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Cyanoborates

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“Umpolung” at Boron by Reduction of $[B(CN)_4]^-$ and Formation of the Dianion $[B(CN)_3]^{2-}$**

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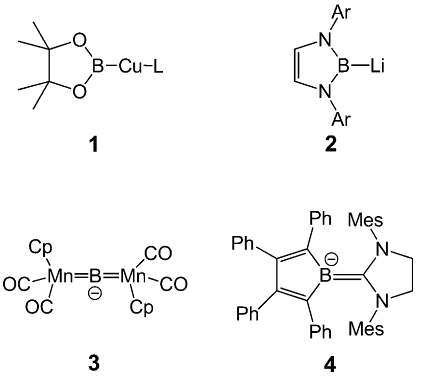
Dedicated to Professor Reint Eujen on the occasion of his 65th birthday

Species containing nucleophilic boron, which, for example, convert protons into hydridic hydrogen atoms in B–H bonds, are well-investigated. For instance, nucleophilic boron in metal borides (e.g., MgB_2[1]) and clusters (e.g., $[B_{11}H_{13}]^{2-}$ [2]) are common, but in the remaining boron chemistry they are more scarce.[3,4] In 1924, Krause reported the first compound containing a nucleophilic boron atom.[5,6] In the reaction of sodium with triphenylboron in diethyl ether, formation of “$NaBPh_3$” was postulated. Later this reaction was elucidated,[7] and “$NaBPh_3$” was identified as a mixture of dimers (e.g. $Na_2[Ph_3B{-}C_6H_5{=}BPh_2]$, $Na_2[Ph_3B{-}C_6H_4{-}BHPh_2]$, Scheme S1). In the reaction of sodium with triphenylboron $[BPh_3]^{-}$ [8] was indeed detected as intermediate and it was found that the radical anions $[BAr_3]^-$ are generally unstable.[8,9] Only the radical anion with mesityl ligands at boron can be isolated, because its dimerization is kinetically hindered.[10,11] The blue $[Li([12]crown\text{-}4)_2][BMes_3]$ is stable up to 230 °C, and its structure was determined by single crystal X-ray diffraction.[10] The dianions $[B(C_{10}H_7)_3]^{2-}$ [12,13] and $[BMes_3]^{2-}$ [14] are scarcely characterized, and their existence is doubtful.[7] Moreover, the claimed syntheses of $[Ph_2B]^-$,[15] $[Bu_2B]^-$,[16] and $[Bu_2BNEt_3]^-$ [17,18] turned out to be questionable.[3,19–22] Nevertheless during the last 20 years, besides “$(C_6H_{11})_3PBH_2Li$” as intermediate,[23,24] some examples for nucleophilic boron species have been described (Scheme 1), which are fully characterized and have found use in organic synthesis.[3,4]

Herein we describe an unprecedented dianion in the salts $M_2[B(CN)_3]$ (M = Li, Na, K), which contains nucleophilic boron in the formal oxidation state +1. This tricyanoborate anion was obtained by reductive B–C bond fission in $[B(CN)_4]^-$ by alkaline metals in liquid ammonia according to Equation (1).

$$M[B(CN)_4] + 2\,M \rightarrow M_2[B(CN)_3] + MCN \tag{1}$$



Scheme 1. Nucleophiic boron species **1**,[25] **2**,[26] **3**,[27] and **4**.[28]

In liquid ammonia at temperatures below −40 °C in an exothermic reaction a yellow precipitate and a red solution were formed. Washing the potassium salt with ammonia and drying the residue in vacuum yields pure $K_2[B(CN)_3]$. The more soluble sodium salt is more difficult to separate from NaCN. Single crystals of $K_2[B(CN)_3]$ [29] (Table 1, Table S1 in the Supporting Information, and Figure 1) and

Table 1: Structural parameters of $[B(CN)_3]^{2-}$ compared with calculated data and those of $[B(CN)_4]^-$ and $[C(CN)_3]^-$.

r [Å] angle [°]	$[B(CN)_3]^{2-}$ [a] calculated	$K_2[B(CN)_3]$ experimental	$K[B(CN)_4]$ [b]	$K[C(CN)_3]$ [c]
av B(C)–C	1.526	1.513	1.595	1.39
av C–N	1.181	1.165	1.142	1.17
av C-B(C)-C	120.0	120.0	109.5	120.0
av B(C)-C-N	180.0	178.4	178.7	177.9

[a] B3LYP/6-311++G(d,p). [b] Ref. [33]. [c] Ref. [31,32].

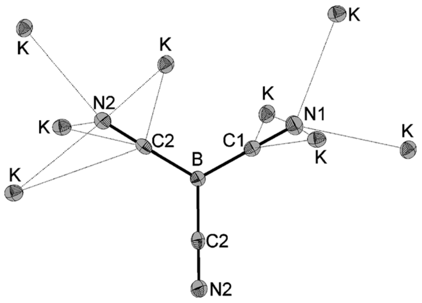


Figure 1. View of a part in the crystal structure of $K_2[B(CN)_3]$ (50 % thermal vibrational ellipsoids). Selected bond lengths: C1–N1 1.167(2), C2–N2 1.1652(15), B–C1 1.509(2), B–C2 1.5152(14) Å. Interionic contacts between two CN groups and K^+ are marked.

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$Na_2[B(CN)_3]\cdot 3\,NH_3$[30] (Table S1 and Figure S1 in the Supporting Information) were obtained by slow evaporation of ammonia from the saturated solution at 0 °C.

The crystal structures of both salts have been obtained by X-ray diffraction at low temperatures (Figure 1 and Figure S1 in the Supporting Information). In both salts the anion is planar (D_{3h} symmetry), and there are interionic contacts (in the K salt: $r(\text{K–N}) = 2.86–3.03$ Å; $r(\text{K–C}) = 3.02–3.44$ Å) directed to the CN ligands and weaker ones to the boron atom ($r(\text{K–B}) = 3.57$ Å). In Table 1 the structural parameters of the anion are compared with those of the isoelectronic $[C(CN)_3]^-$ carbanion[31,32] and of $[B(CN)_4]^-$.[33] Owing the higher negative charge in the borate dianion in comparison to the carbanion there is a strong flow of charge from the occupied boron p_z orbital into the antibonding orbitals of the CN groups. Thus the CN bonds become longer, the BC bonds become shorter, and the charge in the anion is delocalized. In the $[B(CN)_4]^-$ anion there is no back-bonding to CN, and consequently the C–N bonds are very short and the B–C bonds notably long.

When the Li salt is kept in ammonia solution, or if the remaining solvent is removed in vacuum at room temperature, the yellow color vanishes. It turned out that even under these mild conditions solvolysis occur. This reaction is kinetically hindered at low temperature and becomes slower in the Na and K salts (it takes several days at room temperature in liquid NH_3). As products $[HB(CN)_3]^-$,[34,35] $[HB(CN)_2(C\{NH\}_2)]^{2-}$[36] (Table S1 and Figure S2 in the Supporting information), and $[H_2B(CN)_2]^-$[34] have been detected. They are formed by umpolung of protons into hydridic H atoms in B–H bonds.

An alternative route to salts of the tricyanoborate anion consists of treatment of $M[B(CN)_4]$ with strong bases [Eq. (2)].

$$M[B(CN)_4] + 3\,MNH_2 \rightarrow M_2[B(CN)_3] + M_2[CN_2] + 2\,NH_3 \qquad (2)$$

Pure $Li_2[B(CN)_3]$ can be obtained according to Equation (3):

$$Li[B(CN)_4] + 2\,LiBu \rightarrow Li_2[B(CN)_3] + Li[Bu_2CN] \qquad (3)$$

$Li_2[B(CN)_3]\cdot THF$ was isolated from THF suspension. The solvate molecule cannot be removed even at 100 °C in vacuum. At 120 °C the dianion reacts with THF under O–C bond cleavage and formation of $Li_2[B(CN)_3(CH_2)_4O]$ (after aqueous workup, $K[B(CN)_3(CH_2)_4OH]$ is formed;[37] see the NMR spectroscopy data in Table S2 and structural data in Table S1 and Figure S3 in the Supporting Information).

The yellow, thermally stable salts $M_2[B(CN)_3]$ (M = Na, K) decompose above 230 °C and become brown (T_{onset} for the K salt in differential scanning calorimetry (DSC) analysis). The salts are well soluble in $NH_3(l)$ but are insoluble in $(C_2H_5O)_2CO$, $((CH_3)_2N)_2CO$, $(CH_2)_4O$ (THF).

Table 2: IR and Raman band positions (cm^{-1}) and relative band intensities of $K_2[B(CN)_3]$ compared with calculated vibrational data for the free $[B(CN)_3]^{2-}$ dianion.

IR[a]	Raman	Calcd[b]	Int_{IR}[c]	Int_{Raman}[d]	Assignment[e]
	2098 vs	2121	0	17163	ν_1, A_1', ν_{sym} CN
	2040 s				combi
2023 vvs	2022 vs	2057	1222	599	ν_6, E′, ν_{asym} CN
	1997 s				ν_6' ν_{asym} CN
	1137 w	1105	1	3	ν_7, E′, ν_{asym} BC ^{10}B
1073 s	1115 w				2×551
1058 s	1083 w	1064	3.5	15	ν_7, E′, ν_{asym} BC ^{11}B
568 w		587	11	0.01	ν_4, A_2'', π (BCN) ^{10}B
559 m		576	45	0.03	ν_4, A_2'', π (BCN) ^{11}B
		563	0	1.5	ν_8, E′, δ_{asym} (BCN)
	561/551 m	526	0	300	ν_2, A_1', ν_{sym} BC
	502/494 w	486	0	11.5	ν_{10}, E″, δ_{asym} (BCN)
		417	0	0	ν_3, A_2'', ρ (BCN)
	164 vs	136	2.6	20	ν_9, E′, δ_{asym} (CBC)
	113 m	116	12	0.05	ν_5, A_2'', π (CBC)

[a] KBr pellet. [b] B3LYP/6-311++G(d,p), see the Supporting Information for further details. [c] km mol^{-1}. [d] Raman activity in $Å^4\,amu^{-1}$. [e] Approximate description of mode in D_{3h} symmetry.

Furthermore, the salts were characterized by IR and Raman spectroscopy and in solution by ^{11}B and ^{13}C NMR spectroscopy. IR and Raman spectroscopy data of solid $K_2[B(CN)_3]$ are compared in Table 2 with data calculated for the free dianion (for Raman spectra of the Li and Na salts, see Figures S4–S6 in the Supporting Information). In spite of interionic interactions in the salt, observed and calculated band positions and intensities agree surprisingly well. The spectra match the selection rules for D_{3h} symmetry [Eq. (4)]:

$$\Gamma_{\text{vib}} = 2\,A_1'(\text{Ra}) + A_2'(-) + 2\,A_2''(\text{IR}) + 4\,E'(\text{IR, Ra}) + E''(\text{Ra}) \qquad (4)$$

There are seven Raman-active (all observed) and six IR-active (four observed) bands. The vibrational spectrum is disturbed by Fermi resonances in the regions around 2030 and 1100 cm^{-1}, and the E modes (ν_6, ν_7, ν_9, ν_{10}) are split into two components. This latter observation speaks for a lower symmetry than D_{3h} for the dianion in the lattice. It is interesting to compare the average ν(CN) vibrational frequencies of $K_2[B(CN)_3]$ (2040 cm^{-1}) with that of KCN (2076 cm^{-1}) and $K[B(CN)_4]$ (2234 cm^{-1}[33]).

The transfer of electrons from the negatively charged boron atom of $[B(CN)_3]^{2-}$ into the CN π* orbitals leads to small ν(CN) vibrational frequencies. In contrast, owing to the positively charged boron atom in $[B(CN)_4]^-$, there is almost no π back-bonding but strong σ-donor bonding, resulting in a high ν(CN) frequency. On the other hand the average ν(BC) frequency in $[B(CN)_3]^{2-}$ (890 cm^{-1}) is higher than in $[B(CN)_4]^-$ (713 cm^{-1}). The large frequency separation between the symmetrical and asymmetrical ν(CN) vibrations in $[B(CN)_3]^{2-}$ indicates a strong π-bond interaction between B and CN. In contrast, in $[B(CN)_4]^-$ the two ν(CN) vibrational frequencies are equal.

NMR spectra of $K_2[B(CN)_3]$ in liquid ND_3 at −40 °C have been recorded ($\delta(^{11}B) = -45.3$, $\delta(^{13}C) = 158.5$ ppm, $J(^{11}B,^{13}C) = 94$ Hz, internal standard $K[B(CN)_4]$). The data can be compared with those of $K[B(CN)_4]$ in CD_3CN ($\delta(^{11}B) = -38.6$, $\delta(^{13}C) = 123.1$ ppm, $J(^{11}B,^{13}C) = 71.2$ Hz). The $\delta(^{11}B)$ chemical shift of the dianion is 7 ppm lower than that of the monoanion, as expected for the more negative charge at the boron atom. However, the 35 ppm higher ^{13}C

chemical shift for $[B(CN)_3]^{2-}$ may be due to the higher paramagnetic contribution of the more negatively charged CN groups. The s-orbital contribution of the Fermi contact term in the B–C bond of $[B(CN)_3]^{2-}$ is larger than in $[B(CN)_4]^-$, and accordingly the $J(^{11}B,^{13}C)$ coupling constant is 23 Hz larger (see the Supporting Information, Tables S3 and S4 for further data).

In conclusion, the new, reactive $[B(CN)_3]^{2-}$ dianion is fully characterized and its salts are nucleophilic reagents with promising chemistry. Consequently, transfer of the $B(CN)_3$ group to different substrates and its selective oxidation under formation of the $[B(CN)_3]^-$ radical anion may be possible. The high calculated first electron affinity (330 kJ mol^{-1}) of the strong Lewis acid $B(CN)_3$ and the endothermic uptake of the second electron speaks for this possibility. The unexpected high stability of $[B(CN)_3]^{2-}$ is attributed on the extreme acidity of the underlying, uncharged Lewis acid $B(CN)_3$.

Experimental section

The synthesis of $M_2[B(CN)_3]$ (M = Na, K) was accomplished in a glass reactor consisting of two tubes (Ø = 2.3, l = 15 cm), closed at the bottom, each fitted on top with a Young valve and connected in the upper part with a tube and a frit (Ø = 2 cm, G3). The reactor was dried in vacuum, and in a dry box one cylinder was loaded with $M[B(CN)_4]$ (30 mmol),[33,38–40] freshly cut alkaline metal M (M = Na, K, 60 mmol, Merck KGaA), and a magnetic stirring bar. After the transfer of dry, liquid ammonia (40 mL) in vacuum, the reaction mixture was kept at −40 °C, stirred, and shaken. In an exothermic reaction, the blue color of dissolved alkaline metal appeared and then vanished, while a yellow solid was formed. The reaction was finished when the mixture consisted of a red solution and a yellow precipitate. KCN was removed from $K_2[B(CN)_3]$ by repeated washing with liquid ammonia at −70 °C. $Na_2[B(CN)_3]$ is more soluble in liquid ammonia, and NaCN is more difficult to remove. Liquid ammonia was removed under reduced pressure, and the solid residue was dried in vacuum at 50 °C.

Synthesis of $Li_2[B(CN)_3]$: The reactor described above was charged with $Li[B(CN)_4]$ (0.283 g, 2.32 mmol) suspended in THF (10 mL) and *n*BuLi (5 mL, 2 M in hexane), and the mixture was stirred for 16 h. The obtained yellow precipitate was filtered and washed several times with THF. The residue was dried in vacuum. Yield: 0.183 g (1.05 mmol, 45 %). ^{11}B and ^{1}H NMR spectra in D_2O: 0.2–0.4 % $[B(CN)_4]^-$, > 99.5 % $[DB(CN)_3]^-$, from ^{1}H NMR spectroscopy a ratio $[HB(CN)_3]^-$/THF = 1:1 is deduced. For the Raman spectra of $M_2[B(CN)_3]$ (M = Li, Na, K) see the Supporting Information.

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[29] Crystal structure analysis of $K_2[B(CN)_3]$ (for details of measurements and structure solution see the Supporting Information, Table S1): $C_3BN_3K_2$, Mo (λ = 0.71073 Å) sample temperature 150 K, yellow crystal (0.21 × 0.42 × 0.54 mm^3) obtained from ammonia at 0 °C, orthorhombic, space group *Fdd*2 (Nr. 43), $a = 13.4507(8)$, $b = 10.5300(6)$, $c = 8.9576(5)$ Å, $V = 1268.72(12)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.749$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 1.387$ mm^{-1}, $F(000) = 656$, 4251 measured, 784 independent reflections [$R_{int} = 0.0295$, $R_\sigma = 0.0171$], thereof 778 with $I > 2\sigma(I)$ ($3.35 < \theta < 29.13°$), completeness 99.7 % (to $\theta = 26.40°$, $d = 0.8$ Å). Refinement of the structure based on F^2 with 784 independent reflections, 44 variables, and 1 restraint. All atoms were refined anisotropically. $R_1 = 0.0144(I > 2\sigma(I))$, Goodness-of-fit on F^2 1.063. CCDC 840245 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
[30] Crystal structure analysis of $Na_2[B(CN)_3]\cdot 3NH_3$ (for details about measurements and structure solution, see the Supporting Information, Table S1, Figure S1): $C_3H_9BN_6Na_2$, Cu (λ = 1.54184 Å), sample temperature 110 K, yellow crystal (0.23 × 0.23 × 0.26 mm^3) obtained from ammonia at 0 °C, orthorhombic, space group *Cmc*2(1) (Nr. 36), $a = 7.9941(6)$, $b = 10.6256(9)$, $c = 11.5336(8)$ Å, $V = 979.69(13)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.261$ Mg m^{-3}, μ-

($Cu_{K\alpha}$) = 1.484 mm^{-1}, $F(000) = 384$, 2923 measured, 827 independent reflections [$R_{int} = 0.0296$, $R_{\sigma} = 0.0241$], thereof 813 with $I > 2\sigma(I)$ ($7.68 < \theta < 62.38°$), completeness = 98.2 % (to $\theta = 62.38°$, $d = 0.87$ Å). Refinement of the structure based on F^2 with 827 independent reflections, 83 variables, and 6 restraints. All atoms (except H atoms) were refined anisotropically. $R_1 = 0.0231$ ($I > 2\sigma(I)$), Goodness-of-fit on F^2 1.086. CCDC 840246 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[36] Compound $Na_2[BH(CN)_2(C(NH)_2)]\cdot 7/6\,NH_3$ was characterized by crystal structure analysis (details about measurements and structure solution see the Supporting Information, Table S1, Figure S2). CCDC 840247 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[37] Compound $K[B(CN)_3(CH_2)_4OH)]$ was characterized by crystal structure analysis (details about measurements and structure solution see the Supporting Information, Table S1, Figure S3). CCDC 840248 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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