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Mechanism of the opening of the *closo*-NB_{11} clusters by bases*

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Abstract: The icosahedral aza-*closo*-dodecaboranes $RNB_{11}H_{11}$ (R = H, Me, Ph) are opened by neutral bases L or anionic bases X^- to give the *nido*-species $RNB_{11}H_{11}L$ or $[RNB_{11}H_{11}X]^-$, respectively, with a nonplanar pentagonal aperture; the N atom and a BHB hydrogen bridge are situated at opposite sides of the aperture. The BL or the BX vertex is found in the aperture either adjacent to the hydrogen bridge (type **1**; C_1) or adjacent to nitrogen (type **2**; C_1) or off the aperture adjacent to nitrogen on a mirror plane (type **3**; C_s). At any rate, the isomer of type **1** is the primary product, which may rearrange to yield an isomer of type **3** via an isomer of type **2**. Working in deuteromethanol shows that the bridging H atom originates from the primarily attacked BH vertex. The process from $RNB_{11}H_{11}$ to its base adduct of type **3** includes the opening and the closure of skeletal BN bonds and the jumping of the extra-H atom from endo into bridging positions and vice versa, whereas the base does not alter its position. The application of the opening process to a series of aza-*closo*-dodecaboranes with non-hydrogen boron ligands confirms that only atoms of the *ortho*-belt of the starting material are involved in structural changes. The elementary steps from the *closo*-species to the three isomers are identified as a [3c,1c] collocation and subsequent [3c,2c] translocations in the picture of molecular orbitals localized over three or two centers or to one center (lone pair).

INTRODUCTION

The well-known icosahedral aza-*closo*-dodecaborane, $NB_{11}H_{12}$ (C_{5v}) [1], is expected to give the hypothetical *nido*-borate $[NB_{11}H_{12}]^{2-}$ (C_s) upon a two-electron reduction. Two adjacent BN bonds of the *closo*-species would be opened by this process, reducing the connectivity c of the N atom from $c = 5$ to $c = 3$, a more convenient value for nitrogen, and that of the corresponding B atoms from $c = 5$ to $c = 4$ (Fig. 1). The *nido*-anion is formally derived from the hypothetical aza-*closo*-tridecaborane, $NB_{12}H_{13}$

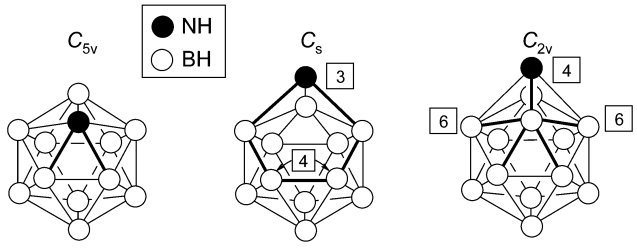

Fig. 1 The structure of *closo*-$NB_{11}H_{12}$ (bold lines: bonds to be opened), *nido*-$[NB_{11}H_{11}]^{2-}$ (bold lines: pentagonal aperture), and *closo*-$NB_{12}H_{13}$ (bold lines: bonds to be opened on BH^{2+} removal); numbers in squares indicate connectivities different from 5.

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(C_{2v}), by removing a BH^{2+} unit with $c = 5$, adjacent to the N atom, thus leaving a nonplanar pentagonal aperture in the *nido*-anion with the N atom on the mirror-plane; this formal BH^{2+} removal reduces the unfavorable connectivity of two B atoms from $c = 6$ to $c = 5$.

Whereas the two-electron reduction has been unknown up to now, the *closo*/*nido* transformation of the NB_{11} skeleton can be achieved by adding the lone pair of a neutral (L) or an ionic Lewis base (X^-) to the *closo*-skeleton of $RNB_{11}H_{11}$ (R = H, Me, Ph), giving the *nido*-species $RNB_{11}H_{11}L$ or $[RNB_{11}H_{11}X]^-$, respectively [2–4]. The base replaces a H atom as a boron-bound *exo*-ligand, and the H atom moves into a bridging position between the two B atoms of the lowest connectivity, $c = 4$, as could have been expected. The base may be bound to one of three boron vertices: the vertex in the aperture at the hydrogen bridge (isomer **1**; C_1), the vertex in the aperture off the hydrogen bridge (isomer **2**; C_1), and the vertex adjacent to nitrogen on a mirror plane (isomer **3**; C_s) (Fig. 2).

Experiments described below show that **1** is the primary product and **3** is formed from **1** via **2**. The question is: What is the mechanism of these isomerizations? Is it an exchange of the base and a hydride anion between adjacent boron vertices (ligand exchange) or is it a migration of the bridging hydrogen under opening and closure of skeletal BN bonds (skeletal rearrangement)?

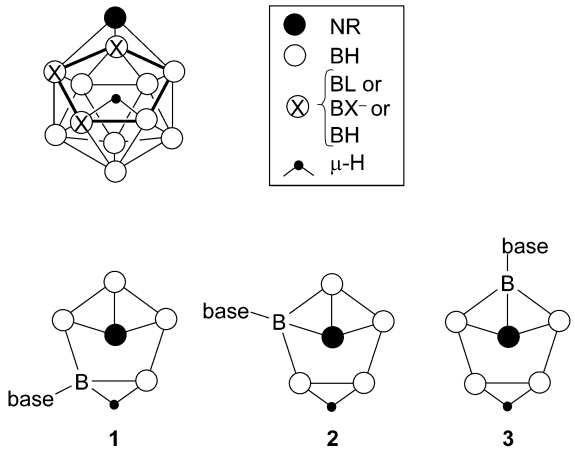

Fig. 2 The structure of $RNB_{11}H_{11}L$ or $[RNB_{11}H_{11}X]^-$ with three positions, to which the base, L or X^-, could be attached, representing the isomers **1**, **2**, **3**, only the upper halves of which are shown.

EXPERIMENTAL RESULTS FOR $RNB_{11}H_{11}L$ AND $[RNB_{11}H_{11}X]^-$

At first glance, products of type **3** seem to be generally formed when anionic bases are applied. Twelve bases X^- are mentioned in Table 1.

Table 1 List of products $M[RNB_{11}H_{11}X]$ of type **3**: R, X, M, and S (solvent of preparation) [M^1 = K(18-crown-6), $M^2 = S(NMe_2)_3$, $M^3 = N(PPh_3)_2$, $M^4 = Li(tmen)_2$, mcl = CH_2Cl_2].

R:	Me	Me	Me	Ph	Ph	Ph	H	Me	Me	Me	Me	Me	Me
X:	H	F	Cl	Br	N_3	OH	OMe	OMe	O*t*Bu	NEt_2	Me	Bu	$FeCp(CO)_2$
M:	M^1	M^2	M^3	NEt_4	M^3	M^1	M^3	M^3	M^1	NH_2Et_2	M^4	M^4	Na
S:	thf	thf	mcl	mcl	mcl	thf	mcl	mcl	thf	mcl	Et_2O	Et_2O	thf

The neutral bases $NHEt_2$ and NH_2tBu give also type **3** products (R = Me). The tertiary amines NMe_3 and NEt_3, however, lead to type **1** products (R = Ph), which are not transformed into isomers, not even in boiling xylene.

The products can be characterized unambiguously by ^{11}B NMR: the correct number and intensities of the signals with respect to type **1** (C_1) and **3** (C_s), assignment of the peaks by 2D-^{11}B/^{11}B NMR methods, characteristic shift values within the type **1** and type **3** series. The products $PhNB_{11}H_{11}(NEt_3)$ (type **1**) and $[N(PPh_3)_2][MeNB_{11}H_{11}(OMe)]$ (type **3**) had also been characterized by crystal structure analysis [2,3].

A particular situation was followed by NMR with pyridine as the neutral base in THF. At –50 °C, a type **1** product is formed and characterized by 2D-NMR. After 1 h at 0 °C, a 1:1 mixture of type **1** and **2** is identified by 2D-^{11}B/^{11}B NMR. After one week at ambient temperature, a 1:1:1 mixture of all three of the isomers **1**, **2**, and **3** is present, and the isomer **3** can again be characterized by NMR in the mixture. The ^{11}B NMR findings are supported by the 2D-^{1}H/^{11}B-HMQC NMR-spectroscopic results. The constant final 1:1:1 ratio of the three isomers $MeNB_{11}H_{11}$(py) indicates accidental equality in free energy.

When we recorded the product $Na\{MeNB_{11}H_{11}[FeCp(CO)_2]\}$ by NMR 10 min after its formation at room temperature, a 1:3 mixture of type **1** and **3** product was observed. It took three days to isomerize the compound **1** completely into **3**. The situation is similar with NH_2tBu as a neutral base. After 10 min in [D_8]THF at –50 °C, the type **1** product is the only one; its complete transformation into **3** takes one week at –50 °C. No indication for the presence of **2** was observed in both cases, probably due to a rapid isomerization **2** → **3**.

The reaction of $MeNB_{11}H_{11}$ with $NHEt_2$ at –50 °C also yields exclusively the type **1** product after 10 min. After 3.5 h, however, the NMR peaks of **1** have disappeared and **2** is now present, which completely isomerizes into **3** within two days.

The type **1** products $MeNB_{11}H_{11}L$ with the bases $NHEt_2$ and NH_2tBu could not structurally be identified in a straightforward way, because a 2:2:1:2:2:1:1 ^{11}B NMR intensity ratio (from high to low field) indicates C_s symmetry. All of the type **3** products (C_s), however, give a 1:2:2:1:2:2:1 ratio, including the type **3** products with the two amines in question. Moreover, the type **1** adduct with L = $NHEt_2$ could be crystallized at low temperature, and the structure could be confirmed by a crystal structure analysis [4]. The observed peak pattern could be explained by an equilibration, according to Fig. 3, which is rapid with respect to the NMR time scale and thus causes C_s pseudosymmetry, the couples of B vertices 2/4, 5/9, 7/10, and 11/13 becoming equivalent. The corresponding ^{11}B NMR shift values of the comparable, but rigid type **1** molecule $PhNB_{11}H_{11}(NEt_3)$ are almost averaged, when going from there to $MeNB_{11}H_{11}(NHEt_2)$: δ = 6.0/–10.6 → –2.7 (B2/4), –4.3/13.0 → 1.0 (B5/9), –19.9/–19.9 (accidental degeneracy) → –19.7 (B7/10), –18.4/–28.7 → –22.7 (B11/13), and a similar situation is met with the NMR peaks of the *exo*-H atoms.

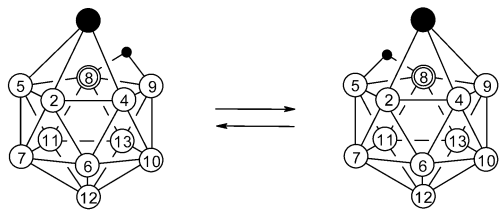

Fig. 3 Equilibration of $MeNB_{11}H_{11}L$ (L = $NHEt_2$, NH_2tBu in position 8).

The question, why the type **1** adducts with the bases NMe_3 and NEt_3 do not enantiomerize, according to Fig. 3, must go back to the lack of a mobile H atom. A mechanism of the enantiomerization is suggested in Fig. 4, which involves an exchange between the bridging and the amine hydrogen. The process is rapid enough to bring corresponding ^{11}B NMR signals to coalescence, but not the NMR signals of H and H′, which strongly differ in frequency: δ = –1.01 (μ-H) and 4.85 (NH).

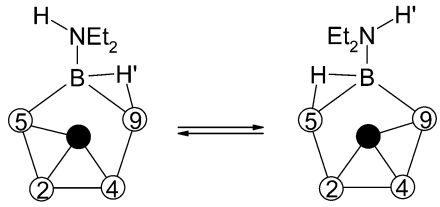

Fig. 4 Mechanism of the equilibration, according to Fig. 3 (only the upper half of the *nido*-cluster is shown).

The generalization of our observations means that type **1** adducts are the primary products, which are either stable or isomerize into **3** via **2**.

OPENING AND REARRANGEMENT MECHANISM

Localized molecular orbitals (LMOs), with restriction to (2c2e) and (3c2e) bonds, are a useful tool in boron chemistry for obtaining qualitative insight into the bonding situation. Figure 5 presents such an LMO description of $HNB_{11}H_{11}$. All of the 60 valence orbitals of the 24 atoms are distributed over t (3c2e) and y (2c2e) bonds: $3t + 2y = 60$; all of the 50-valence electrons are found in these bonds, according to $2t + 2y = 50$. Hence, $t = 10$ and $y = 15$. Since no BHB-(3c2e) bonds are present, we have to consider 10 BBB- and BNB-(3c2e) bonds. Besides the 1 NH and the 11 BH bonds, we have to take into account 3 skeletal BB- or BN-(2c2e) bonds.

It is reasonable to assume that the lone pair of the base, L or X^-, attacks one of the five boron atoms in the *ortho*-belt of $HNB_{11}H_{11}$, which contains the most positively charged B atoms [5]. The (1c2e) lone pair gives a BL- or BX-(2c2e) bond, respectively, and the electron octet at the attacked B atom is maintained, when the corresponding BNB-(3c2e) bond becomes a BN-(2c2e) bond. We call such an elementary reaction, the transformation of a (3c2e) bond and a (1c2e) lone pair into two (2c2e) bonds, a *[3c,1c] collocation* and would call the reversed reaction a *[2c,2c] dislocation* [6]. The H atom at the attacked B atom is shifted from an exo into an endo position, the base being too large for the endo position. An intermediate is formed by this adopted process with a tetragonal aperture, represented in Fig. 6.

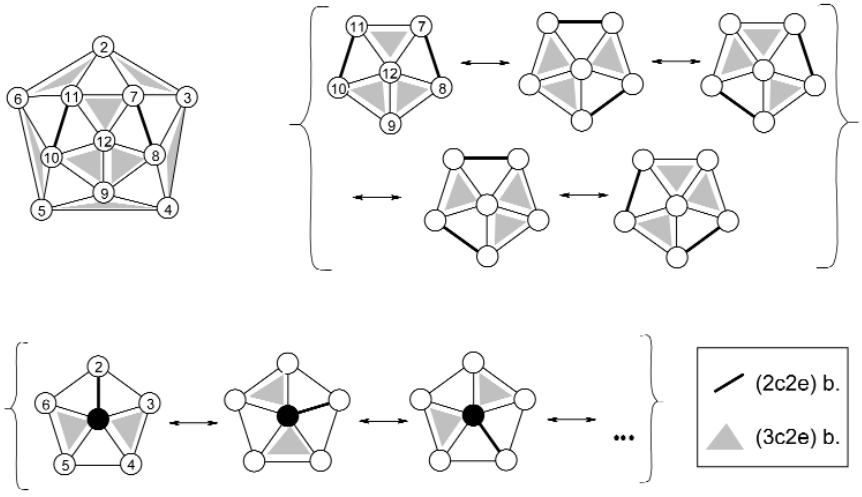

Fig. 5 Distribution of 10 (3c2e) and 3 (2c2e) bonds in the NB_{11} skeleton of $HNB_{11}H_{11}$. Upper left: planarized B_{11} skeleton; upper right: 5 canonical formulae of the B_6 unit B7–B12, the first one taken from the upper left representation; below: 5 canonical formulae of the NB_5 unit.

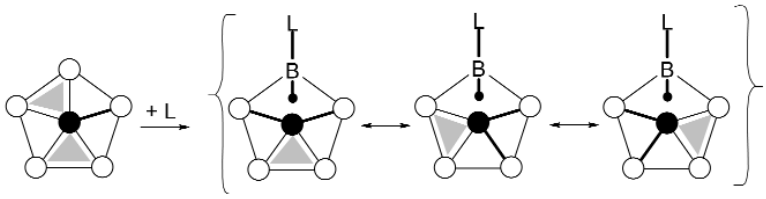

Fig. 6 First step of the attack of $HNB_{11}H_{11}$ (upper half represented) by a base to give an intermediate (three canonical structures).

This intermediate will be stabilized to give a type **1** product by an elementary process, by which a BNB-(3c2e) is transformed into a BN-(2c2e) bond, while a BH-(2c2e) bond generates a BHB-(3c2e) bond. We call such a process a *[3c,2c] translocation* [6] (Fig. 7). The shift of a H atom from an endo into a bridging position and vice versa seems to be a process of low activation energy in bigger *nido*-borane clusters, e.g., in *nido*-undecaborates [7].

The same intermediate as in Fig. 6 could be formed by a two-step mechanism, when the base attacks a B–B edge in the *ortho*-belt of the *closo*-cluster, the lone pair giving a BLB- or BXB-(3c2e) bond, while the corresponding two BN bonds are opened, leaving the N atom bound to three B atoms by (2c2e) bonds; from there the intermediate of Fig. 6 could be formed by a [3c,2c] translocation. Note that the BBB-(3c2e) bond, which connects the B atoms of the attacked B–B edge (see Fig. 5, upper left side), will not be altered during that process.

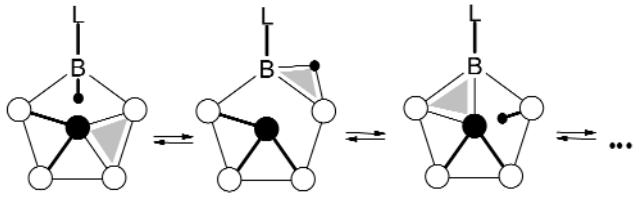

Fig 7 [3c,2c] Translocations during the rearrangement of $RNB_{11}H_{11}L$.

The type **1** product may again undergo a [3c,2c] translocation, by which another intermediate with an *endo*-H atom and with four BN connections is formed (Fig. 7), and from there the way is open for the formation of the products **2** and **3** by a series of altogether five [3c,2c] translocations (Fig. 8).

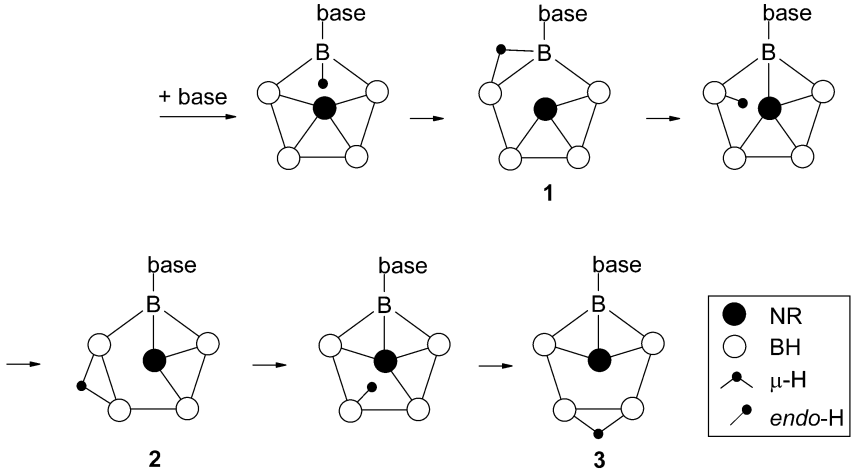

Fig. 8 Overall mechanism of the reaction of $RNB_{11}H_{11}$ with a base to give the adduct **3** via **1** and **2**.

The alternative mechanism for the formation of **2** and **3** from **1** would be an exchange of the base and the *exo*-H atom at adjacent B atoms. The BL or BX bond would necessarily be opened, and the adjacent *exo*-H atom would be shifted into a bridging position by a [2c,2c] dislocation, giving two adjacent hydrogen bridges. The isomer **2** could then be formed by another attack of the base during a [3c,1c] collocation. The NB_{11} skeleton and the original BHB bridge would not be involved in such a three-step mechanism. We do not believe in this mechanism, because the opening of a BL or a BX bond would afford more energy than the electron shifts of a [3c,2c] translocation.

The opening of *closo*-$MeNB_{11}H_{11}$ with CH_3OD gives the same product, $[MeNB_{11}H_{11}(OMe)]^-$ (type **3**), as with CH_3OH; no deuterium was found in the ligand sphere [2], confirming that the bridging H atom originates from the cluster and not from the medium and, moreover, that there is no proton exchange between the adduct and the medium. Note that in the opening process under consideration, the counterion of the type **3** anion is a proton, in a mixture of CH_2Cl_2 and excess CH_3OH as the medium; efforts to isolate pure $H[MeNB_{11}H_{11}(OMe)]$, obviously a strong acid, gave a degradation of the cluster.

OPENING OF DERIVATIVES OF $RNB_{11}H_{11}$

We opened the halo-derivatives *closo*-$MeNB_{11}H_{10}Hal$ (with Hal = Cl, Br, I in the *para*-position 12) [8] by NEt_3 and obtained *nido*-$MeNB_{11}H_{10}Hal(NEt_3)$ of type **3** with Hal still in position 12, whereas the same base had given a stable type **1** product with the unsubstituted *closo*-$MeNB_{11}H_{11}$ [3,4]. The electronic effect of *para*-substituents in icosahedral clusters is well known ("antipodal effect" [9]). Even in the opened *nido*-clusters $RNB_{11}H_{10}HalL$, the Hal substituent in position 12 still exerts an electronic effect on the N atom, obviously, that supports BN bond openings during the transformation of **1** into **3**.

In the *closo*-species $RNB_{11}H_5Me_5(OTrf)$ [4,8], the five Me groups occupy the *meta*-belt, the triflate group is found in *para*-position, and the five H atoms in the *ortho*-belt invite the attack of bases. We applied the bases NMe_3 (in CH_2Cl_2, R = Me) and OH^- (H_2O in CH_3OD, R = Ph) and obtained type **3** products in both cases [4]. The cluster skeleton apart from the upper NB_5 pyramid of the starting material was again not affected by the opening procedure.

An interesting starting material is the *closo*-cluster [–CH_2–CH_2–NEt_2–BH_2–$NB_{11}H_{10}$–] (Fig. 9) [10]. The stericly demanding base *t*$BuNH_2$ attacks a B atom in the *ortho*-belt, which is nonadjacent to the B atom that carries the side chain. Out of five hypothetical isomers with respect to the position of the hydrogen bridge, only that one is found, whose bridging H atom connects two BH vertices. All of the skeletal alterations during the formation of the product are again restricted to the *ortho*-belt of the starting material. The product provides another type **2** example with the characteristic series of ^{11}B NMR signals [4].

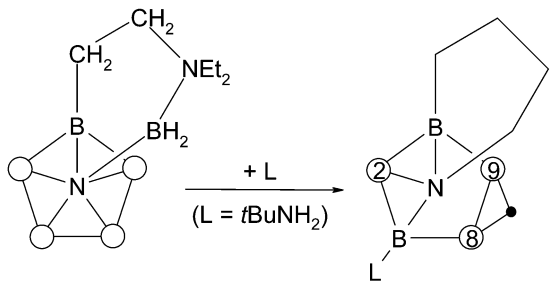

Fig. 9 Opening of [–CH_2–CH_2–NEt_2–BH_2–$NB_{11}H_{11}$–] by *t*$BuNH_2$.

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