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Diverse chemistry of the dianion $[closo\text{-}B_9H_9]^{2-}$: synthesis and reactivity of its mono-anionic derivative $[arachno\text{-}B_9H_{12}\text{-}4,8\text{-}Cl_2]^-$†

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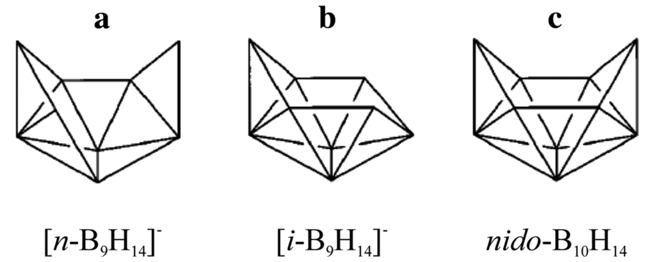
Attempted protonation of the dianion $[closo\text{-}B_9H_9]^{2-}$ under moisture-free conditions did not afford its mono-protonated form $[closo\text{-}B_9H_{10}]^-$. The reaction of the former *closo*-borate with CH_3COOH in dichloromethane yielded a monoanionic product $[B_2O(MeCO_2)_5]^-$. The treatment of $[closo\text{-}B_9H_9]^{2-}$ with HCl in dichloromethane afforded its *arachno*-derivative $[arachno\text{-}B_9H_{12}\text{-}4,8\text{-}Cl_2]^-$ in a high yield. The experimental solution and quantum-chemically calculated ^{11}B and ^1H NMR spectra of the latter monoanion were found to be in a good agreement; its structure in the solid state was studied by the single crystal X-ray diffraction experiment for the crystal $(PPh_4)[arachno\text{-}B_9H_{12}\text{-}4,8\text{-}Cl_2]\cdot0.04HCl$. The reaction of $[arachno\text{-}B_9H_{12}\text{-}4,8\text{-}Cl_2]^-$ with liquid ammonia caused its quantitative conversion into the parent $[closo\text{-}B_9H_9]^{2-}$.

Borates $[closo\text{-}B_nH_n]^{2-}$ ($n > 4$) are fundamental building blocks of the boron cluster chemistry (see for example[1–4]) and these borates with n = 6–12 were synthesized in 1959–1967.[5–9] $[closo\text{-}B_nH_n]^{2-}$ have three-dimensional aromaticity, while the organic aromatic compounds have two-dimensional aromaticity[10,11] (and literature cited therein). Among the $[closo\text{-}B_nH_n]^{2-}$ (n = 6–12), those with n = 7–9 are the least explored.

Borates with an *arachno* nine-vertex are described in literature since 1960.[12–16] The existence of the monoanion $[arachno\text{-}B_9H_{14}]^-$ has been postulated by Lipscomb,[1] while the first X-ray structural characterization in the form of its cesium(I) salt has been performed by Greenwood *et al.*;[4,5] two possible conformations of this monoanion (a and b) are shown in Scheme 1.

Its *i*-configuration appears to be a deviation from Williams theory. The Williams theory postulates that for the generation of the *arachno*-boranes or carboranes from the *nido*-clusters, a vertex with the highest connectivity should be removed.[18,19] The examples of the *n*-configuration of the monoanion $[arachno\text{-}B_9H_{14}]^-$ (in contrast to those of its *i*-configuration) are very rarely reported in literature. They include the dianion $[n\text{-}B_9H_{15}]^{2-}$ [11] as well as the organometallic and coordination compounds, such as $[\eta^6\text{-}(C_6Me_6)RuB_8H_{14}]$,[20] $[(dppe)Pt_2B_7H_{11}]$[21] and $[(PMe_2Ph)_2PtB_7H_{10}NHEt]$.[14] The structure with *i*-geometry, on the other hand, is obtained by removing a corner with a lower connectivity of $nido\text{-}B_{10}H_{14}$ (Scheme 1c). Such geometry has been however observed for numerous members of the borates, including the dianion $[i\text{-}B_9H_{15}]^{2-}$ [11] and a series of neutral coordination compounds $[arachno\text{-}B_9H_{13}L]$.[15] The borate $nido\text{-}B_{10}H_{14}$ has been also assigned to this geometry (see ref. 17 and references therein). The *n*-configuration has been observed[17] only for one of its halogen-containing derivative, *viz.*, $[arachno\text{-}B_9H_{12}\text{-}4,8\text{-}Br_2]^-$, which is a by-product of the synthesis of $anti\text{-}B_{18}H_{22}$ by the reaction of $[nido\text{-}B_9H_{12}]^-$ with $HgBr_2$ in dichloromethane.[17,22] In the present communication, we describe the products of the reactions of $[closo\text{-}B_9H_9]^{2-}$ with various acids and the reactivity of these products.



Scheme 1 Known nine-vertex conformations of the monoanion $arachno\text{-}B_9H_{14}^-$ (a and b) and that of $nido\text{-}B_{10}H_{14}$ (c).[17]

In the first stage of our investigation, we attempted to protonate $[closo\text{-}B_9H_9]^{2-}$ with acetic acid under anhydrous conditions. Dry acetic acid was added to the red-orange solution of $(PPh_4)_2[closo\text{-}B_9H_9]$ in dichloromethane and then, the reaction mixture was left under pentane atmosphere for 3 days. This reaction resulted in

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the complete destruction of a polyhedral boron cluster, thus affording the monoanion $[B_2O(MeCO_2)_5]^-$ as a major product, which crystallizes as $(PPh_4)[B_2O(MeCO_2)_5]$ in colorless crystals.[23] The heteroleptic products $[B_2O(MeCO_2)_5]^-$ and $B_2O(MeCO_2)_4$ were already detected spectroscopically few years ago.[24–27] It should be noted that the homoleptic compounds $[B(MeCO_2)_4]^-$ and $B(MeCO_2)_3$ were not described in literature till date.

We also studied the reaction of $(PPh_4)_2[closo\text{-}B_9H_9]$ with HCl in dichloromethane. Indeed, the bromine-containing compound $[arachno\text{-}B_9H_{12}\text{-}4,8\text{-}Br_2]^-$ has been prepared[6] using the reaction of the $[nido\text{-}B_9H_{12}]^-$ with $HgBr_2$. The treatment of $(PPh_4)_2[closo\text{-}B_9H_9]$ with purified gaseous HCl (the oxygen impurities were removed using three condensation–argon saturation cycles) in dichloromethane at −78 °C (the latter makes it possible to remove the remaining moisture impurities) under inert atmosphere afforded the chlorine-containing monoanion $[arachno\text{-}B_9H_{12}\text{-}4,8\text{-}Cl_2]^-$ as per the following eqn (1):

$$(PPh_4)_2[closo\text{-}B_9H_9] + 3HCl \rightarrow (PPh_4)[arachno\text{-}B_9H_{12}\text{-}4,8\text{-}Cl_2] + (PPh_4)Cl \qquad (1)$$

The calculated structure of this monoanion with a labeling scheme of its atoms is shown in Fig. 1.

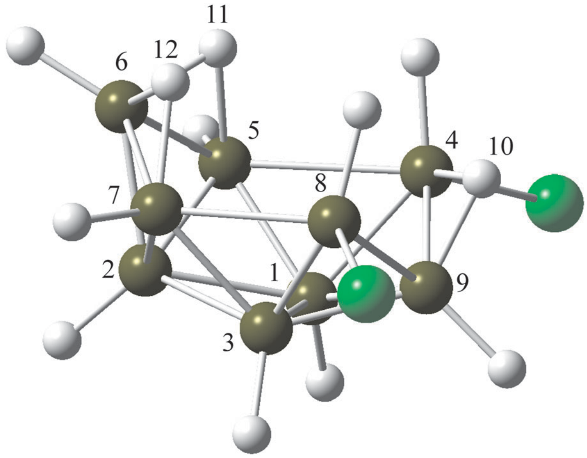

Fig. 1 Labeling scheme of the atoms in the anion $[arachno\text{-}B_9H_{12}\text{-}4,8\text{-}Cl_2]^-$ and its quantum-chemically calculated structure.

The initial red-orange solution of $(PPh_4)_2[closo\text{-}B_9H_9]$ in dichloromethane underwent an immediate decolouration after the addition of HCl. The resultant reaction mixture was carefully mixed with a five-fold volume of pentane and colorless crystals were formed after 3 days with high yield (83%).

The reaction of a suspension of $(PPh_4)[arachno\text{-}B_9H_{12}\text{-}4,8\text{-}Cl_2]$ with liquid ammonia at r.t.[19] resulted in the re-closing of this *arachno*-compound into the initial $[closo\text{-}B_9H_9]^{2-}$: after 10 min, the initially colorless reaction mixture turned yellow, following which NH_3 escaped from the mixture and the intensity of its color increased, thus indicating the formation of the *closo*-borate dianion according to eqn (2):

$$2(PPh_4)[arachno\text{-}B_9H_{12}\text{-}4,8\text{-}Cl_2] + 6NH_3 \rightarrow (PPh_4)_2[closo\text{-}B_9H_9] + (NH_4)_2[closo\text{-}B_9H_9] + 4NH_4Cl \qquad (2)$$

The yield of the orange solid product, based on its NMR spectra, was quantitative.

The initial *closo*-borate compound and the products of its transformations were characterized using multinuclear NMR spectroscopy and by the single crystal X-ray diffraction study as; their ^{11}B NMR spectra are shown in Fig. 2 and 3.

In the spectrum b of new compound $(PPh_4)[arachno\text{-}B_9H_{12}\text{-}4,8\text{-}Cl_2]$, the signals of its ^{11}B nuclei split in the integral ratio 2 : 1 : 2 : 2 : 1 : 1; the two chlorine-substituted boron atoms have a singlet character. An assignment of the above signals was made

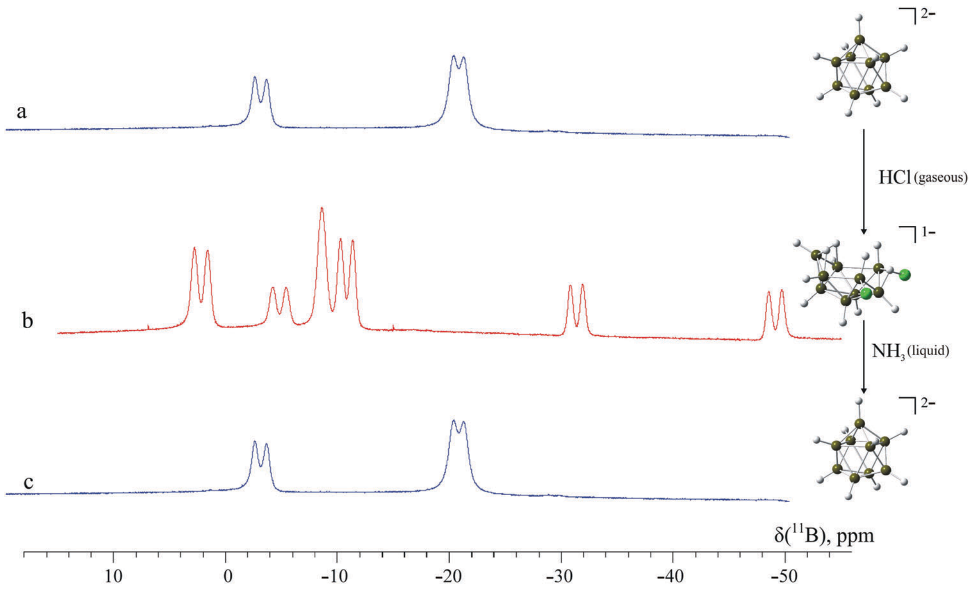

Fig. 2 ^{11}B NMR spectra of the CD_3CN solutions of the initial $[closo\text{-}B_9H_9]^{2-}$ (a), the chlorine-containing derivative $[arachno\text{-}B_9H_{12}\text{-}4,8\text{-}Cl_2]^-$ (b) and the product of its reaction with liquid ammonia (c).

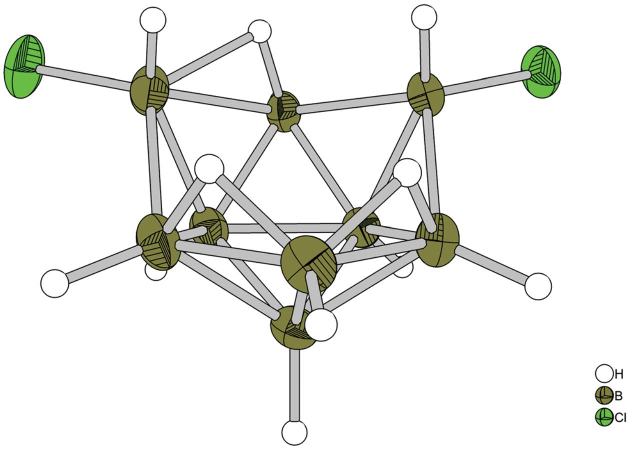

Fig. 3 General view of the monoanion $[arachno\text{-}B_9H_{12}\text{-}4,8\text{-}Cl_2]^-$ in the crystal $(PPh_4)[arachno\text{-}B_9H_{12}\text{-}4,8\text{-}Cl_2]$. Thermal ellipsoids are shown with 50% probability.

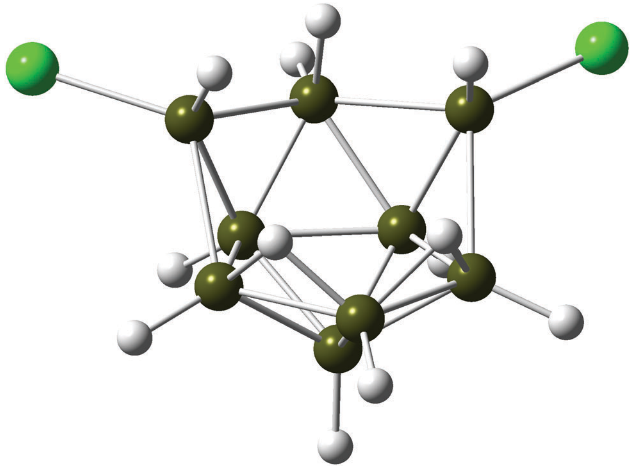

Fig. 4 Quantum-chemically calculated structure of the monoanion $[arachno\text{-}B_9H_{12}\text{-}4,8\text{-}Cl_2]^-$ having C_s symmetric arrangement.

Table 1 Experimental NMR data for the CD_3CN solution of the chlorine-containing monoanion $[arachno\text{-}B_9H_{12}\text{-}4,8\text{-}Cl_2]^-$ in CD_3CN and those quantum-chemically calculated using GIAO//B3LYP/6-311G[20]

Assignment	$\delta_{^{11}B}$ (ppm)	$^1J_{^{11}B-^1H}$ (Hz)	$\delta_{^1H}$ (ppm)
B5, B7	2.2 (−1.3)[ab]	149	3.05 (2.53)[bc]
B6	−4.9 (−14.5)	153	2.86 (2.14)
B4, B8	−8.6 (−10.0)[b]		−0.41 (1.13)[bc]
B1, B3	−10.9 (−17.3)[b]	142	2.04 (1.58) [b]
B9	−31.4 (−35.5)	145	0.82 (0.32)
B2	−49.1 (−56.3)	152	−0.41 (1.13)[c]
H10			(−2.35)
H11			(−3.20)
H12			(−4.22)

[a] In parentheses: the calculated NMR parameters; ^{11}B NMR data relative to $BF_3{\cdot}OEt_2$ with $\delta_{^{11}B} = 0$ ppm; $\delta_{^{11}B} = 101.63 - \sigma_{^{11}B}$; ^1H NMR data relative to Me_4Si with $\delta_{^1H} = 0$ ppm; $\delta_{^1H} = 31.97 - \sigma_{^1H}$. [b] The averaged calculated $\delta_{^{11}B}$. [c] The averaged calculated $\delta_{^1H}$ for the atoms H2, H4 and H8.

using the theoretically calculated ^{11}B NMR values, which are also collected in Table 1.

The bridging hydrogen atoms of $[arachno\text{-}B_9H_{12}\text{-}4,8\text{-}Cl_2]^-$ were not detected at room temperature using ^1H NMR method due to substantial broadening (due to the dynamic behavior)of the peaks. The same effect is also observed[6] in its bromine-containing analog $[arachno\text{-}B_9H_{12}\text{-}4,8\text{-}Br_2]^-$. The calculated values of $\delta_{^{11}B}$ for the boron-based framework of $[arachno\text{-}B_9H_{12}\text{-}4,8\text{-}Cl_2]^-$ were found to be in a good agreement with those experimentally observed (except that for the atom B_6).

The colorless single crystals of the salt $(PPh_4)[arachno\text{-}B_9H_{12}\text{-}4,8\text{-}Cl_2]$ were also characterized using the single crystal X-ray diffraction method;[21] the molecular structure of its *arachno*-anion is shown in Fig. 3.

This structure is very similar to that of the parent anion $[arachno\text{-}B_9H_{14}]^-$, having the same arrangement of both the backbone and the bridging protons. Two of the residual electron peaks observed in this spectrum were assigned to the HCl molecule with about 4% occupancy. In addition, peaks attributed to 3 μ-H and 2 *endo*-H could be found. The bridging proton H10 was evidenced to be deviated from the centrum of the corresponding boron–boron bond, while the same was not observed for the two other bridging protons. The bond distance B9–H10 (1.126 (12) Å) is smaller than that of B4–H10 (1.508 (13) Å). The quantum-chemical B3LYP/6-311G calculations[20] showed that such arrangement of the bridging hydrogen atoms in the crystal $(PPh_4)[arachno\text{-}B_9H_{12}\text{-}4,8\text{-}Cl_2]$ is energetically preferable by 5.83 kJ mol^{-1} as compared with its C_s-symmetric arrangement (Fig. 4).

Such calculated C_s-symmetric structure contains two μ-H and three *endo*-H atoms and it was not experimentally detected using the NMR method.

Thus, the dianion $[closo\text{-}B_9H_9]^{2-}$ was found to react with gaseous HCl in dichloromethane under anhydrous conditions, affording its halogen-containing derivative $[arachno\text{-}B_9H_{12}\text{-}4,8\text{-}Cl_2]^-$, which undergoes re-closing with NH_3 to form an initial *closo*-borate dianion.

Conflicts of interest

There are no conflicts to declare.

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