not be covalently attached to a receptor and it does not require the addition of a detergent to enhance fluorescence intensity.

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[15] Reagent: A solution containing $EuCl_3 \cdot 6H_2O$ (9.6 mg) and tetracycline hydrochloride (4 mg) in a MOPS buffer (200 mL, 10 mmol L^{-1}) of pH 6.9. The absorbance at 405 nm is $\approx 0.78 \pm 0.01$ cm^{-1}. The reagent is stable for at least 1 month if stored at 4 °C in the dark.

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[19] Assay protocol for H_2O_2: The aqueous sample (1 mL; containing 1 to 2 $\mu g \cdot mL^{-1}$ of H_2O_2) was added to the [Eu(tc)][15] (1 mL) in a cuvette, and the increase in luminescence intensity at > 616 nm was measured after 10 min (excitation at 405 nm). If a time-resolving reader was available, the lag time was adjusted to > 30 μs and the integration time to 100 μs.

[20] GOx assay procedure: The following solutions were placed in the wells of a microtiterplate: a) A [Eu(tc)] solution (in the ten-fold concentration of that given in [15], except for the buffer concentration); b) a solution of GOx (of unknown activity) in the same buffer; c) enough buffer to fill up to a volume of 200 μL; d) β-D-glucose (50 μL, 28 mmol L^{-1}) in buffer, to start the reaction. The increase in fluorescence intensity between 610 and 630 nm was measured over 10 min (ΔI_{10min}). The activity of GOx was calculated by use of a calibration graph, established by plotting ΔI_{10min} versus known activities of GOx. Note: citrate and phosphate interfere.

[21] Procedure for glucose assay: The [Eu(tc)] reagent solution[15] (1 mL) was placed in a cuvette, to which a solution of GOx (2 mL, 15 units, from Sigma, product no. G 2133) in MOPS buffer (10 mL) was added. The reaction was initiated by adding 2 mL of a sample containing between 2 and 10 mmol L^{-1} of glucose. The increase in luminescence intensity after 10 min (ΔI_{10min}) at 616 nm (excitation at 400–440 nm) was measured, and ΔI_{10min} used to read off the glucose concentration using a calibration graph established with β-D-glucose. Note: citrate and phosphate interfere.

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Conversion of *arachno*-Nonaborane into Azanonaborane: Unexpected Loss of a Firmly Integrated Boron Atom**

Mohamed E. El-Zaria,* Udo Dörfler, Matthias Hofmann, and Detlef Gabel

The polyhedral azanonaborane $(RH_2N)B_8H_{11}NHR$ (R = *i*Pr, **1**) is easily prepared by treating dimethylsulfido *arachno*-nonaborane 4-$(Me_2S)B_9H_{13}$ with three equivalents of a primary amine.[1] The reaction has been shown to proceed stepwise, by an initial ligand exchange to give 4-$(RH_2N)B_9H_{13}$, which reacts with an additional amine NH_2R^1 to give the mixed species $R^1H_2NB_8H_{11}NHR$.[1b] These compounds have been shown to constitute a good entry into azacarbaborane[2] and azametallaborane chemistry[3] and may also be useful in neutron capture therapy.[4] The transformation of $(Me_2S)B_9H_{13}$ to $(RH_2N)B_8H_{11}NHR$ involves the loss of one boron atom and cluster rearrangement. Herein we report the conversion of boron-substituted nonaboranes into azanonaboranes. These experiments make it possible to determine which boron atom is eliminated, and to speculate on the mechanism of the cluster rearrangement.

A variety of B-substituted $B_{10}H_{14}$ derivatives are known.[5] These can be converted readily by a two-step process via 6,9-$(Me_2S)_2B_{10}H_{12}$ derivatives into the corresponding *arachno*-nonaborane system.[6] We prepared some ethyl, bromine, and deutero derivatives of decaborane(14), which are stable under the reaction conditions (neither the bromine atom nor the ethyl group can be removed by Et_3N,[6a] and no deuterium exchange has been noted on heating the tetradeuterated $(Me_2S)B_9H_{13}$ with diethylamine under reflux in benzene[6c]).

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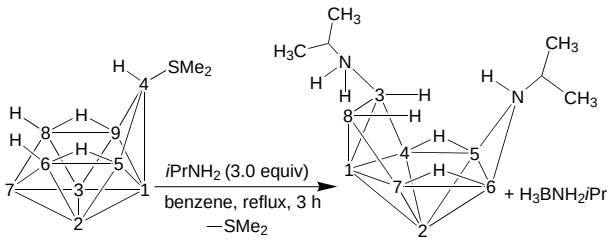
The following $(Me_2S)B_9H_{13}$ compounds with labeled B-atoms were prepared (Scheme 1, Table 1): Et at B^2 (**2**) or B^7 (**3**), Br at B^2 (**4**) or B^6 (**5**) or B^1 (**6**), D at B^1, B^2, B^3, and B^7 (**7**). The presence and the positions of the substituents were confirmed by NMR and IR spectroscopy and mass spectrometry.



Scheme 1. Conversion of the B_9 clusters **2**–**7** into the B_8N clusters **1**, **8**—**12**. The numbering of the clusters is given in Table 1, (*exo*-H atoms are omitted for clarity.

Table 1. Position of the substituents on the B_9 and B_8N clusters (see Scheme 1).

B_9	Substituent	Position on B_9 cluster	Position on B_8N cluster	B_8N
2	Et	2	2	**8**
3	Et	7	6	**9**
4	Br	2	2	**10**
5	Br	6	7	**11**
6	Br	1	–	**1**
7	D	1, 2, 3, 7	2, 5, 7 or 2, 4, 6	**12**

The labels of the B_9 cluster appeared in the following positions of the B_8N cluster after reaction with isopropylamine (Scheme 1, Table 1): Et at B^2 of **2** ⇒ B^2 in **8**; Et at B^7 of **3** ⇒ B^6 in **9**; Br of B^2 in **4** ⇒ B^2 in **10**, and the Br of B^6 in **5** ⇒ B^7 **11**, the Br of B^1 in **6** ⇒ bromine free B_8N cluster **1**. The 1,2,3,7-tetradeuterated nonaborane **7** was transformed to either the 2,4,6- or the 2,5,7- trideuterated B_8N cluster **12**. The NMR spectroscopy results show clearly the loss of one deuterium atom (Table 2) while it was not possible to determine whether the remaining three deuterium atoms were at B^2, B^5, and B^7, or at B^2, B^4, and B^6.

Thus, the boron atoms B^2, B^3, B^6, and B^7 in the B_9 cluster end up at the positions B^2, B^4, B^7, and B^6 in B_8N, respectively, while B^1 of the B_9 cluster is lost during the conversion (Scheme 1).

According to these results we suggest the following stepwise mechanism for the conversion starting with the amino-substituted B_9 cluster (Scheme 2):

a) Initially, an R^1NH_2 molecule attacks the 4-$(RH_2N)B_9H_{13}$ cluster at B^9 or B^5. This proposal is supported by two observations: 1) A 5-$(RH_2N)B_9H_{13}$ intermediate can be isolated from the reaction of 4-$(Me_2S)B_9H_{13}$ with RNH_2.[7] 2) No reaction is observed when 5-OMe-4-(iPrH$_2$N)B_9H_{12} is heated under refluxed with excess iPrNH$_2$ in benzene.
b) The RNH_2 moiety of B^4 exchanges its position from *exo* to *endo* as described in the literature[8] possibly aided by a weakened bond between B^9 and B^4.
c) The RNH_2 moiety migrates from B^4 to form a bridge between B^7 and B^8. This assumption is supported by the reaction rate of **3** (with Et on B^7) which is slower than that of **2** (with Et on B^2). In addition, the R^1NH_2 moiety migrates from B^9 to the *exo* position of B^4.[7] (See also ref. [6b] for an analogous migration.)
d) A third amine, R^2NH_2, attacks at B^9.
e) The B^8–B^9 and B^7–B^3 bonds opens and a diamond-square-diamond (DSD) rearrangement[9] which involves the atoms B^2, B^3, B^7, and B^8 yields a bond between B^2 and B^8.
f) Migration of R^1NH_2 from B^4 to B^1 leads to loss of the B^1-NH_2R^1 unit together with two additional H atoms. Specific elimination of B^1 was shown by reactions of the deuterium substituted **7** and the bromine substituted compound **6**. Closing the B^5–B^3, B^5–B^9, and B^6–B^4 connections completes the formation of the azanonaborane cluster.

The experimental basis for the proposed mechanism is the fate of the boron atoms B^1, B^2, B^6, and B^7 (on the basis of the

Table 2. ^{11}B and ^1H NMR spectroscopic data ($CDCl_3$ at 20 °C, 200 MHz) for B_8N clusters **1**, **8**–**12**.[a]

B_8N	B^1	B^2	B^3	B^4	B^5	B^6	B^7	B^8	μ-H(4,5) μ-H(6,7)	NH
1	1.82	−55.61	−21.46	−31.76	−11.11	−11.11	−33.41	−30.76		
	[2.57]	[−0.65]	[1.29]	[0.86]	[2.51]	[2.51]	[0.86]	[0.55]	[−2.04]	[−1.56]
								[−0.64]	[−1.99]	
8	2.94	−43.91	−20.06	−32.3	−9.88	−10.6	−31.65	−30.62		
	[2.58]	[−]	[1.28]	[0.84]	[2.34]	[2.49]	[0.84]	[0.56]	[−1.9]	[−1.55]
								[−0.48]	[−1.75]	
9	0.76	−53.79	−21.73	−31.67	−10.6	0.76	−32.91	−30.68		
	[2.48]	[−0.55]	[1.26]	[0.77]	[2.21]	[−]	[0.77]	[0.52]	[−2.24]	[−1.36]
								[−0.55]	[−1.89]	
10	3.46	−41.77	−20.58	−28.8	−10.08	−10.08	−28.8	−28.8		
	[3.06]	[−]	[1.21]	[1.25]	[2.75]	[2.86]	[1.25]	[0.73]	[−1.34]	[−1.34]
								[−0.41]	[−1.34]	
11	12.06	−47.28	−18.09	−28.77	−7.41	−4.72	−38.92	−23.25		
	[3.59]	[−0.29]	[1.18]	[0.82]	[2.70]	[2.93]	[−]	[0.77]	[−2.47]	[−0.95]
								[−0.51]	[−1.72]	
12	1.64	−55.64	−21.46	−32.53	−10.65	−11.14	−31.82	−30.65		
	[2.49]	[−]	[1.36]	[0.74][b]	[−][c]	[2.55][c]	[−][b]	[0.46]	[−2.21]	[−1.64]
								[−0.61]	[−2.09]	

[a] All entries in ppm, δ(1H) in square parentheses All spectra measured on a Bruker DP 200 spectrometer. [b], [c] A clear assignment of the deuterium substitutes to either B^5 or B^6 or to B^4 or B^7 is not possible.

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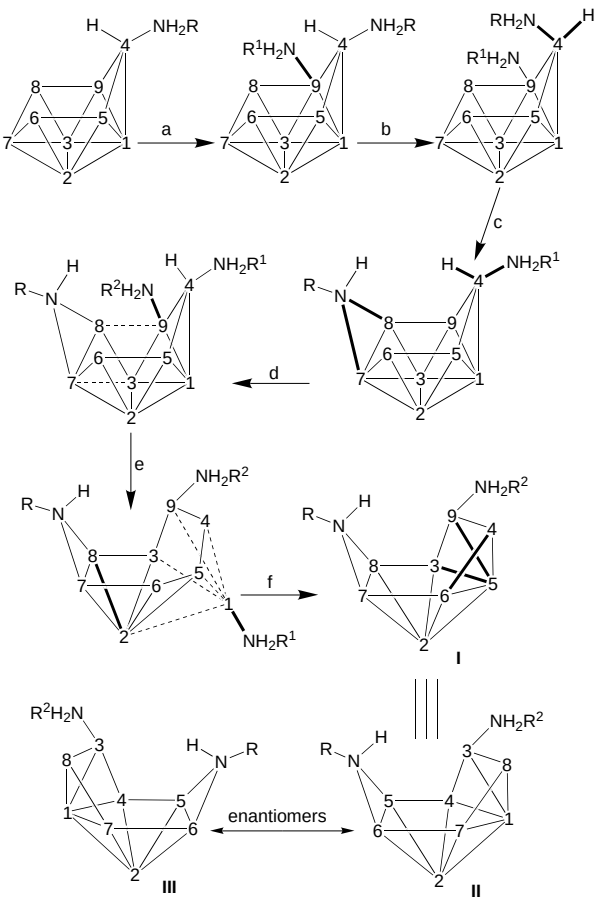

Scheme 2. Mechanistic pathway of the conversion of the nonaborane cluster into the azanonaborane cluster (**I** IUPAC numbering of the B_9 cluster, **II** and **III** IUPAC numbering of the B_8N cluster).[10] Bold lines: new bonds; dashed lines: bonds to be broken.

experiments with the Et- and Br-substituted clusters) and B^3 (concluded from the experiments with a tetradeuterated cluster). Computed ^{11}B NMR chemical shifts, supported by 2D–^{11}B COSY and ^1H CW ^{11}B NMR spectra showed the Et group to be connected to B^6, opposite to the *exo*-amino ligand at B^3 in the B_8N cluster **9**; the data further indicated that the Br atom at B^6 in the B_9 cluster **5** is located at B^7 and not at B^4 in the B_8N cluster **11**. The fate of the boron atoms B^5, B^8, and B^9 has not been clarified, but the proposed mechanism would require only a minimal rearrangement of the bonds (one DSD rearrangement and the closing of the cluster after the loss of B^1). The loss of B^1, which is *not* part of the open face, is surprising. Quantum-mechanical computations might give indications about the feasibility of the proposed pathway, the relative stability of the proposed intermediates, the origin of the H atoms which leave together with B^1, and the rearrangement of the other H atoms.

Experimental Section

1, **8**–**12**: Isopropylamine (0.1 g, 1.74 mmol) was added to a solution of $(Me_2S)B_9H_{13}$ in dry benzene (10 mL, 0.1 g) at room temperature. The mixture was heated to reflux for 3 h. All volatile components were removed under vacuum and the resulting substance was recrystallized from ethanol:water (1:1). Compounds **8** and **9** were purified by TLC by using CH_2Cl_2 as eluent ($R_f = 0.31$). For further purification the substance was dissolved in $CHCl_3$:hexane (1:3) at −20 °C. The solution was filtered and the resulting filtrate was evaporated to dryness to yield the purified product. **1** (DCI): *m*/*z* (%) 214 (95) [M^+]; **8**, **9** MS (EI, 750 eV, 200 °C): *m*/*z* (%) 242 (24) [M^+]; **10**, **11**, (EI, 750 eV, 200 °C): *m*/*z* (%) 293 (18) [M^+]; **12** (FAB$^+$): *m*/*z* (%) 217 (100) [M^+].

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Fluorous Biphasic Catalysis without Perfluorinated Solvents: Application to Pd-Mediated Suzuki and Sonogashira Couplings**

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In catalytic reactions easy handling of the catalyst together with its straightforward recovery and possible reuse remain an important topic. A widespread solution to reach these goals is the application of immobilized catalysts. Immobilization can be achieved by covalent attachment to organic polymers or inorganic support materials.[1] Alternatively, catalysts can be adsorbed on silica gel[2–4] or on reversed-phase silica gel.[5] In some cases the immobilization has a beneficial effect on the catalyst's stability.[6,7] One profound advantage of such supported catalysts is the easy separation from the reaction

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