VIP **B–H Activation** *Very Important Paper*

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Bismuth Undecahydro-*closo*-dodecaborane: A Retainable Intermediate of B–H Bond Activation by Bismuth(III) Cations

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Abstract: *The $[B_{12}H_{12}]^{2-}$ anion shows an extensive substitutional chemistry based on its three-dimensional aromaticity. The replacement of functional groups can be attained by electrophilically induced substitution caused by Brønsted or Lewis acidic electrophiles (e.g. Pt^{2+}). Until now, it was impossible to structurally characterize a metal-substituted $[B_{12}H_{12}]^{2-}$ cage. When an aqueous solution containing both Bi^{3+} cations and $[B_{12}H_{12}]^{2-}$ anions was heated, the charge-neutral bismuth undecahydro-closo-dodecaborane $BiB_{12}H_{11}$ was obtained, representing a new class of metalated $[B_{12}H_{12}]^{2-}$ clusters. The title compound was characterized by single-crystal X-ray diffraction and NMR spectroscopic methods. Compared to the typical B–H bond, the short B–Bi single bond (230 pm) exhibits inverted polarity.*

Derivatives of benzene and other aromatic compounds, in which a hydrogen atom is replaced with a metal atom, have been known for many years.[1] Nevertheless, related compounds of the dodecahydro-*closo*-dodecaborate dianion $[B_{12}H_{12}]^{2-}$, which often behaves similar to benzene due to its three-dimensional aromaticity, are more or less unknown.[2] The only exception are reports about an entirely saturated product with mercury(II) cations, where all hydrogen atoms are replaced by mercury.[3] These results, however, should be viewed critically, since the compounds were only partially characterized by NMR spectroscopy. Furthermore the replacement of four or more hydrogen atoms, where at least two metal atoms are in *ortho*-position to each other, is difficult to achieve for geometric reasons.

In 1960 it was already realized that cations which are easy to polarize like Cu^+, Ag^+, and Hg^{2+} show interaction with the soft $[B_{12}H_{12}]^{2-}$ anion, thus forming poorly water-soluble salts.[4] In the case of the homologous $[B_{10}H_{10}]^{2-}$ anion, the copper(I) derivative $Cu_2[B_{10}H_{10}]$ displayed rather short Cu···H–B distances, and therefore a significant interaction between the hydrogen atoms and the copper cations was concluded.[5]

In the case of the thallium salt $Tl_2[B_{12}H_{12}]$, which crystallizes isotypically to the alkali-metal salts $A_2[B_{12}H_{12}]$ (A = K–Cs),[6] the bond between the Tl^+ cations and the negatively polarized hydrogen atoms was deduced to have significant covalent character based on the red shift of the thallium luminescence.[7] The crystal structures of other cations containing a $6s^2$ lone pair, for example, $[Pb(H_2O)_3][B_{12}H_{12}]\cdot 3H_2O$ and $[Bi_6O_4(OH)_4][B_{12}H_{12}]_3\cdot 10H_2O$, also display close contacts between the hydrogen atoms and metal cations.[8,9] If one assumes that the formation of these interactions (which can also be interpreted as the coordination of B–H bonds by metal cations) is the first step in B–H bond activation, these salts represent precursors for the synthesis of metalated boron clusters.[10]

Consistent with this hypothesis, we discovered that the thermal dehydration of the basic salt $[Bi_6O_4(OH)_4][B_{12}H_{12}]_3\cdot 10H_2O$ and the reaction of the free acid $(H_3O)_2[B_{12}H_{12}]$ with an equimolar amount of bismuth(III) oxide carbonate at about 40 °C lead to the neutral $BiB_{12}H_{11}$ (**1**) molecule (Figure 1), which can be isolated in the form of three different crystalline solvates (**1**·6 H_2O, **1**·3 H_2O, and **1**·4 CH_3OH). Each of these solvates displays a yellow color, whose intensity decreases with increasing degree of solvation.

Single-crystal X-ray structure determinations (see the Supporting Information) of all three compounds reveal slightly distorted boron icosahedra. The B–B distances are in the range of 177–180 pm and correspond to the distances within salt-like dodecahydro-*closo*-dodecaborates.[6] One boron atom of each B_{12} cluster is connected to the bismuth atom. The Bi–B distances (231 pm for the hydrates and 224 pm for the methanol solvate) are in good agreement with the only published Bi–B bond length (232 pm in a boryl-substituted dibismuthene[11]) as well as with the sum of the covalence radii (232 pm)[12] and thus can be interpreted as Bi–B single bonds.

Whereas the neutral molecule **1** manifests the same structure in all three structures, the bismuth atom is coordinated differently. In compound **1**·6 H_2O, the Bi^{3+} coordination sphere is built up by the covalently bound boron atom and five coplanar oxygen atoms of corresponding water molecules

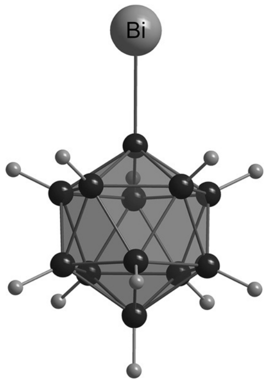

Figure 1. Structure of the neutral $BiB_{12}H_{11}$ molecule (**1**).

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with distances from 238 to 266 pm. The O–Bi–O angles are between 67 and 78°, so that a slightly distorted pentagon can be observed and the overall coordination is pentagonal bipyramidal (Figure 2 a). This coordination is also realized for compound $\mathbf{1}\cdot 3\,H_2O$ (Figure 2 b) and here two corners of the pentagon are occupied by hydridic hydrogen atoms of two adjacent $BiB_{12}H_{11}$ molecules. These molecules protrude out of the oxygen-built coordination plane by 27 pm. The Bi–O distances range between 251 (2 ×) and 258 pm and the Bi–H distances correspond to 228 pm (2 ×). Within the methanol solvate $\mathbf{1}\cdot 4\,CH_3OH$ the bismuth atom is coordinated by three oxygen atoms from methanol molecules with distances from 239 to 246 pm; the bismuth center additionally maintains contacts to three hydridic hydrogen atoms of the same neighboring $BiB_{12}H_{11}$ cluster (Figure 2 c). Two of these three hydrogen atoms with distances of 260 and 306 pm can be found roughly in the same plane as the oxygen atoms; thus, a pentagonal pyramid arises as resulting coordination polyhedron. The interaction to the third hydrogen atom with a distance of 317 pm is solely caused by the rigid structure of the icosahedral molecule (**1**).

The Bi–B distance obtained from X-ray structure determinations can be compared very well with the value of 234 pm calculated by optimization of the molecular structure of $B_{12}H_{11}(H_2O)_5$ ($\mathbf{1}\cdot 5\,H_2O$) using the B3LYP/def2-SVP standard.[13,14] The results of an NBO analysis indicate the existence of a localized Bi—B bond with considerable covalent bonding character as well as a bismuth-centered stereochemically active lone pair (Figure 3). The formation of the Bi—B bond can be explained by a mixture of ligand-orbital-induced interactions between Bi–s and Bi–p atomic orbitals and is a typical feature in many Bi^{III}-containing compounds.[17] This offers a facile explanation for the pentagonal-pyramidal coordination geometry, which is also established by theoretical calculations. The estimated NBO charges ($q(Bi) = 15.3$, $q(B) = -0.48$)) confirm that, as expected, the Bi—B bond shows an inverted polarity compared to the B—H bonds.

The ^{11}B and $^{1}H\{^{11}B\}$ NMR spectra of **1** show three distinguishable signals each, which can be clearly assigned by means of 2D ^{1}H, ^{11}B HMQC, ^{11}B and $^{1}H\{^{11}B\}$ COSY, and TOCSY spectra (see the Supporting Information). Furthermore the spectra always contain signals belonging to the $[B_{12}H_{12}]^{2-}$ and $[B_{12}H_{11}(OH)]^{2-}$ anions, which are known to be products of the thermal dehydration of the free acid $(H_3O)_2$-$[B_{12}H_{12}]$.[4] The ^{11}B NMR signal of the metal-bonded boron atom ($\delta^{11}B$: +72.1 ppm) of **1** has a significant low-field shift, whereas the signals of the equivalent *ortho*- and *meta*-positioned boron atoms ($\delta^{11}B$: −13.8 and −12.3 ppm) display values typical for *closo*-borates. The signal of the boron atom in *para*-position ($\delta^{11}B$: −13.9 ppm) shows overlaps with the signals of the *ortho*-disposed boron atoms and thus can only be identified by 2D NMR techniques. This potent deshielding of the bismuth-bonded boron atom in **1** differs from the situation in mercurated carboranes, in which the metalation induces only very weak increases in the chemical shift.[10] Similar low-field shifts are known in literature for boryl- and borylene-metal complexes.[18,19] First indications that the deshielding of the bismuth-bonded boron atom of **1** is caused by relativistic effects are currently under investigation.

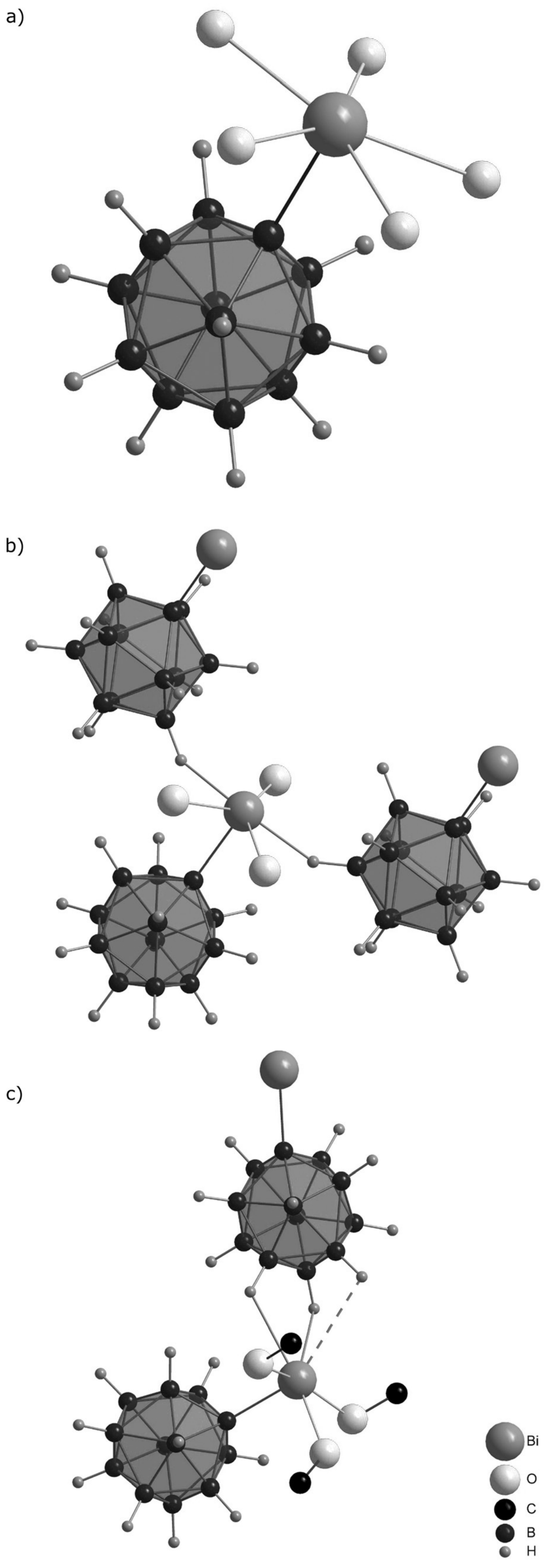

Figure 2. Coordination spheres of the bismuth atom in $\mathbf{1}\cdot 6\,H_2O$ (a), $\mathbf{1}\cdot 3\,H_2O$ (b), and $\mathbf{1}\cdot 4\,CH_3OH$ (c).

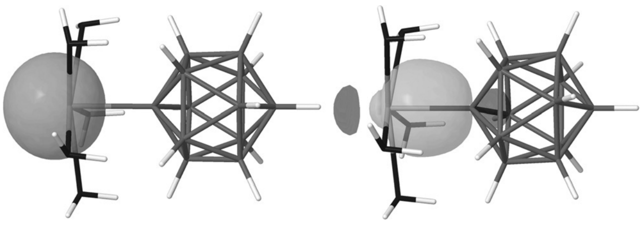

Figure 3. Visualization of the B3LYP/def2-SVP-calculated NBOs for the lone pair on Bi (left) and the Bi–B bond (43 % Bi, 57 % B, right) in $B_{12}H_{11}Bi(H_2O)_5$ (**1**·5 H_2O).[11,12]

The formation of the bismuth undecahydro-*closo*-dodecaborate $BiB_{12}H_{11}$ (**1**) reveals analogies to the C–H bond activation with heavy (and soft) metal ions like Hg^{2+} and Pt^{2+}.[20] The fact that the polarity of the Bi–B bond is inversed relative to the H–B bond introduces completely new synthetic routes to substituted *closo*-dodecaborates. In addition to the higher reactivity of the Bi–B bond, **1** compensates for the negative charge of *closo*-borates by its electronic neutrality, and in this way a general substitution should be even easier to perform.

Experimental Section

$BiB_{12}H_{11}\cdot n\,H_2O$ ($n = 3$ and 6): The dehydration of a mixture containing bismuth(III) cations from bismuth oxide carbonate $Bi_2O_2(CO_3)$ (255 mg, 0.5 mmol) and a solution of the free acid $(H_3O)_2[B_{12}H_{12}]$ of the corresponding dodecahydro-*closo*-dodecaborate (180 mg, 1 mmol) in 25 mL of water at 40 °C led to the two hydrates of **1**. The obtained yellow solid was subsequently dissolved in water and recovered by filtration as the hexahydrate in the form of pale yellow, needle-like crystals through isothermal evaporation at room temperature. These crystals weather upon further contact with dry air to provide lath-shaped crystals of the trihydrate.

$BiB_{12}H_{11}\cdot 4\,CH_3OH$: The methanol derivative was obtained by drying **1**·3 H_2O (300 mg, 0.74 mmol) at 40 °C under argon atmosphere, then dissolving the resulting brownish orange solid in 5 mL of absolute methanol and evaporating the excess solvent in a stream of dry argon at room temperature. The compound thereby precipitates in the form of pale yellow crystals.

Keywords: B–H activation · bismuth · boranes · borates · umpolung

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