
- ¹² H. Plotová, S. Heřmánek and J. Plešek, *Coll. Czech. Chem. Commun.* in press.
- ¹³ H. Plotová, *Thesis*, Institute of Chemical Technology: Prague (1973).
- ¹⁴ J. Plešek, B. Štíbr and S. Heřmánek, to be published.
- ¹⁵ S. Heřmánek, J. Plešek and B. Štíbr, Second International Meeting on Boron Compounds, Abstracts, p 38. Leeds, England (25-29 March 1974).
- ¹⁶ B. Štíbr, J. Plešek and S. Heřmánek, *Coll. Czech. Chem. Commun.* **38**, 338 (1973).
- ¹⁷ S. Heřmánek and J. Plešek, to be published.
- ¹⁸ W. J. Evans and M. F. Hawthorne, *J. Amer. Chem. Soc.* **93**, 3063 (1971).
- ¹⁹ M. F. Hawthorne, *Pure Appl. Chem.* **33**, 475 (1973).
- ²⁰ B. Štíbr, J. Plešek and S. Heřmánek, *Chem. & Ind. (London)*, 649 (1972).

- ²¹ B. Štíbr, J. Plešek and S. Heřmánek, *Coll. Czech. Chem. Commun.* **39**, 1805 (1974).
²² R. E. Williams, *Inorg. Chem.* **10**, 210 (1971).
²³ R. W. Rudolph and W. R. Pretzer, *Inorg. Chem.* **11**, 1974 (1972).
²⁴ M. F. Hawthorne and A. R. Pitochelli, *J. Amer. Chem. Soc.* **81**, 5519 (1959).
²⁵ S. Heřmánek and J. Plešek, *Z. Anorg. Allgem. Chem.* in press.
²⁶ W. N. Lipscomb, *Pure Appl. Chem.* **29**, 493 (1972).
²⁷ J. Plešek and S. Heřmánek, *Chem. & Ind. (London)*, 890 (1972).
²⁸ Z. Janoušek, *Thesis*, Institute of Inorganic Chemistry: Řež near Prague, Czechoslovakia (1973).
²⁹ J. A. Dupont and M. F. Hawthorne, *J. Amer. Chem. Soc.* **86**, 1643 (1964).
³⁰ Z. Janoušek, S. Heřmánek, J. Plešek and B. Štíbr, *Coll. Czech. Chem. Commun.* **39**, 2363 (1974).
³¹ D. C. Young, D. V. Howe and M. F. Hawthorne, *J. Amer. Chem. Soc.* **91**, 859 (1969).
³² M. F. Hawthorne, R. L. Pilling and P. F. Stokely, *J. Amer. Chem. Soc.* **87**, 1893 (1965).
³³ D. V. Howe, C. J. Jones, R. J. Wiersema and M. F. Hawthorne, *Inorg. Chem.* **10**, 2516 (1971).
³⁴ A. R. Siedle, G. M. Bodner and L. J. Todd, *J. Organometal. Chem.* **33**, 137 (1971).
³⁵ B. L. Chamberland and E. L. Muettterties, *Inorg. Chem.* **3**, 1450 (1964).
³⁶ Z. Janoušek, J. Plešek, B. Štíbr and S. Heřmánek, to be published.
³⁷ J. Plešek, B. Štíbr and S. Heřmánek, *Chem. & Ind. (London)*, 662 (1974).
³⁸ S. Heřmánek, J. Plešek, B. Štíbr and F. Hanousek, *Coll. Czech. Chem. Commun.* **33**, 2177 (1968).
³⁹ P. M. Garrett, F. N. Tebbe and M. F. Hawthorne, *J. Amer. Chem. Soc.* **86**, 5016 (1964).
⁴⁰ J. S. Roscoe, S. Kongpricha and S. Papetti, *Inorg. Chem.* **9**, 1561 (1970).
⁴¹ J. Plešek and S. Heřmánek, *Chem. & Ind. (London)*, 381 (1973).