Angewandte
International Edition Chemie

**Diborane(6)**

International Edition: DOI: 10.1002/anie.201504579
German Edition: DOI: 10.1002/ange.201504579

# The Hexacyanodiborane(6) Dianion $[B_2(CN)_6]^{2-}$

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*Dedicated to Professor Manfred Scheer on the occasion of his 60th birthday*

***Abstract:*** *Diborane(6) dianions with substituents that are bonded to boron via carbon are very reactive and therefore only a few examples are known. Diborane(6) derivatives are the simplest catenated boron compounds with an electron-precise B–B σ-bond that are of fundamental interest and of relevance for material applications. The homoleptic hexacyanodiborane(6) dianion $[B_2(CN)_6]^{2-}$ that is chemically very robust is reported. The dianion is air-stable and resistant against boiling water and anhydrous hydrogen fluoride. Its salts are thermally highly stable, for example, decomposition of $(H_3O)_2[B_2(CN)_6]$ starts at 200°C. The $[B_2(CN)_6]^{2-}$ dianion is readily accessible starting from 1) $B(CN)_3^{2-}$ and an oxidant, 2) $[BF(CN)_3]^-$ and a reductant, or 3) by the reaction of $B(CN)_3^{2-}$ with $[BHal(CN)_3]^-$ (Hal = F, Br). The latter reaction was found to proceed via a triply negatively charged transition state according to an $S_N2$ mechanism.*

Electron-precise boron compounds with a boron–boron single, double, or triple bond and related oligomers or polymers that for example contain {B−B} units are of growing interest because of their unusual properties, which make them attractive building blocks for a variety of different applications.[1] Salts of the dianion $[B_2H_6]^{2-}$, which is the simplest species with a B−B σ-bond, were described as early as 1935[2] but later they were found to be mixtures of $[BH_4]^-$ and $[B_3H_8]^-$ salts.[3] In contrast to $[B_2H_6]^{2-}$, salts of a few related diborane(6) dianions were isolated,[4] for example, $[B_2(NCS)_6]^{2-}$.[5] Only five of these derivatives have solely hydrogen substituents and groups that are bonded via carbon to boron (Scheme 1). Among these, molecule **I**[4d] is the only air-stable compound, which may be rationalized by 1) compensation of the negative charge and 2) steric protection of the B−B bond. The B−B core of the dianions $\mathbf{IIa}^{2-}$,[4e] $\mathbf{IIb}^{2-}$,[4f] and $\mathbf{III}^{2-}$ [4g] is sterically shielded as well. Dianion $\mathbf{IV}^{2-}$ [4h] that is obtained by stepwise reduction of the respective bisborane via radical anion $\mathbf{IV}^{\cdot-}$ is stabilized by the bridging substituent of the B−B fragment. So far, only $\mathbf{IV}^{\cdot-}$ [4h] and $\mathbf{V}^{\cdot-}$ [6] (Scheme 1) were structurally characterized, while other similar radical anions have only been observed by spectroscopic or electrochemical methods.[7]

Cyano groups that are bonded to boron often result in an enhanced stability compared to related boron compounds. Thus, the homoleptic cyanoborate anion $[B(CN)_4]^-$ (**2**, Scheme 2)[8] is chemically more robust than $[BH_3(CN)]^-$, and salts with reactive cations such as $H^+$, $H_3O^+$,[9] and $Ph_3C^+$ [10] are accessible. The tricyanoborate dianion $B(CN)_3^{2-}$ (**3**), which is the only dianionic nucleophilic boron species known, is another example for a homoleptic cyanoboron derivative that exhibits an unprecedented stability.[11] In addition to the well-defined anions **2** and **3**, a few further homoleptic cyano boron species are known. The Lewis acid $B(CN)_3$ is a polymer $\{B(CN)_3\}_n$[8b] and the radical species $B(CN)_2^{\cdot}$ and $B(CN)_3^{\cdot-}$ were generated from $[B(CN)_4]^-$ and studied by ESR spectroscopy.[12] A number of heteroleptic B−CN derivatives have been fully characterized, for example, simple borate anions as $[(CF_3)_3B(CN)]^-$ [13] and the diborene $B_2(CAAC)_2(CN)_2$ (CAAC = 1-(2,6-diisopropylphenyl)-3,3,5,5-tetramethylpyrrolidin-2-ylidene).[14]

In the course of our studies on the chemistry of the dianion $B(CN)_3^{2-}$ (**3**), we observed the formation of the new homoleptic cyanoborate dianion $[B_2(CN)_6]^{2-}$ (**1**). Salts of dianion **1** were obtained in good to excellent yields using different synthetic strategies (Scheme 3).[15] Oxidation of dianion **3** in THF with chlorine, bromine, iodine, or thallium(I) chloride resulted in the formation of $[B_2(CN)_6]^{2-}$ (**1**), which was isolated as tetrabutylammonium or potassium salt in yields of 44–96%. Reaction of $K[BF(CN)_3]$[16] with *t*BuLi or $KC_8$ as reductant in THF gave $[n\mathrm{Bu}_4\mathrm{N}]_2\mathbf{1}$ and $[\mathrm{Ph}_4\mathrm{P}]_2\mathbf{1}$ in 42% and 66% yield, respectively. Reactions of $[BHal(CN)_3]^-$ salts (Hal = F, Br) with alkali metal salts of dianion **3** in THF provide a further entry to hexacyanodiborates with yields of 68–89% (Scheme 3; Supporting Information, Figure S1).

Theoretical studies show that **1** is formed from $B(CN)_3^{2-}$ (**3**) and $[BF(CN)_3]^-$ via a concerted nucleophilic substitution reaction (Figure 1). The calculated free activation energy $\Delta G^{\neq}$ amounts to only 185.2 and 127.2 kJ mol$^{-1}$ with solvent corrections for THF and $\varepsilon_r = 78.4$ ($\varepsilon_r$ of $H_2O$), respectively (B3LYP(CPCM)). Most likely, in solution the highly charged transition state is stabilized not only by the solvent but also by the countercations. Owing to the very low solubility of alkali

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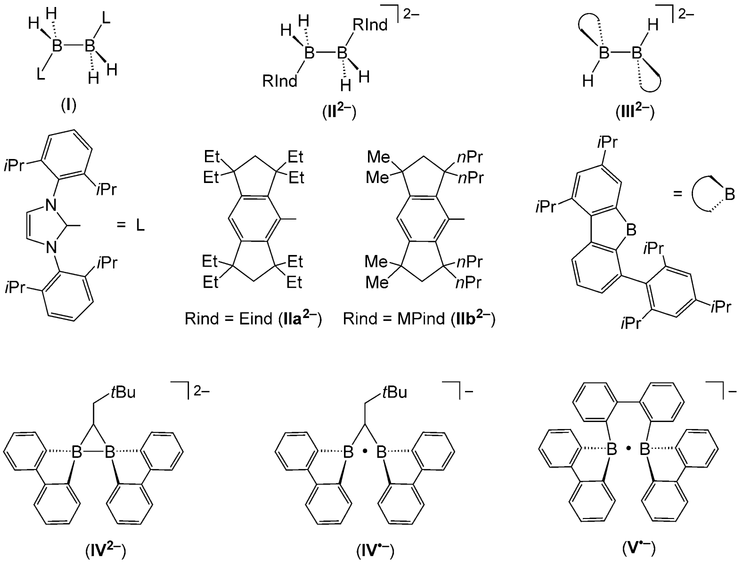
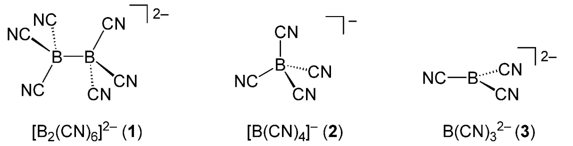
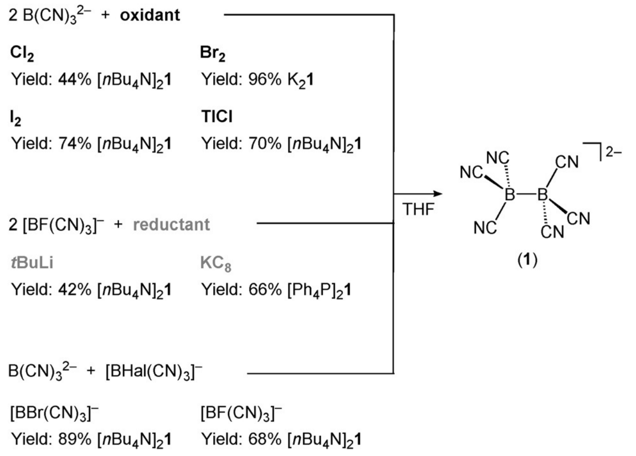
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201504579.



*Scheme 1.* Structurally characterized diborane(6) derivatives with hydrogen substituents or groups bonded via carbon to boron.



*Scheme 2.* Homoleptic cyanoborate anions that have been fully characterized.



*Scheme 3.* Syntheses of salts of the dianion $[B_2(CN)_6]^{2-}$ (**1**).

metal salts of **3** in THF at room temperature and at elevated temperatures, which is below the detection limit of NMR spectroscopy, a kinetic study that could provide experimental proof for an $S_N2$ mechanism is not possible. Therefore, a detailed study with $^{11}B$ and $^{10}B$ isotopically labeled compounds was conducted. The reaction of $K_2{}^{11}B(CN)_3$ with $K[^{10}BF(CN)_3]$ yielded solely the isotopologue $[^{10}B^{11}B(CN)_6]^{2-}$ as evident from the spectroscopic data, which supports the predicted $S_N2$ mechanism. Alternatively, a two-step reaction with initial formation of $B(CN)_3^{\bullet -}$ from **3** and $[BF(CN)_3]^-$ followed by combination of two radical anions to give **1** might be considered. However, this radical mechanism should result in all possible isotopologues, including $[^{10}B_2(CN)_6]^{2-}$ and $[^{11}B_2(CN)_6]^{2-}$, which is not the case. Another alternative is an $S_N1$ mechanism that requires dissociation of $[BF(CN)_3]^-$ into $B(CN)_3$ and $F^-$. According to theoretical data, $B(CN)_3$ is a very strong Lewis acid[16d,17] that is experimentally only known as polymeric $\{B(CN)_3\}_n$.[8b] In agreement with the theoretically predicted strong B–F bond, $[BF(CN)_3]^-$ was found to be chemically very stable and its salts are thermally very robust.[16a,d] Thus, an $S_N1$ mechanism is also unlikely.

To the best of our knowledge, the reaction of $B(CN)_3^{2-}$ (**3**) with $[BF(CN)_3]^-$ to give **1** is the first example for the formation of a diborane(6) derivative via an $S_N2$ reaction. The reaction of **3** with $[BBr(CN)_3]^-$ probably also proceeds via an $S_N2$ mechanism. Furthermore, at least some if not all other syntheses of **1** shown in Scheme 3 can be rationalized by an $S_N2$ reaction. Syntheses employing salts of **3** and an halogen containing oxidant may in the first step yield $[BHal(CN)_3]^-$, which subsequently reacts with dianion **3** to give **1**. Reactions of $K[BF(CN)_3]$ with a reducing agent can be explained by the initial formation of dianion **3** followed by a nucleophilic substitution reaction with $[BF(CN)_3]^-$.

$K_2[B_2(CN)_6]$ ($K_2$**1**) undergoes an irreversible oxidation ($E_{pa}$) at 1.21 V in $CH_3CN$ and 0.92 V in THF (versus Fc/Fc$^+$; scan rate: 15 mV s$^{-1}$), respectively (Figure S8). The experimental redox potential is well reproduced by DFT and MP2 calculations (Table S9). Dianion **1** is unprecedentedly resistant against oxidation compared to other dianionic diborane(6) derivatives, for example, $\mathbf{IV}^{2-}$ (Scheme 1) is oxidized at

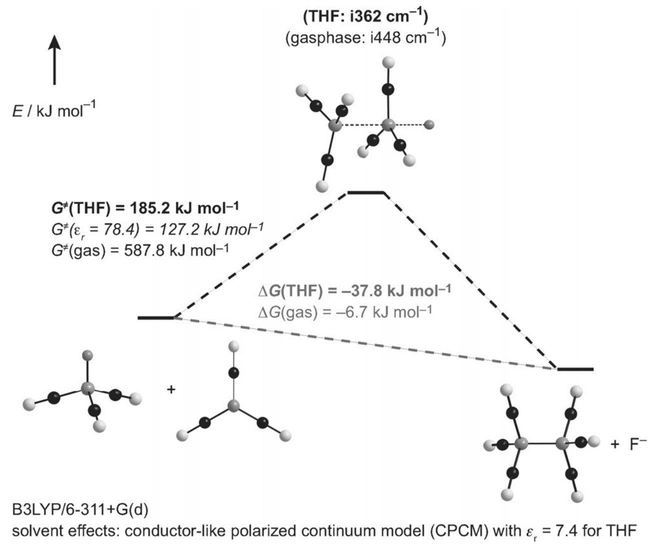
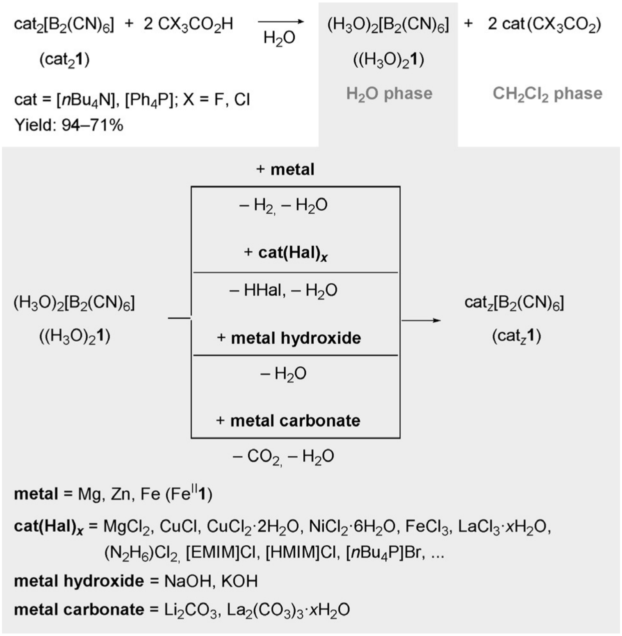


*Figure 1.* Calculated transition state for the $S_N2$ reaction of $B(CN)_3^{2-}$ (**3**) with $[BF(CN)_3]^-$ to give **1**.

$E_{1/2} = -1.76$ V to yield $\mathbf{IV}^{\bullet-}$.[4h] Removal of one electron from the HOMO of **1** should result in the radical monoanion $[B_2(CN)_6]^{\bullet-}$. The calculated B–B bond length of $[B_2(CN)_6]^{\bullet-}$ (2.259 Å) is similar to the experimental B–B distance of $\mathbf{IV}^{\bullet-}$ (2.166(4) Å) but much longer than the calculated B–B distance of **1** (1.806 Å). Since $\mathbf{IV}^{\bullet-}$ is only stable because of the bridging unit between the two boron atoms, the irreversibility of the oxidation of **1** is expected.

Salts of dianion **1** are stable in air for more than one year. No decomposition of **1** was observed by $^{11}$B NMR spectroscopy after stirring for one day in boiling water under air or anhydrous hydrogen fluoride at room temperature. This robustness is in sharp contrast to the properties of the related dianionic diborane(6) derivatives $\mathbf{II}^{2-}$–$\mathbf{IV}^{2-}$ that are air-sensitive (Scheme 1).[4e–h] The high chemical stability of **1** allowed the preparation of a wealth of salts with different organic and inorganic cations. Dianion **1** is most conveniently isolated as $[n\text{Bu}_4\text{N}]^+$ or $[\text{Ph}_4\text{P}]^+$ salt (Scheme 3). $[n\text{Bu}_4\text{N}]_2\mathbf{1}$ and $[\text{Ph}_4\text{P}]_2\mathbf{1}$ are readily transformed into $(H_3O)_2\mathbf{1}$ (Scheme 4). The unprecedented stability of salts of dianion **1** is exemplified by $(H_3O)_2\mathbf{1}$ that is stable up to 200 °C in the solid state and that is a strong two-protic acid in water. $(H_3O)_2\mathbf{1}$ serves as starting material for the preparation of many different salts of **1** in water that exhibit high thermal stabilities in general (Scheme 4). Crystals of selected salts of the $[B_2(CN)_6]^{2-}$ dianion (**1**) were studied by X-ray diffraction (Table S1). Representative structures of salts with different types of cations are depicted in Figure 2. In all of the crystals studied, dianion **1** exhibits almost $D_{3d}$ symmetry. The experimental B–B distance in **1** ($[Cu(dmso)_6]\mathbf{1}$: 1.782(4) Å; $(N_2H_6)\mathbf{1}$: 1.7840(4) Å) is well reproduced by theoretical methods (Table 1; Table S11). The B–B bonds of all diborane(6) derivatives shown in Scheme 1 are significantly longer (**I** 1.828(4) Å,[4d] $\mathbf{IIa}^{2-}$ 1.924(3) Å,[4e] $\mathbf{IIb}^{2-}$ 1.905(3) Å,[4f] $\mathbf{III}^{2-}$ 1.83(2) Å,[4g] $\mathbf{IV}^{2-}$ 1.906(3) Å[4h]). So, the short B–B distance in **1** is indicative for a strong B–B bond that compares well to the chemical robustness of dianion **1** and the high thermal stabilities of its salts.



***Scheme 4.*** $(H_3O)_2[B_2(CN)_6]$ ($(H_3O)_2\mathbf{1}$), an easy accessible and versatile starting material for the preparation of salts of dianion **1**. EMIM = 1-ethyl-3-methylimidazolium, HMIM = 1-hexyl-3-methylimidazolium.

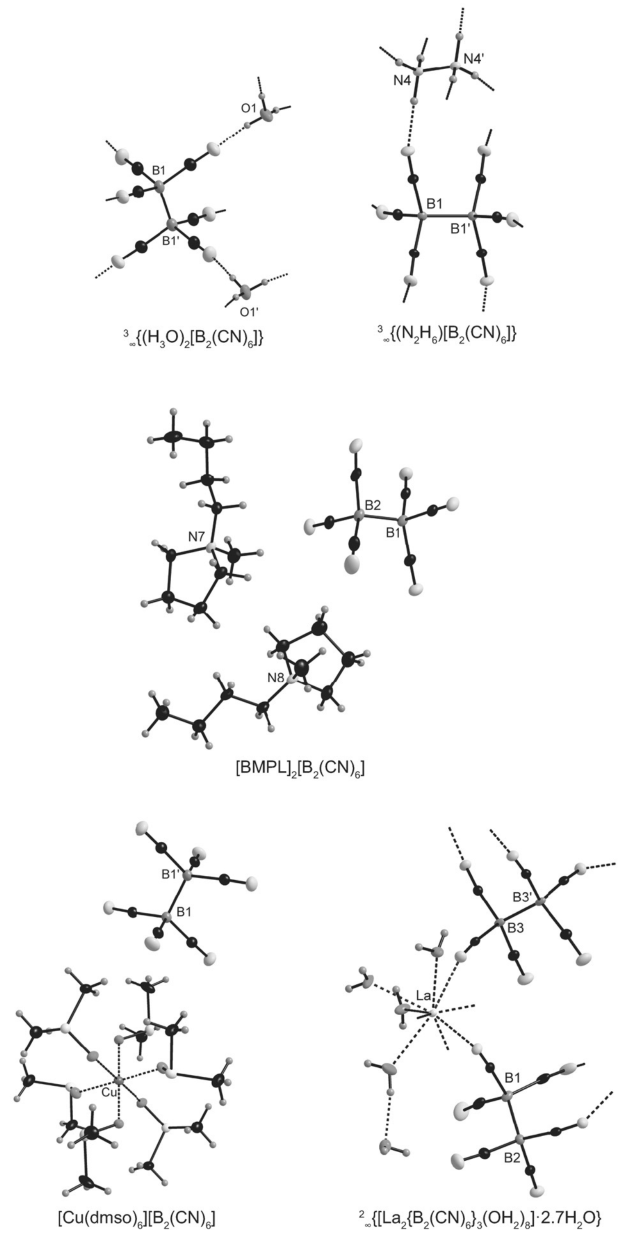


***Figure 2.*** Selected crystal structures of salts of dianion **1**. Elllipsoids are set at 50% probability for ${}^3_\infty\{(N_2H_6)\mathbf{1}\}$, $[Cu(dmso)_6]\mathbf{1}$, ${}^2_\infty\{[La_2\mathbf{1}_3(OH_2)_8]\cdot 2.7\,H_2O\}$, at 35% probability for $[BMPL]_2\mathbf{1}$, and at 25% probability for ${}^3_\infty\{(H_3O)_2\mathbf{1}\}$. BMPL = 1-butyl-1-methylpyrrolidinium.

Experimental and calculated $d$(CN) and $d$(BC) of $[B_2(CN)_6]^{2-}$ (**1**) and $[B(CN)_4]^-$ (**2**) are very close (Table 1) with $d$(CN) being marginally longer and $d$(BC) being slightly shorter in **1**. In contrast, the B–C and C–N bonds in $B(CN)_3^{2-}$ (**3**) are significantly shorter and longer, respectively. The differences between $d$(CN) and $d$(BC) in **2** and **3** were rationalized by partial delocalization of the negative charge

***Table 1:*** Selected properties of homoleptic cyanoborate anions.[a]

| Property | $[B_2(CN)_6]^{2-}$ (**1**) $(N_2H_6)$**1**[b] | B3LYP[c] | $[B(CN)_4]^-$ (**2**) K**2**[d] | B3LYP[c] | $B(CN)_3{}^{2-}$ (**3**) $K_2$**3**[d] | B3LYP[c] |
|---|---|---|---|---|---|---|
| Symmetry | $C_i$ | $D_{3d}$ | $S_4$ | $T_d$ | $C_{2v}$ | $D_{3h}$ |
| $d$(B-B) | 1.7840(4) | 1.820 | – | – | – | – |
| $d$(B-C) | 1.5795(4) | 1.592 | 1.595(1) | 1.596 | 1.512(2) | 1.526 |
| $d$(C-N) | 1.1533(11) | 1.159 | 1.142(1) | 1.156 | 1.166(2) | 1.181 |
| ∡(B-B-C) | 108.33(2) | 110.5 | – | – | – | – |
| ∡(C-B-C) | 110.60(2) | 108.3 | 109.5(1) | 109.5 | 120.0 | 120.0 |
| ∡(B-C-N) | 175.96(5) | 179.8 | 178.7(1) | 180.0 | 178.4 | 180.0 |
| $\tilde{\nu}$(CN)[e] | 2212 | 2275 | 2233 | 2315 | 2048 | 2079 |
| $\tilde{\nu}$(BB) | 877[f] | 836[f] | – | – | – | – |
| $\delta(^{11}B)$ | −35.9 | −39.2 | −38.6 | −42.4 | −45.3 | −61.0 |
| $\sigma(^{11}B)$[g] | 25 |  | 0.07 |  | 13 |  |
| $\delta(^{13}C)$ | 131.5 | 137.2 | 127.9 | 127.4 | 158.5 | 168.5 |
| $^1J(^{11}B,^{11}B)$ | 33.2[h] | 35.1 | – | – | – | – |
| $^1J(^{13}C,^{11}B)$ | 63.2[h] | 69.8 | 71.3 | 73.8 | 94 | 103.6 |
| $^2J(^{13}C,^{11}B)$ | −3.5[h] | −3.6 | – | – | – | – |

[a] $d$ in Å; ∡ in°, $\tilde{\nu}$ in cm$^{-1}$; $\delta$ and $\sigma$ in ppm; $^nJ$ in Hz. [b] IR and Raman: $K^+$; NMR: $[nBu_4N]^+$ in $CD_3CN$. [c] B3LYP/6-311+G(d); NMR: B3LYP/6-311+G(3df) using geometries calculated at the B3LYP/6-311+G(d) level of theory. [d] K**2** in $CD_3CN$, 25 °C;[8a] $K_2$**3** in $ND_3$, −40 °C.[11a] [e] Mean value. [f] $\nu$(BB) mixed with $\nu$(BC) at 398 ($\tilde{\nu}_{exptl}$) and 368 cm$^{-1}$ ($\tilde{\nu}_{calcd}$). [g] Line width. [h] Coupling constants derived from simulated $^{13}C$ NMR spectrum (ABX pattern, Figure 3) of $[^{11}B_2(^{13}CN)(CN)_5]^{2-}$ with a line width of $\sigma(^{13}C) = 32.5$ Hz.

through the π-framework of the trigonal-planar dianion **3**, whereas B−C π-bond contributions in the tetracyanoborate anion are negligible.[11a] Thus, presumably B−C π-bond contributions are small in **1** as well.

Salts of $[B_2(CN)_6]^{2-}$ (**1**) were studied by (−)-ESI and (−)-MALDI mass spectrometry. Neither the signal of dianion **1** nor of the radical monoanion $[B_2(CN)_6]^{\bullet-}$ was observed but the radical anion $B(CN)_3{}^{\bullet-}$ was detected. These findings are in agreement to calculations at the CCSD(T)/aug-cc-pvtz level of theory that predict **1** to be unstable in the gas phase with respect to homolysis ($\Delta G = +54.4$ kJ mol$^{-1}$). In contrast to the gas phase, homolysis of **1** in solution to give $B(CN)_3{}^{\bullet-}$ does not occur (EPR spectroscopy). (−)-ESI mass spectra taken on solutions of $[nBu_4N]_2$**1** and the respective $^{11}B$ and $^{10}B$ enriched salts show the

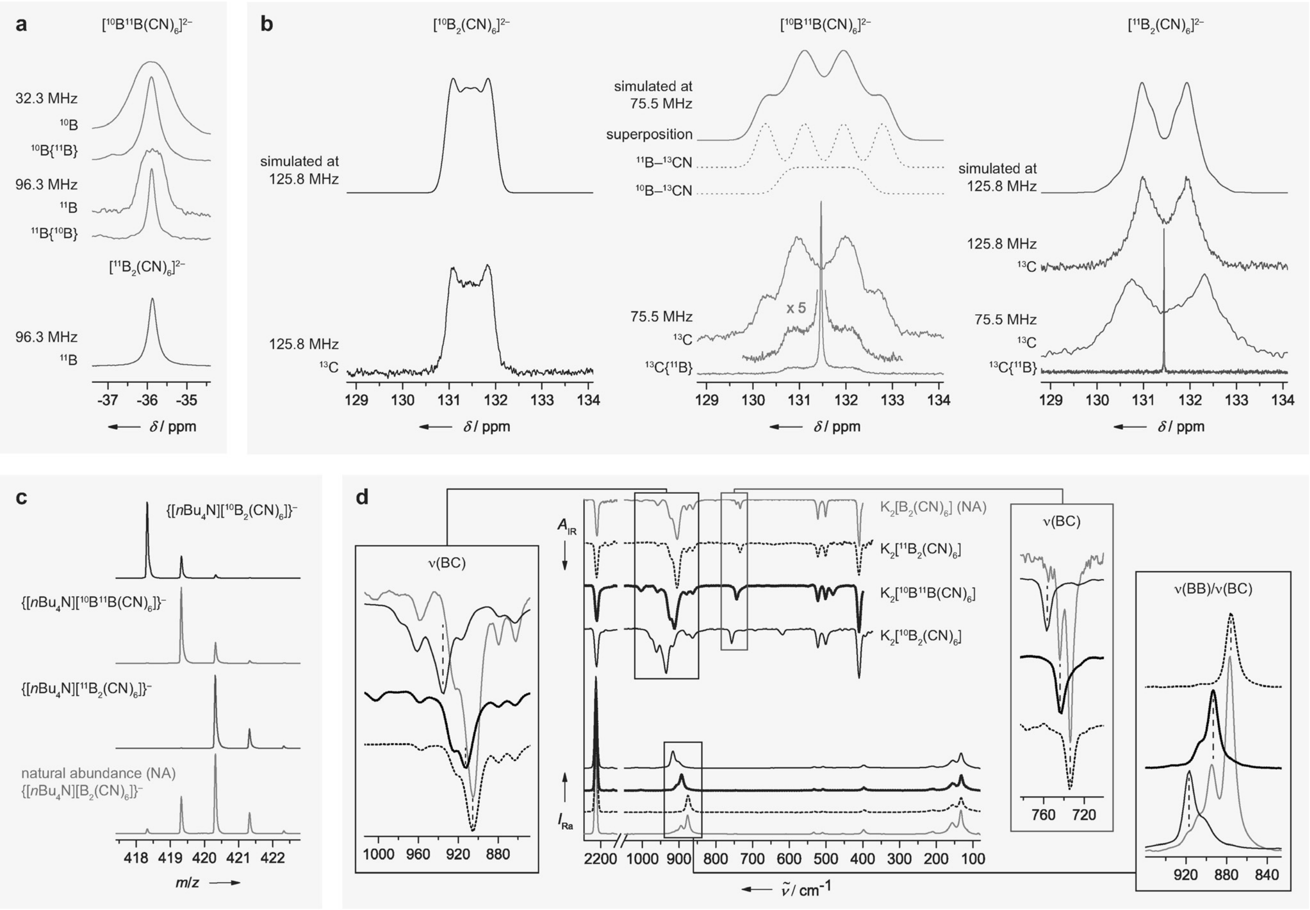


***Figure 3.*** a) $^{11}B$ and $^{10}B$ and b) $^{13}C$ NMR spectra of isotopically enriched **1**, c) (−)-ESI mass spectra of the ion pair $\{[nBu_4N]\mathbf{1}\}^-$, and d) IR and Raman spectra of $K_2$**1**.

signal of the ion pair $\{[n\text{Bu}_4\text{N}]\mathbf{1}\}^-$ with the expected isotopic distribution (Figure 3c).

The $^{11}$B NMR signal of $[^{11}\text{B}_2(\text{CN})_6]^{2-}$ at −35.9 ppm is a broad singlet. The signal of the mixed isotopologue $[^{10}\text{B}^{11}\text{B}(\text{CN})_6]^{2-}$ is broader because of the $^1J(^{11}\text{B},^{10}\text{B})$ of about 11 Hz (Figure 3a). The $^{13}$C NMR signal of $[^{11}\text{B}_2(\text{CN})_6]^{2-}$ at 131.5 ppm shows an ABX coupling pattern that is transformed into a sharp singlet upon $^{11}$B decoupling (Figure 3b). Spectra simulation gave coupling constants of $^1J(^{13}\text{C},^{11}\text{B}) = 63.2\ \text{Hz}$, $^2J(^{13}\text{C},^{11}\text{B}) = -3.5\ \text{Hz}$, and $^1J(^{11}\text{B},^{11}\text{B}) = 33.2\ \text{Hz}$ that are in excellent agreement to values derived from DFT calculations (Table 1). The $^{13}$C NMR spectrum of $[^{10}\text{B}^{11}\text{B}(\text{CN})_6]^{2-}$ in Figure 3b is a superposition of the spectra of $[(\text{N}^{12}\text{C})_2(\text{N}^{13}\text{C})^{10}\text{B}{-}^{11}\text{B}(^{12}\text{CN})_3]^{2-}$ and $[(\text{N}^{12}\text{C})_3{}^{10}\text{B}{-}^{11}\text{B}(^{13}\text{CN})(^{12}\text{CN})_2]^{2-}$. Therefore, the $^{13}\text{C}\{^{11}\text{B}\}$ NMR signal of $[(\text{N}^{12}\text{C})_3{}^{10}\text{B}{-}^{11}\text{B}(^{13}\text{CN})(^{12}\text{CN})_2]^{2-}$ is a sharp singlet, whereas for $[(\text{N}^{12}\text{C})_2(\text{N}^{13}\text{C})^{10}\text{B}{-}^{11}\text{B}(^{12}\text{CN})_3]^{2-}$ a plateau-like signal is found.

The IR and Raman spectra of the potassium salts of $^{10}$B and $^{11}$B labeled and non-labeled **1** are shown in Figure 3d. The assignment of the bands observed is based on a comparison to calculated displacement vectors, $^{10}\text{B}/^{11}\text{B}$ isotopic shifts, and the selection rule (Table S2). The $D_{3d}$ symmetry of **1** in crystalline $\text{K}_2$**1** is confirmed by the vibrational data. The four $\nu$(CN) vibrations overlap at 2213 $\text{cm}^{-1}$ because vibrational coupling between the cyano groups is very weak, similar to $\text{K}[\text{B}(\text{CN})_4]$ (K**2**)[8a] and in contrast to $\text{K}_2\text{B}(\text{CN})_3$ ($\text{K}_2$**3**).[11a] The average $\tilde{\nu}$(CN) of $\text{K}_2$**1** is slightly smaller than of K**2** but much larger than of $\text{K}_2$**3** (Table 1). Thus, the CN bonds in **1** are a little weaker than in **2** and stronger than in **3**. The bands in the region 1000–730 $\text{cm}^{-1}$ are attributed to BB and BC stretching modes, with the band at 877 $\text{cm}^{-1}$ having the strongest contribution of $\nu$(BB). As expected, these skeleton vibrations show large $^{10}\text{B}/^{11}\text{B}$ isotopic shifts (Figure 3d).

In summary, the hexacyanodiborate dianion $[\text{B}_2(\text{CN})_6]^{2-}$ (**1**) is an easily accessible dianionic diborane(6) derivative with an unprecedented chemical and electrochemical stability and its salts are thermally highly stable. These properties distinguish **1** from related diborane(6) dianions and make it an attractive building block for material science and applications. The formation of dianion **1** by an $\text{S}_\text{N}2$ reaction and a transition state in which a dianion ($\text{B}(\text{CN})_3{}^{2-}$, **3**) reacts with a monoanion ($[\text{BHal}(\text{CN})_3]^-$ (Hal = F, Br)) that results in accumulation of a triply negative charge is highly unusual and unknown for the synthesis of catenated boron compounds.

## Acknowledgements

Financial support by Merck KGaA and the Deutsche Forschungsgemeinschaft (FI 1628/4-1) is gratefully acknowledged.

**Keywords:** borates · boron · cyanoborates · diborane(6)

**How to cite:** *Angew. Chem. Int. Ed.* **2015**, *54*, 11259–11264
*Angew. Chem.* **2015**, *127*, 11411–11416

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Received: May 20, 2015
Revised: June 19, 2015