

The chemistry of the undecaborates

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Dedicated to M. Frederick Hawthorne on the occasion of his 75th birthday in recognition of his outstanding contributions to boron chemistry

Abstract

The formation, structure, and reactivity of the *nido*-11-vertex species $B_{11}H_{15}$, $B_{11}H_{14}^-$, $B_{11}H_{13}^{2-}$, $B_{11}H_{12}^{3-}$ and of the *closo*-11-vertex species $B_{11}H_{12}^-$, $B_{11}H_{11}^{2-}$ are reviewed. The reactivity includes the behavior towards acids, bases, and oxidants as well as cluster expansion reactions, giving *closo*-12-vertex species of the type $EB_{11}H_{11}^{n-}$ or $[B_{11}H_{11}M]^{n-}$.

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1. Introduction

The deltahedral *closo*-borates, $B_nH_n^{2-}$, have obtained text-book importance, representing aesthetically pleasing examples of electron-deficient molecular structures. The ‘electron deficiency’, represented in the simple picture of localized molecular orbitals by three-center-two-electron (3c2e) bonds, increases with the cluster size n . The connectivity k of a given atom, i.e. the number of adjacent skeletal atoms, increases as well. The sum of the connectivities for all of the n skeletal atoms, Σ_k , is related to the cluster size n by the relationship $\Sigma_k = 6n - 12$, a sum, that covers a range from 12 ($n = 4$; tetrahedron) to 60 ($n = 12$; icosahedron). Note, that all of the vertices of the deltahedral Platonic bodies (regular polyhedra) are characterized by the same connectivity, which is 3 (‘ $3k$ ’) for the tetrahedron ($n = 4$), 4 (‘ $4k$ ’) for the octahedron ($n = 6$), and 5 (‘ $5k$ ’) for the icosahedron ($n = 12$). However, mixed connectivities are found for vertices in the intermediate polyhedra. The 11-vertex *closo*-structure (‘cl-11’), an octadecahedron, may be derived from the classical 10-vertex skeleton of *nido*-

decaborane (ni-10<VI>), $B_{10}H_{14}$, by capping the hexagonal aperture. (A Roman number with the cluster symbol denotes the size of the aperture in deltahedral *nido*- or *arachno*-skeleton.) The cl-11 structure has the lowest symmetry of all known *closo*-structures and is the only deltahedron, containing vertices of three different connectivities, namely: $6k$ for B1 (on the C_2 -axis), $4k$ for B2 and B3 (on one of the mirror planes) and $5k$ for B4–B11 (Fig. 1).

The *nido*-11-vertex clusters are formally derived from the $B_{12}H_{12}^{2-}$ icosahedron by removing a BH_2^+ vertex, thus leaving a hypothetical anion $B_{11}H_{11}^{4-}$ with a pentagonal aperture, ni-11<V>. This anion was called ‘ollide’ because of its pot-like structure (from Spanish ‘olla’, water jar [1]). More or less well characterized ni-11<V> clusters are the anions $B_{11}H_{12}^{3-}$, $B_{11}H_{13}^{2-}$, $B_{11}H_{14}^-$ and the neutral species $B_{11}H_{15}$, with one to four extra-H atoms, which fluctuate along the pentagonal aperture so rapidly that the NMR spectra indicate C_{5v} pseudo-symmetry.

Whereas *arachno*-11-vertex clusters with heteroatoms in the skeleton are well known [2], homo-boranes with a $B_{11}H_{11}^{6-}$ skeleton and a few additional extra-protons are unknown up to now. An ar-11<VI> structure was suggested for $B_{11}H_{16}^-$, which is derived from the ni-11<V> skeleton by opening of one bond at the aperture [3]. Such structures are found in the hetero-undecaborate series.

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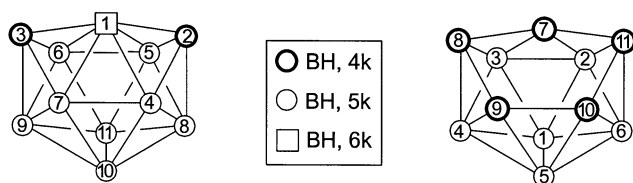
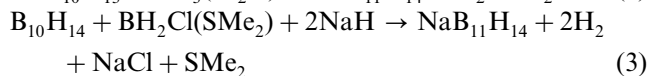
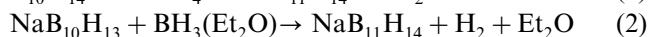
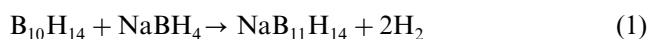


Fig. 1. Structure and numbering of *closo*- $B_{11}H_{11}^{2-}$ (cl-11; C_{2v}) and (hypothetical) *nido*- $B_{11}H_{11}^{4-}$ (ni-11<VI>; C_{5v}).

In this article, we survey the chemistry of the known B_{11} clusters with a cl-11 or a ni-11<V> structure. Undecaborates with one or more non-boron atoms in the 11-vertex skeleton are not considered.

2. Formation and structure of *nido*- $B_{11}H_{15}$ and its conjugated anions

The key substances for entry into undecaborate chemistry are salts containing the anion $B_{11}H_{14}^-$. The first synthesis of $B_{11}H_{14}^-$ started from decaborane, whose *nido*- B_{10} skeleton was expanded by the action of BH_4^- (80–90 °C, in dioxane; Eq. (1)). Such an expansion can also be achieved by adding BH_3 to the $B_{10}H_{13}^-$ anion (45 °C, diborane in Et_2O ; Eq. (2)). The same anion may be an intermediate during the reaction, according to Eq. (1) [4]. The addition of $BH_2Cl(SMe_2)$ to $B_{10}H_{14}$ in the presence of NaH gives the same product Eq. (3) [5].



Reaction (3) yields the 7-alkyl derivatives, when 6-alkyl decaborane, $B_{10}H_{13}R$ ($R = Me, CHMeiPr, CMe_2iPr$), is the starting material [5]. In all cases, the B_{10}/B_{11} cluster expansion is a structurally transparent reaction (see Fig. 2).

When pentaborane(9) is available, its deprotonation with an alkali metal hydride or with a metal alkanide (Li^iBu , e.g.) offers a high-yield one-pot preparation of *nido*-undecaborate, a reaction, which is assumed to proceed through $B_9H_{14}^-$ as an intermediate (85–90 °C, in glyme; Eq. (4)) [6].

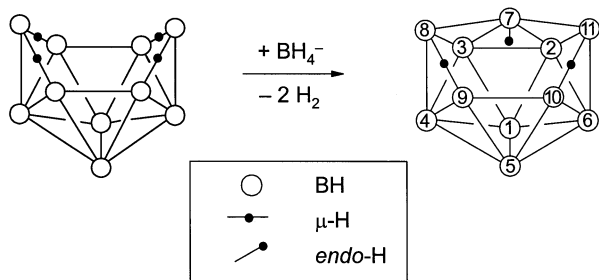
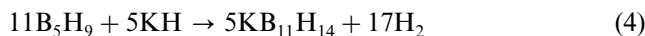
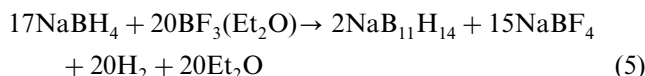


Fig. 2. Formation of *nido*- $B_{11}H_{14}^-$ from *nido*- $B_{10}H_{14}$.



The most convenient synthesis of $B_{11}H_{14}^-$ starts from the readily available substances $NaBH_4$ and $BF_3(Et_2O)$ (105 °C, in diglyme; Eq. (5)) [7]; this reaction proceeds via triborate, $B_3H_8^-$, the salts of which can also be used as starting material. The adduct $BF_3(Et_2O)$ can be successfully replaced in reaction (5) by other halogenated species, such as $BCl_3, CHCl_3, CH_2Cl_2, BuCl, C_5H_{11}Br, C_6H_{13}Br,$ or $SiCl_4$ [8].



In crystalline $[PHMe_3]B_{11}H_{14}$, the two of three extra-H atoms of the anion are found in bridging positions and the third H atom in an *endo*-position (see Fig. 2) [9]. In solution, these extra-H atoms fluctuate so rapidly around the pentagonal aperture, that no decoalescence of the NMR signals can be observed on cooling down the solution, establishing C_{5v} pseudo-symmetry. A theoretical study of this structural process by ab initio methods showed that a concerted transformation of *endo*-into bridging H atoms and vice versa takes place with an activation energy of only 5.9 kJ mol⁻¹ [10].

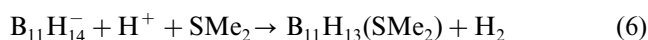
The anion $B_{11}H_{14}^-$ can be protonated (–78 °C, anhydrous HCl) to give the neutral parent borane $B_{11}H_{15}$, which is unstable above 0 °C [9]. A dioxane-adduct of $B_{11}H_{15}$ is formed, when HCl acts on $B_{11}H_{14}^-$ in dioxane [11]. The NMR spectra of $B_{11}H_{15}$ reveal again C_{5v} pseudo-symmetry because of fluctuation of the four extra-H atoms [9]. An ab initio calculation gives a ground state with four adjacent hydrogen bridges at the pentagonal aperture, from B7 to B11. The boron atoms B8–B10 adopt the rare over-all coordination number 7 in the ground state [12].

The deprotonation of $B_{11}H_{14}^-$ in aqueous alkaline solution yields salts with the anion $B_{11}H_{13}^{2-}$ [4]. The anion exhibits the typical ni-11<V> structure, whose aperture is hydrogen-bridged at B7–B8 and B9–B10 in crystals of $Cs[NMe_4]B_{11}H_{13}$ [13], whereas the two extra-H atoms fluctuate along the aperture in solution.

Two protons can be removed from $B_{11}H_{14}^-$ by using Li^iBu as a base (in tetrahydrofuran, thf, or tetrahydropyran, thp) [14]. The extra-H atom might be found in a bridging (A) or in an *endo*-position (B) at the pentagonal aperture; both of these structures are minima on the potential energy hypersurface with structure A by 13.0 kJ mol⁻¹ better than structure B. The transition state is only 0.5 kJ mol⁻¹ above the flat minimum B, so that the rapid fluctuation of the extra-H atom can be understood, inducing C_{5v} pseudo-symmetry with respect to the NMR spectra in solution. The observed ¹H and ¹¹B-NMR shifts are in good agreement with the GIAO-calculated shift values, when these values are averaged, according to the equivalences of the C_{5v} pseudo-symmetry [14].

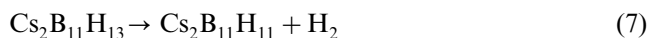
The removal of a third proton from $B_{11}H_{14}^-$ could not be achieved. The anion $B_{11}H_{12}^{3-}$ must be an extremely weak Brønsted acid for electrostatic reasons, and the ollide anion $B_{11}H_{11}^{4-}$ remains unknown. Owing to increasing lattice energies, the solubility decreases in the series $MB_{11}H_{14} > M_2B_{11}H_{13} > M_3B_{11}H_{12}$ [14].

Neutral *nido*-undecaboranes of the type $B_{11}H_{13}L$ can be obtained by the action of a Lewis base L and a Brønsted acid on $B_{11}H_{14}^-$. The base SMe_2 and HCl/dioxane [11] or a two-phase mixture SMe_2/H_2SO_4 [15] can be used Eq. (6). Presumably, $B_{11}H_{15}$ is an intermediate. The structure of $B_{11}H_{13}(SMe_2)$ in the crystal exhibits a ni-11<V> skeleton with SMe_2 as *exo*-ligand at B7 and three extra-H atoms as in $B_{11}H_{14}^-$ (see structure (g) in Fig. 7) [15].

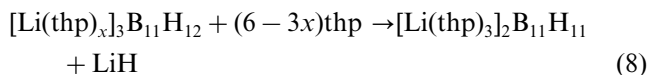


3. Formation and structure of *closo*- $B_{11}H_{11}^{2-}$ and $-B_{11}H_{12}^-$

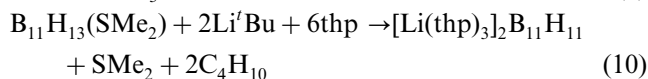
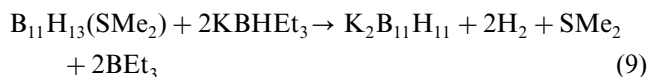
A *closo*-undecaborate was first synthesized by the thermal elimination of H_2 from solid $Cs_2B_{11}H_{13}$ (268 °C; Eq. (7)) [16]. Only two B–B bonds need to be formed in this structurally transparent process: a bond from B7 to B9 and one from B7 to B10 of $B_{11}H_{13}^{2-}$ to give the bonds B1–B7 and B1–B4 of $B_{11}H_{11}^{2-}$, respectively (Fig. 1). The *closo*-species $Cs_2B_{10}H_{10}$ and $Cs_2B_{12}H_{12}$ are by-products, which cannot be separated.



Starting from a salt with the anion $B_{11}H_{12}^{3-}$, the thermolysis does not give H_2 , but instead a hydride, at much lower temperature (80 °C, in thp; Eq. (8)) [14].

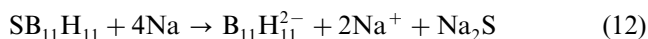


The best access of *closo*- $B_{11}H_{11}^{2-}$ can be achieved by the double deprotonation of $B_{11}H_{13}(SMe_2)$ with bases like $KBHt_3$ (in thf; Eq. (9)) or Li^tBu (in thp; Eq. (10)) [17]. Pure crystals are formed, and the cation can easily be exchanged in order to obtain single crystals, appropriate for X-ray analysis. A 1:1 ratio of $B_{11}H_{13}(SMe_2)$ and base leads to the anion $B_{11}H_{12}(SMe_2)^-$ [18], obviously an intermediate in the reactions (9, 10).



Further interesting ways to the *closo*- B_{11} skeleton have been described. When $B_{11}H_{14}^-$ is oxidized by polyselenide, a *closo*-cluster anion $B_{11}H_9(Se_3)^{2-}$ is formed, in which a Se_3 chain replaces two *exo*-H atoms.

In the solid state, the Se_3 unit connects B4 and B7, thus creating a B_2Se_3 pentagon, fused to the B_{11} skeleton [19]. A possible stoichiometry is suggested in Eq. (11). The *closo*-12-vertex species $SB_{11}H_{11}$ can be desulfurized with alkali metal, yielding $B_{11}H_{11}^{2-}$ (Na in liquid NH_3 ; Eq. (12)) [20].



Moreover, $B_{11}H_{11}^{2-}$ can be formed as a side-product in efforts to obtain *closo*-(CH) $B_{11}H_{11}$ by dihalocarbene addition to $B_{11}H_{14}^-$, using $CHCl_3$ or CHI_3 in the presence of a strong base [21].

The anion $B_{11}H_{11}^{2-}$ can be protonated by acids HX at low temperatures to give $B_{11}H_{12}^-$. This anion reacts above -10 °C with excess HX and yields *nido*- $B_{11}H_{13}X^-$ [17,22].

The C_{2v} structure of the $B_{11}H_{11}^{2-}$ anion was suggested by analogy to well-characterized isoelectronic species (e.g. *closo*-(CH) $_2B_9H_9$) as well as from electronic considerations [23,24] and was later computed by ab initio methods [22,25,26]. The computed geometric data fit well to the results of an X-ray diffraction analysis of $[NBzEt_3]_2B_{11}H_{11}$ [17].

In solution, however, a rapid skeletal fluxionality makes all of the eleven BH vertices equivalent, as indicated by one single peak in the corresponding NMR spectra, even at low temperature [24,27], whereas five sets of non-equivalent BH vertices are present in the computed C_{2v} ground state. A diamond-square-diamond (dsd) mechanism was proposed for the skeletal rearrangement by theoretical arguments [23,24,26,28]. On the way from the type C ground state to the low lying type D transition state (C_s), one of the four equivalent edges from the $6k$ vertex B1 to one of the four equivalent $5k$ vertices B4–B7 is opened (edge B1–B4 in Fig. 3). The subsequent formation of one of the equivalent bonds B1–B4 or B2–B7 along the diagonal of the tetragonal aperture B1–B2–B4–B7 of D^1 gives the ground state C^1 or C^2 , respectively, with equal probability, and from there the $11!/2$ degenerate type C tautomers can be obtained by repetition of such fluxional processes. The lowest computed activation energy for $C \rightarrow D$ was found to be 9.1 kJ mol^{-1} [22]. In the series of closed deltahedral boranes $B_nH_n^{2-}$ ($n = 6–12$), the anions $B_{11}H_{11}^{2-}$ and $B_8H_8^{2-}$ are the only ones that undergo a degenerate dynamic skeletal rearrangement at such a low activation energy. Interestingly, the B_{11} skeleton of the above mentioned anion $B_{11}H_9(Se_3)^{2-}$ undergoes the same dynamic process, revealing one ^{11}B -NMR doublet and one singlet in the ratio 9:2 [19]; the particular tautomer found in the solid state may be due to lattice forces.

The computed geometry of the C_{2v} ground state C represents another example of the power of ab initio

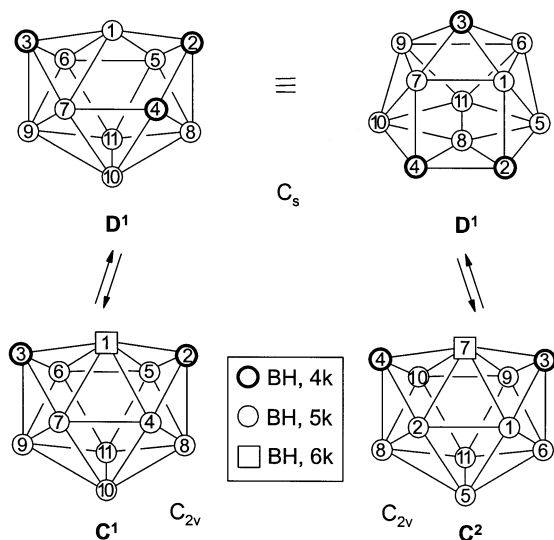


Fig. 3. dsd Mechanism for the $B_{11}H_{11}^{2-}$ skeletal rearrangement with two of the degenerate ground-state structures, C^1 and C^2 , and one of the transition states, D^1 ; numbers denote the identity of each BH unit throughout the rearrangement and correspond to systematic numbering in structure C^1 only.

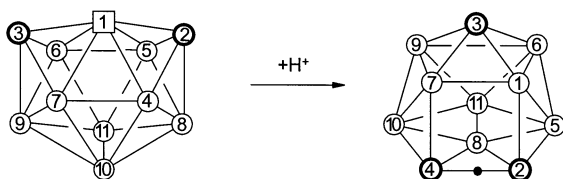
calculations, when the NMR shifts are calculated from the computed geometry and averaged in the ratio 1:2:4:2:2 for B–B11: excellent agreement with the observed data is achieved [$\delta(^1H) = 1.34$ (calc.) and 1.26 (obs.); $\delta(^{11}B) = -17.8$ (calc.) and -17.2 (obs.) [22].

The structure of the *closo*-anion $B_{11}H_{12}^-$ was first deduced from the 2D- $^{11}B/^{11}B$ -NMR spectrum. In contrast to $B_{11}H_{11}^{2-}$, a rigid skeleton was found with the same structural pattern as found for the transition state **D** (Fig. 3) [17]. The additional proton bridges the two adjacent $4k$ vertices B2 and B4 at the tetragonal aperture (Scheme 1). In spite of the *closo*-electron count, the structure does not represent a closed deltahedron. The proposed structure was confirmed by the good agreement of observed and ab initio computed NMR data [22].

4. Reactions of *closo*-undecaborates

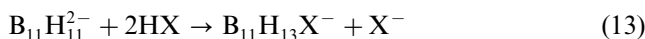
4.1. Reactions with Brønsted acids

The protonation of $B_{11}H_{11}^{2-}$ by Brønsted acids HX generates the well-characterized anion $B_{11}H_{12}^-$ and then the *nido*-cluster $B_{11}H_{13}X^-$, as mentioned in Section 3



Scheme 1.

(Eq. (13)) [17,22].



Reaction (13) may be performed in CH_2Cl_2 with the borate and trifluoroacetic acid in the ratio 1:2 ($X = CF_3COO^-$) [17]. When the borate (e.g. $[NMe_3Ph]_2B_{11}H_{11}$) is suspended in a medium with a limited basicity such as ethanol, addition of CF_3COOH leads to protonation of $B_{11}H_{11}^{2-}$. In a second step, however, EtOH is added to $B_{11}H_{12}^-$ rather than CF_3COOH and $B_{11}H_{13}(OEt)^-$ is obtained [22]. Reaction between $K_2B_{11}H_{11}$ and aqueous hydrochloric acid yields $B_{11}H_{13}(OH)^-$ [22], proving, that HCl acts as the protonation agent in the reaction. However, OH^- is then added in the second step since it is more basic than Cl^- [22]. The protonation of $B_{11}H_{11}^{2-}$ with CF_3COOH at $-78^\circ C$ may be followed by the addition of a neutral base like pyridine, yielding $B_{11}H_{12}(py)^-$ (structure (h) in Fig. 7) [22].

The second step of reaction (13) can easily be understood as a cleavage of the longest bond in $B_{11}H_{12}^-$, connecting the two $5k$ vertices of the tetragonal aperture (calc. 219.0 pm [22]). This gives a BX vertex with displacement of the former *exo*-H atom to the extra-H atom trio together with the bridging H atom of $B_{11}H_{12}^-$ and the H atom from HX; these three H atoms fluctuate around the aperture in solution, but are rigid in the crystal [22] (Fig. 4).

4.2. Reaction with oxidants

The oxidation of $B_{11}H_{11}^{2-}$ had been studied by cyclic voltammetry [29]. A one-electron transfer gives the short-lived radical-anion $B_{11}H_{11}^{\cdot-}$, which rapidly dimerizes to yield the stable anion $B_{22}H_{22}^{2-}$. This anion, previously formed by the oxidation of *nido*- $B_{11}H_{14}$ with H_2O_2 [30], can be synthesized on a preparative scale, when $B_{11}H_{11}^{2-}$ is oxidized by hard cationic species like Fe^{3+} or Ce^{4+} [17,29]. The structure of $B_{22}H_{22}^{2-}$ was established by X-ray analysis of appropriate salts [17,30] and by 2D- $^{11}B/^{11}B$ -NMR analysis [17]. This structure can be understood by assuming an icosahedral $B_{12}H_{10}$ unit (B1–B12 in Fig. 5) and a $B_{10}H_{12}^{2-}$ unit (B1'–B12' in Fig. 5). The $B_{12}H_{10}$ unit is derived from *closo*- $B_{12}H_{12}^{2-}$ by splitting off two H^- ions, leaving two unsaturated B vertices (B1 and B2 in Fig. 5); the $B_{10}H_{12}^{2-}$ unit is derived from *nido*- $B_{10}H_{14}$ by splitting off two bridging protons, leaving two unbridged B–B bonds (B4'–B8' and B5'–B11'). The role of these bridging protons is played by the unsaturated atoms B1 and B2 in $B_{22}H_{22}^{2-}$, so that each of these B atoms is coordinated by seven B atoms.

Oxidants with a soft center can lead to a substitution of H atoms. An early example is dimethylsulfoxide, Me_2SO , which transforms $B_{11}H_{11}^{2-}$ into $B_{11}H_{10}(SMe_2)^-$ and OH^- , when acetic anhydride is used as an OH^- acceptor (Eq. (14)) [31]. In crystals of the product, the

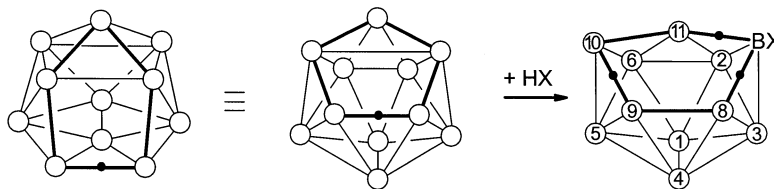
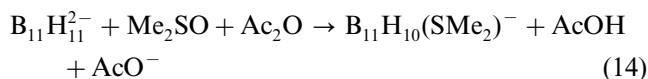
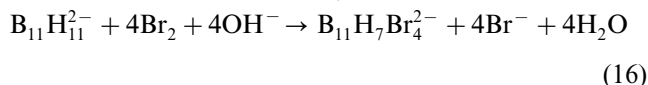
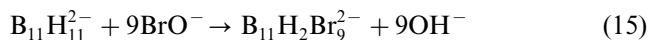


Fig. 4. Structural pathway for the formation of $B_{11}H_{13}X^-$ from $B_{11}H_{12}^-$; bold lines mark the pentagonal aperture of $B_{11}H_{13}X^-$, preformed in $B_{11}H_{12}^-$.

base SMe_2 is bound to B4, whereas the B_{11} skeleton fluctuates in solution, giving a 10:1 ratio of an ^{11}B -NMR doublet and singlet [32].

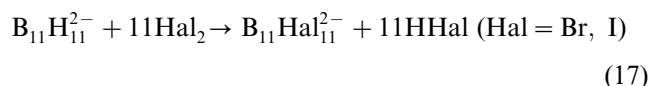


With hypobromite as the oxidant in aqueous solution, an H/Br exchange is achieved to give $B_{11}H_2Br_9^{2-}$ (Eq. (15)) [16]. When bromine in alkaline solution is used, $B_{11}H_{11}^{2-}$ is also brominated to give $B_{11}H_7Br_4^{2-}$ with hypobromite as the probable bromination agent (Eq. (16)) [23]. An ^{11}B -NMR doublet and a singlet in the ratio 7:4 indicate the rapid skeletal rearrangement of the tetrabromoundecaborate.



The perhalogenated undecaborates $B_{11}Hal_{11}^{2-}$ (Hal = Br, I) can be obtained by treatment of solutions of $[NBzIEt_3]_2B_{11}H_{11}$ in CH_2Cl_2 with excess bromine or iodine (Eq. (17)) [29]. Using excess *N*-chlorosuccinimide, $(COCH_2CH_2CO)NCl$, gives $B_{11}Cl_{11}^{2-}$ (Eq. (18)) [29]. However stoichiometric amounts of the chloroi-

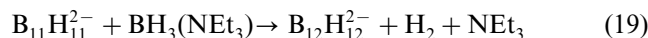
midate and the borate (11:1) give $B_{11}HCl_{10}^{2-}$, whose subsequent iodination leads to $B_{11}Cl_{10}I^{2-}$. All of these halogenated species exhibit skeletal fluctuality in solution. In crystals of $[NBzIEt_3]_2B_{11}Hal_{11}$ (Hal = Br, I), however, a rigid octadecahedral skeleton is observed (Fig. 1) [29].



The oxidation of $B_{11}Hal_{11}^{2-}$ by cyclic voltammetry gives a one-electron transfer, forming $B_{11}Hal_{11}^-$, followed by an irreversible decomposition step at higher potentials. No indications for the formation of a species $B_{22}Hal_{22}^{2-}$, comparable to $B_{22}H_{22}^{2-}$, could be detected probably for steric reason [29].

4.3. Cluster expansion with 2e-donors

Normally the *closo*-cluster anions $B_nH_n^{2-}$ are so stable, that an expansion to closed cluster anions $EB_nH_n^{2-}$ with $n+1$ vertices, where the unit E contributes two skeletal electrons, cannot easily be achieved. The anion $B_{11}H_{11}^{2-}$ is an exception, however. Its enhanced reactivity relates to its easy skeletal rearrangement. A striking example is the incorporation of a BH unit by using $BH_3(NEt_3)$ (Eq. (19)) [17].



We assume that the Lewis acid BH_3 attacks the same bond of the structure **D** (Fig. 3), i.e. the transition state of the skeletal rearrangement of $B_{11}H_{11}^{2-}$, as does a proton (Scheme 1). It is not uncommon for BH_3 to add to a 2c2e bond with formation of a $BBB-3c2e$ bond. A well investigated simple example is the addition of BH_3 to the B–B bond of the three-membered ring $[-NR-BR-BR-]$ (R = *t*Bu) [33]. Subsequently, one of the three B–H bonds of BH_3 in the hypothetical adduct $B_{12}H_{14}^{2-}$ cleaves the same long B–B bond that is cleaved by HX during the addition of HX to $B_{11}H_{12}^-$ (Fig. 4). We assume that the *nido*-anion $B_{12}H_{14}^{2-}$ contains a 3*k* BH_2 vertex with an *endo*-H atom and a 4*k*–4*k* B–B bond with a hydrogen bridge; structures of this type are well known with the heteroborates *nido*- $EB_{11}H_{12}^-$ (E = O

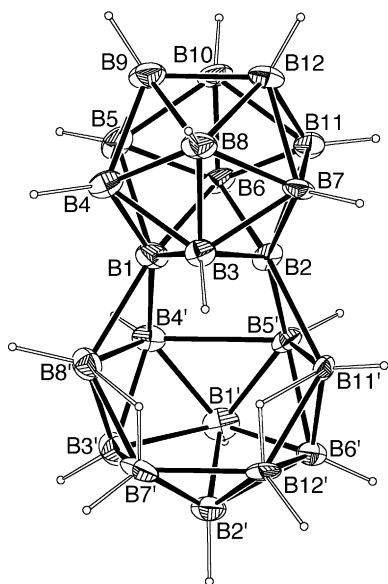


Fig. 5. Structure of $B_{22}H_{22}^{2-}$, consisting of a cl-12 (B1–B12) and a nido-10<VI> unit (primed numbers) [17].

[34], NR [35]; see Fig. 8). The parent anion $B_{12}H_{14}^{2-}$, however, seems to be unstable and is not isolable. Instead it loses H_2 with concurrent formation of two new B–B bonds from the $3k$ to the two $4k$ vertices, yielding the icosahedral $B_{12}H_{12}^{2-}$ anion. The assumed structural pathway of this cluster expansion is depicted in Fig. 6.

A second example of a *closo/closo* cluster expansion is provided by the incorporation of the hypothetical 2e-donor $NiCp^+$ into the closed B_{11} skeleton, when the nickel compound $[Ni(CO)Cp]_2$ is allowed to react with $B_{11}H_{11}^{2-}$ in thf to give $[B_{11}H_{11}(NiCp)]^-$ [36].

5. Reactions of the *nido*-undecaborates

5.1. Reactions with Brønsted acids and Lewis bases

The formation of $B_{11}H_{15}$ from $B_{11}H_{14}^-$ by protonation has been mentioned in Section 2. When this protonation is performed with gaseous HCl in dimethylsulfane solution or by H_2SO_4 in the presence of SMe_2 , the neutral *nido*-species $B_{11}H_{15}$ loses H_2 and $B_{11}H_{13}(SMe_2)$ is isolated (Eq. (6)) [11,15]. The base SMe_2 is found as an *exo*-ligand at the pentagonal aperture (type (g) in Fig. 7). More stable isomers appear to be those with the ligand in position 1 or 2 (type (f) in Fig. 7), because these isomers were formed from the 7-isomer at 170 °C [11]; the mechanism of this rearrangement is unknown.

The ligand SMe_2 in position 7 can easily be exchanged by a series of ligands L in refluxing benzene [$L = RNH_2$ ($R = Cy, ^tBuCH_2, Ph, 4-MeC_6H_4$), py, $PPh_3, PMePh_2$] (Eq. (20)) [18]. The compounds $7-B_{11}H_{13}L$ with $L = ^tBuCH_2NH_2, py$ are also transformed into a mixture of the 1- and 2-isomers at 170 °C [18].

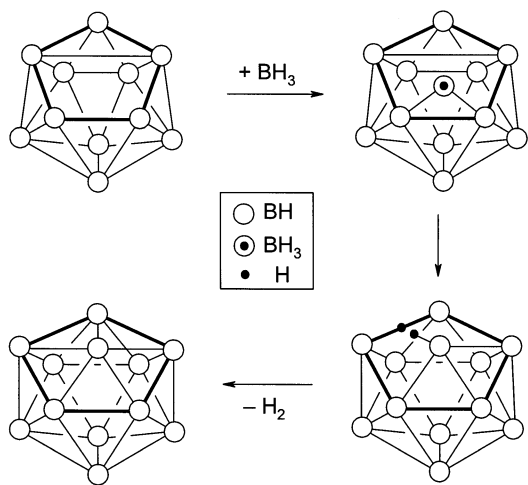


Fig. 6. Structural pathway for the formation of $B_{12}H_{12}^{2-}$ by the addition of BH_3 to the type D structure of $B_{11}H_{11}^{2-}$ (Fig. 3); bold lines connect the same five atoms in each of the structures.

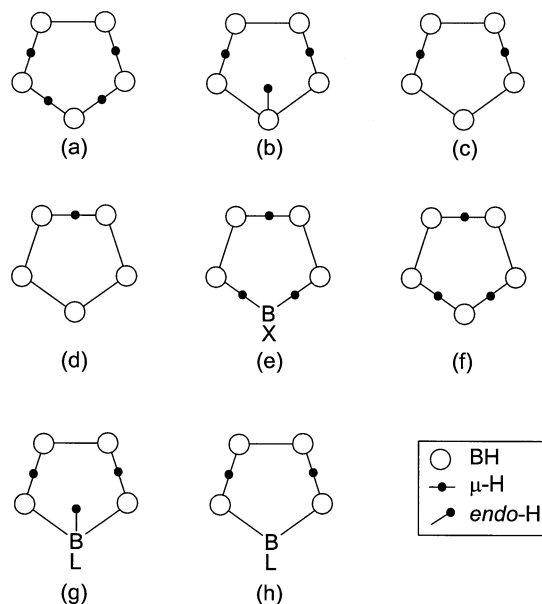
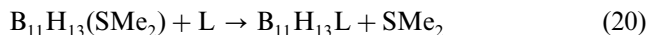


Fig. 7. The pentagonal aperture of *nido*-undecaboranes and borates: (a) $B_{11}H_{15}$ (calc. [12]), (b) $B_{11}H_{14}$ (X-ray [9]), (c) $B_{11}H_{13}^{2-}$ (X-ray [13]), (d) $B_{11}H_{12}^{3-}$ (calc. [22]), (e) $B_{11}H_{13}X^-$ (X-ray; $X = CMe_2CHMe_2$ [5], OEt [22]), (f) $2-B_{11}H_{13}L$ (X-ray; $L = SMe_2$ [15]), (g) $7-B_{11}H_{13}L$ (X-ray; $L = SMe_2$ [15]), (h) $B_{11}H_{12}L^-$ (X-ray; $L = py$ [22]).

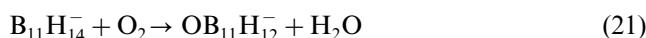


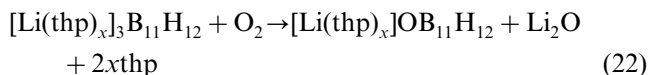
The adduct $7-B_{11}H_{13}(SMe_2)$ can be deprotonated to give $B_{11}H_{12}(SMe_2)^-$ (type (h) in Fig. 7) with bases like $LiBu, Li^tBu, NaH, K[BHET_3]$ or even with amines like $BuNH_2$ [18]. The same deprotonation is possible with other adducts $B_{11}H_{13}L$ ($L = ^tBuCH_2NH_2, py$). A stoichiometric amount of base must be used, otherwise a double deprotonation occurs with elimination of L, leading to *closo*- $B_{11}H_{11}^{2-}$, according to Eq. (9) or Eq. (10).

One, two, three or four extra-H atoms may occur at the pentagonal aperture in solutions, as mentioned above. In the calculated ground-state structure or in the crystal structure, these extra-H atoms are found in fixed positions. A survey on the possible extra-H atom distributions is given in Fig. 7.

5.2. Reactions with oxidants

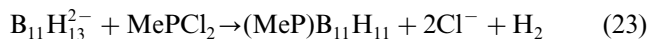
The *nido*- B_{11} skeleton can be expanded to the *nido*- OB_{11} skeleton by the action of O_2 to $B_{11}H_{14}^-$ in alkaline solution (Eq. (21)) [34,37]. The reaction proceeds probably via $B_{11}H_{13}^{2-}$ or even $B_{11}H_{12}^{3-}$, since solid $[Li(thp)_x]_3B_{11}H_{12}$ can also be used as a starting material (Eq. (22)) [14]. The cluster O atom forms linkages to three of the B atoms at the aperture of the B_{11} skeleton (Fig. 8).



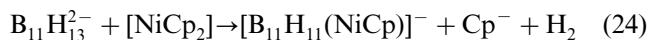


The action of H_2O_2 causes a fusion of two $\text{B}_{11}\text{H}_{14}^-$ units [8]. The anion $\text{B}_{22}\text{H}_{22}^{2-}$ was identified in crystalline material [30]; the structure has been discussed in Section 4.2.

Dehydrogenation of $\text{B}_{11}\text{H}_{13}^{2-}$, formally an oxidation, may be caused by MePCl_2 . The MeP unit is incorporated into the borane skeleton with formation of the closed PB_{11} skeleton (Eq. (23)) [38].



A similar dehydrogenation is observed in the reaction of $\text{B}_{11}\text{H}_{13}^{2-}$ and $[\text{NiCp}_2]$ (Eq. (24)) [39].



5.3. Cluster expansions with 6e-acceptors

The reaction of the *nido*-anions $\text{B}_{11}\text{H}_{14}^-$ and $\text{B}_{11}\text{H}_{13}^{2-}$ with strong bases might formally be expected to give the ollide anion, $\text{B}_{11}\text{H}_{11}^{4-}$, although the existence of this anion has never been proven. The ollide anion should be isolobal with the cyclopentadienide anion, C_5H_5^- (Cp^-), and therefore be able to react, at least formally, with unsaturated species, which complete an 8e-shell or an 18e-shell by accepting six electrons. Formally, such species are E^{3+} ($\text{E} = \text{P}, \text{As}, \text{Sb}, \text{Bi}$), E^{2+} ($\text{E} = \text{Ge}, \text{Sn}, \text{Pb}, \text{BH}, \text{AlMe}$) with respect to the completion of the 8e-shell and transition metal species like $[\text{Rh}(\text{PR}_3)_2]^+$ with respect to the completion of an 18e-shell. In any case, the products are 12-vertex *closo*-heteroboranes of the type $\text{EB}_{11}\text{H}_{11}^{n-}$ or $[\text{B}_{11}\text{H}_{11}\text{M}]^{n-}$ (Fig. 8).

In practice, one can start from salts of $\text{B}_{11}\text{H}_{14}^-$ and add E_2O_3 [$\text{E} = \text{As}, \text{Sb}, \text{Bi}$; Eq. (25)] [38,40] or PbCl_2 (Eq. (26)) [41] in alkaline aqueous solutions.

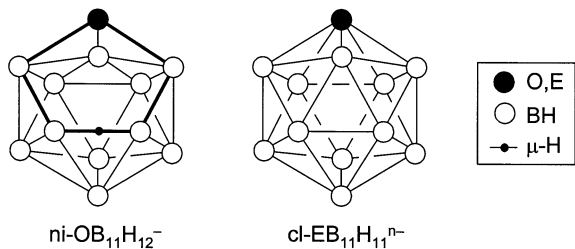
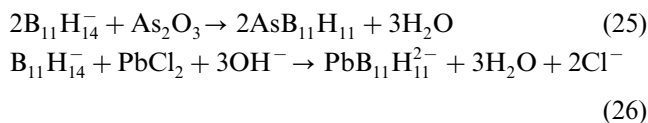
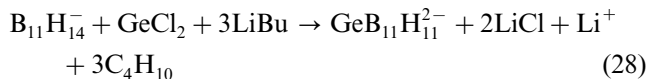
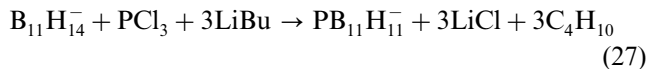
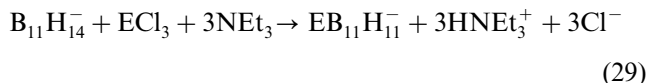


Fig. 8. Structures of *nido*- $\text{OB}_{11}\text{H}_{12}^-$ (*ni*-12<V> type, isoelectronic with $\text{B}_{12}\text{H}_{14}^{2-}$ (Fig. 6); bold lines mark the non-planar pentagonal aperture) and *closo*- $\text{EB}_{11}\text{H}_{11}^{n-}$ ($n = 1$: $\text{E} = \text{P}, \text{As}, \text{Sb}, \text{Bi}, \text{NiCp}$; $n = 2$: $\text{E} = \text{Sn}, \text{Pb}, \text{AlMe}$; $n = 3$: $\text{E} = \text{Rh}(\text{PPh}_3)_2$).

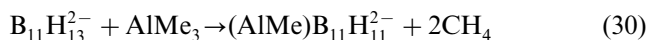
Lithium butanide in thf can be used as a base, starting from $\text{B}_{11}\text{H}_{14}^-$ and ECl_3 ($\text{E} = \text{P}, \text{Bi}$; Eq. (27)) [42,43] or ECl_2 ($\text{E} = \text{Ge}, \text{Sn}$; Eq. (28)) [41].



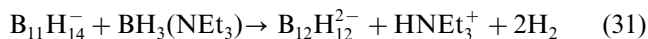
Starting from SbCl_3 or BiCl_3 , the amine NET_3 in thf acts as a sufficiently strong base ($\text{E} = \text{Sb}, \text{Bi}$; Eq. (29)) [42,43].



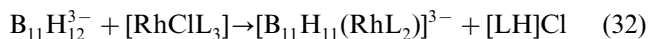
Though itself a Lewis acid, trimethylalane may provide the incorporated moiety, AlMe , the methyl carbanions acting as bases, when starting from $\text{B}_{11}\text{H}_{13}^{2-}$ (100 °C; Eq. (30)) [44].



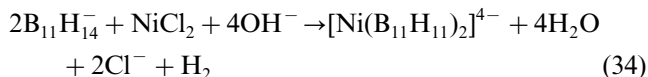
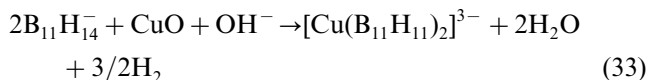
The borane BH_3 works analogous to AlMe_3 . When starting from $\text{B}_{11}\text{H}_{14}^-$ and $\text{BH}_3(\text{NET}_3)$, one proton will be accepted by the amine (Eq. (31)). NaBH_4 in diglyme can be used instead of $\text{BH}_3(\text{NET}_3)$ [45].



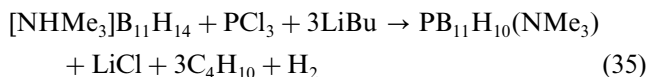
When $[\text{RhClL}_3]$ ($\text{L} = \text{PPh}_3$) is allowed to react with $\text{B}_{11}\text{H}_{12}^{3-}$ in thf, the base L is strong enough to accept a proton (Eq. (32)) [14].



The reaction of $\text{B}_{11}\text{H}_{14}^-$ with CuO or with NiCl_2 in alkaline solutions gives the corresponding sandwich type metallates $[\text{M}(\text{B}_{11}\text{H}_{11})_2]^{n-}$, in which two icosahedra are connected by a common metal atom [46]. The reaction can be formally considered to proceed via $\text{B}_{11}\text{H}_{11}^{4-}$ and the 6e-cations Cu^{5+} or Ni^{4+} , which obtain an 18e-shell by adding two ollide anions. The oxidation of the metal is performed by H^+ , evolved as gaseous H_2 (Eqs. (33) and (34)).



A redox process is also involved, when the cluster expansion reaction with PCl_3 starts from $[\text{NHMe}_3]\text{B}_{11}\text{H}_{14}$; a hydride ligand is replaced by NMe_3 as an additional reaction step (Eq. (35)) [43].



A similar H^-/L exchange and, moreover, an H^-/Br^- exchange is observed, when PdBr_2L_2 ($\text{L} = \text{PMe}_2\text{Ph}$)

reacts with $B_{11}H_{14}^-$. Two molecules L are found at B2 and B5 and the ligand Br at B3 of the closed 12-vertex skeleton of the product $[B_{11}H_8BrL_2(PdBrL)]^-$ [43].

The non-expert in the field may be helped in verifying the skeletal electron-count in this latter example: one BBr and eight BH vertices provide nine times two electrons; two times three electrons come from the two BL vertices; the PdBrL moiety contributes one electron (10+1+2 electrons from Pd, Br, L, respectively, give one cluster and 12 metal electrons); together with the 1^- ionic charge, 26 electrons are available for the cluster, typical for the *closo*-12-vertex count.

6. The localized-bond description of the undecaborates

Many of the experimentally working chemists are using *ab initio* calculations as routine methods with the computer as a black box, comparable to an NMR machine. Nevertheless, the same chemists use 2c2e bonds and 1c2e lone pairs, when they consider actual molecules, built up from non-metal elements. They judge the stability of these molecules initially from the satisfaction of the octet rule (with the elements C, N, O, F, at least) or the doublet rule (with hydrogen). They do not consider, that there are interactions between all the centers of a quantum-mechanical system, and consider a bond between two polyatomic fragments to be a bond between two pseudo-atoms. Such a procedure has served for many years to provide a most useful qualitative description, in spite of the lack of quantitative value. The bond-localization model becomes a bit more complicated, when the electron deficiency in borane clusters requires an extension of the localization picture to 3c2e bonds, as worked out by Lipscomb [47] and others decades ago. Particularly with bigger clusters, like the undecaborates, a description with 2c2e and 3c2e bonds has become out of vogue, possibly because of the current domination of *ab initio* calculations. We used the connections between the vertices in the preceding figures only for the presentation of the topological, not of the electronic situation. There is one useful rule, however, in the localized bond description of boron clusters: a molecular unit, for which an appropriate valence structure cannot be written down, will not be stable. We think it helpful, therefore, to show how the well known procedures can be applied to the localized bond description of the undecaborates.

All of the valence orbitals (four from boron and one from hydrogen) and valence electrons (three from boron and one from hydrogen) are distributed over t 3c2e and y 2c2e bonds. The sum of orbitals, Σ_o , and the sum of electrons, Σ_e , follows for obvious reason the balances $\Sigma_o = 3t + 2y$ and $\Sigma_e = 2t + 2y$, so that the values of t and

y can be unambiguously derived. The t 3c2e bonds consist of t_1 BHB and t_2 BBB bonds, thus $t = t_1 + t_2$. We consider only closed 3c2e bonds, so that the tree centers form a triangle, which is close to equilateral. The y 2c2e bonds are the sum of y_1 BH and y_2 BB bonds. We restrict ourselves to the isoelectronic *closo*-species $B_{11}H_{11}^{2-}$ and $B_{11}H_{12}^-$ and the isoelectronic *nido*-species $B_{11}H_{11}^{4-}$ (hypothetical), $B_{11}H_{12}^{3-}$, $B_{11}H_{13}^{2-}$, $B_{11}H_{14}^-$, and $B_{11}H_{15}$. The substitution of H by X (X = Hal, R, etc.) does not change our picture, because both X and H provide one orbital and one electron. A substitution of H by a neutral Lewis base L does not alter the number of orbitals, but introduces one electron more into the cluster. The valence structure of the cluster skeleton of $B_{11}H_{13}L$, e.g. is the same, therefore, as of $B_{11}H_{14}^-$, etc. For the present, we exclude *endo*-H atoms, so that in an anion $B_{11}H_m^{x-}$ we have 11 *exo*-BH and $m-11$ BHB bonds. Later the *endo*-H atoms are considered. The following table presents the numbers t , t_1 , t_2 , y , y_1 , y_2 for the 11-vertex boranes.

	Σ_o	Σ_e	t	t_1	t_2	y	y_1	y_2
$B_{11}H_{11}^{2-}$	55	46	9	0	9	14	11	3
$B_{11}H_{12}^-$	56	46	10	1	9	13	11	2
$B_{11}H_{11}^{4-}$	55	48	7	0	7	17	11	6
$B_{11}H_{12}^{3-}$	56	48	8	1	7	16	11	5
$B_{11}H_{13}^{2-}$	57	48	9	2	7	15	11	4
$B_{11}H_{14}^-$	58	48	10	3	7	14	11	3
$B_{11}H_{15}$	59	48	11	4	7	13	11	2

The drawings of valence structures make a planarization of the polyhedra or polyhedral fragments necessary. A total planarization of the $B_{11}H_{11}^{2-}$ octadecahedron would obscure the structure, so that we prefer a two-

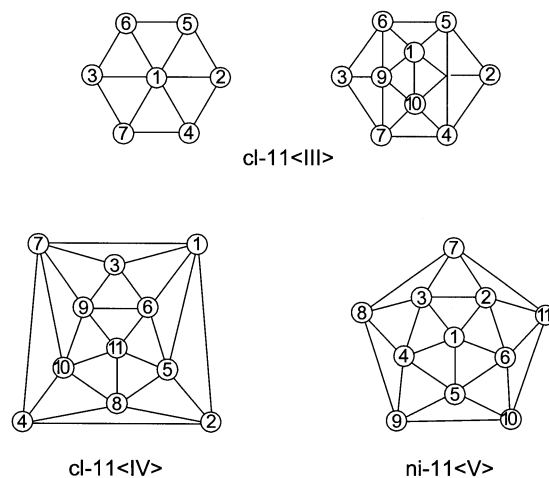


Fig. 9. Planarized structures of $B_{11}H_{11}^{2-}$ (cl-11<III>; upper and lower part), $B_{11}H_{11}^{2-}$ (cl-11<IV>; numbering like cl-11<III>, with the B1–B4 bond opened), and $B_{11}H_{11}^{4-}$ (ni-11<V>).

sketch presentation of the upper and the lower sides separately (Fig. 9).

In constructing valence formulae, we consider two principles, as usual: (a) each vertex participates in three skeletal bonds, 3c2e or 2c2e bonds, besides the one 2c2e *exo*-B–H bond (octet rule). (b) Each edge of a given deltahedron or deltahedral fragment must participate in one 2c2e, in one 3c2e bond or in two 3c2e bonds. A participation in two 2c2e bonds or one 2c2e and one 3c2e bond by a single edge is not considered to be possible.

We start with $B_{11}H_{11}^{2-}$ (C_{2v} ; 9 BBB and 3 BB bonds). The upper part of the anion is built up from three BBB bonds (Fig. 10); two equivalent resonating valence structures are possible. Four resonance structures of principally different weight can be constructed for the lower part of the cluster; each of these four formulae is part of a quadruple of equivalent formulae, which are derived from the given formula by applying the symmetry operations of C_{2v} . The lower part is, therefore, totally represented by 16 resonance formulae; eight of these fit to the one and eight to the other of the upper part formulae. In Fig. 10, each deltahedral vertex means a BH unit. The 2c2e bonds are symbolized by bold lines in Figs. 10–12, the 3c2e bonds by grayish triangles.

The open cl-11<IV> structure of the transition state $B_{11}H_{11}^{2-}$ (C_s ; again 9 BBB and 3 BB bonds) is described by 16 non-equivalent resonance structures. No equivalent resonance structures are possible for the first two

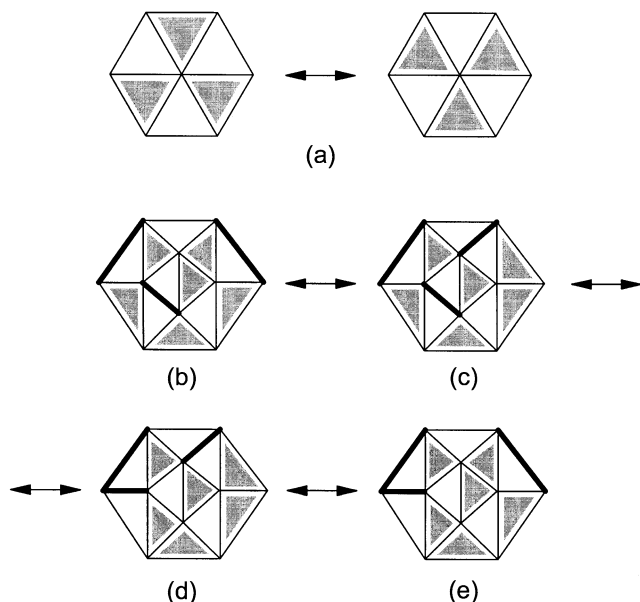


Fig. 10. Two formulae of the upper part (a) and four symmetrically non-equivalent formulae of the lower part (b)–(e) of $B_{11}H_{11}^{2-}$; eight formulae (b)–(e) and those obtained from (b) to (e) by reflexion at the mirror plane through B10 and B11 fit to the left formula (a) and eight others (obtained from (b) to (e) by rotation around the C_2 axis through B1 and by reflexion at the mirror plane through B1–B3) fit to the right formula (a).

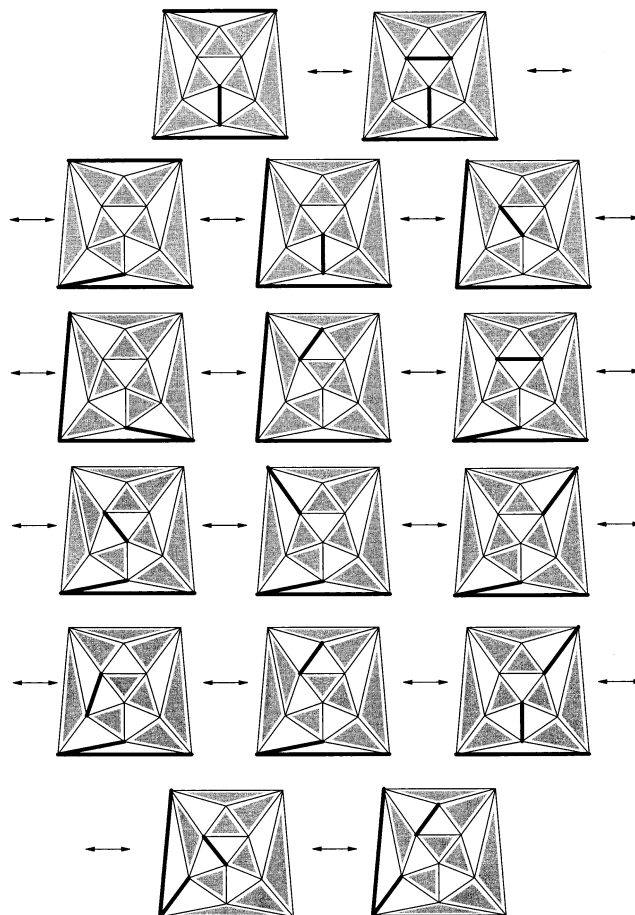


Fig. 11. Sixteen non-equivalent resonance structures of the cl-11<IV> structure of $B_{11}H_{11}^{2-}$.

symmetric formulae in Fig. 11, but two equivalent structures are possible for each of the following unsymmetrical formulae, so that a total of 30 resonance structures result.

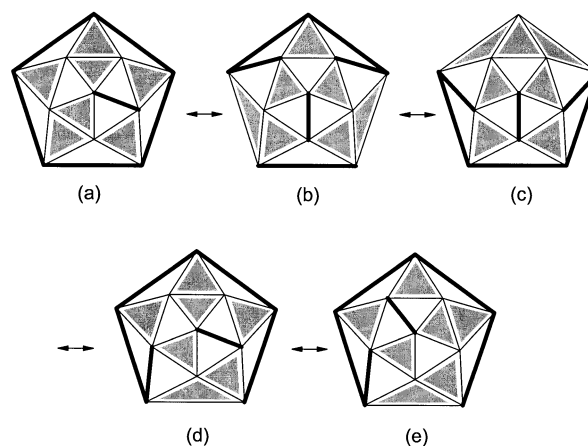


Fig. 12. Five non-equivalent resonance structures (a)–(e) of the ni-11<V> structure of $B_{11}H_{11}^{4-}$; four further equivalent resonance structures can easily be generated from each of the structures (a)–(c) and nine for each of the structures (d) and (e).

Five non-equivalent resonance structures can be drawn for the ni-11<V> structure of the hypothetical $B_{11}H_{11}^{4-}$ (C_{5v} ; 7 BBB and 6 BB bonds; Fig. 12). Five equivalent structures can be generated from each of the symmetric formulae (a)–(c) by applying the C_5 operations and ten equivalent structures from each of the unsymmetrical formulae (d) and (e) by applying all the symmetry operations of C_{5v} , giving a total amount of 35 resonance structures.

The valence structures of $B_{11}H_{11}^{2-}$ and $B_{11}H_{11}^{4-}$ in Figs. 10–12 are built up from BH vertices only. Valence structures, that include BHB bridges, can easily be generated from the given structures by adding one or more protons to appropriate 2c2e bonds with formation of BHB 3c2e bonds. Appropriate for the generation of the cl-11<VI> structure of $B_{11}H_{12}$ is the addition of H^+ to the 2c2e bond B2–B4, which is present in 14 out of the 16 resonance structures of Fig. 11. Appropriate for the generation of valence structures of $B_{11}H_{12}^{3-}$, $B_{11}H_{13}^{3-}$, $B_{11}H_{14}$, and $B_{11}H_{15}$ are the structures of Fig. 12: (a)–(e) for $B_{11}H_{12}^{3-}$, (a)–(e) for $B_{11}H_{13}^{3-}$, (a), (b), (d), (e) for $B_{11}H_{14}$, and (a), (d), (e) for $B_{11}H_{15}$.

Valence structures, which include *endo*-BH bonds, can be derived from the corresponding bridged structures. Let us start, e.g. from a $B_{11}H_{14}$ structure with three BHB bridges and transform this structure into one with two non-adjacent BHB bridges and one *endo*-BH bond, which is the real ground-state structure. The tri-bridged structure of Fig. 13 is derived from structure (d) of Fig. 12 by adding three protons, thus transforming the hypothetical $B_{11}H_{11}^{4-}$ into a non-ground state structure of $B_{11}H_{14}$. The transformation into the ground-state structure involves the transformations of a BHB into a BH and of a BB into a BBB bond. Such elementary reactions are frequently found in boron hydride chemistry. More generally, the transformation of a 3c2e into a 2c2e and, simultaneously, of a 2c2e into a 3c2e bond have been called a [3c, 2c]-translocation [48]. Our simple localizing orbital description is certainly not suitable to compare the energy of the two isomers of Fig. 13.

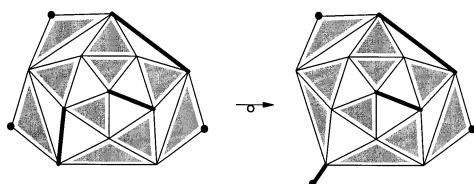


Fig. 13. Transformation of a BHB–3c2e into a BH–2c2e bond by a [3c,2c]-translocation with *nido*- $B_{11}H_{14}$.

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