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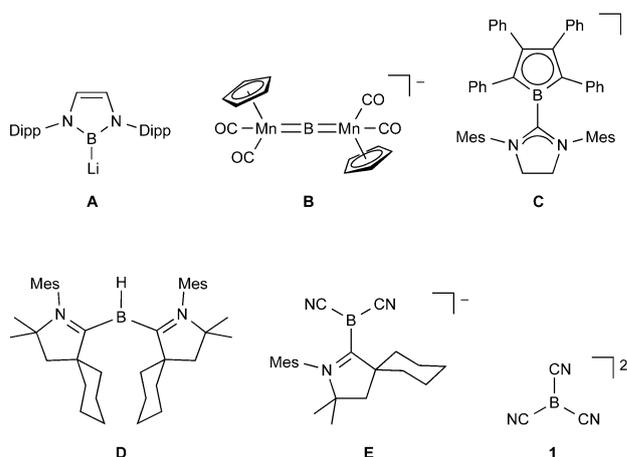
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## Convenient access to the tricyanoborate dianion $B(CN)_3^{2-}$ and selected reactions as a boron-centred nucleophile†

 Johannes Landmann,<sup>a</sup> Jan A. P. Sprenger,<sup>a</sup> Rüdiger Bertermann,<sup>a</sup> Nikolai Ignat'ev,<sup>b</sup> Vera Bernhardt-Pitchougina,<sup>a,c</sup> Eduard Bernhardt,<sup>c</sup> Helge Willner<sup>c</sup> and Maik Finze<sup>\*a</sup>

Alkali metal tricyanoborates  $M_2B(CN)_3$  ( $M = Na, K$ ) are accessible by the reaction of tricyanofluoroborates with alkali metals (i) in liquid  $NH_3$  or (ii) in THF–naphthalene. The  $M_2B(CN)_3$  are versatile starting materials for the synthesis of  $K[RB(CN)_3]$  ( $R = Et, C_6F_5, CH_2=CHCH_2$ ).

So far, only a few well-defined boron-centred nucleophiles have been isolated and characterized in detail. Their nucleophilic character has been demonstrated by reactions with selected electrophiles. Relevant examples for such boron species are summarized in Scheme 1. The unusual lithiated boryl anion **A** was reported in 2006.<sup>1</sup> Since then a number of related anions have been described and their chemistry has been studied.<sup>2</sup> Furthermore, related transition metal boryl complexes are highly valuable starting materials for transition metal catalysed transformations and they exhibit a certain degree of nucleophilic character at the boron atom, as well.<sup>3</sup> The anionic dimanganese borylene complex **B** reveals a nucleophilic behavior at the linear coordinated boron centre.<sup>4</sup> The carbene-stabilized  $\pi$ -boryl anion **C** was found to react with methyl iodide to yield the corresponding methyl substituted donor-stabilized borole<sup>5</sup> and with  $[Et_3NH]^+$  to give the respective protonated derivative.<sup>6</sup> Both reactions provided some evidence for a nucleophilic reactivity of **C**. However, recently an alternative non-nucleophilic pathway for reactions of **C** via a radical intermediate was discussed.<sup>7</sup> Further examples for nucleophilic boron derivatives are the molecule **D**,<sup>8</sup> the dicyanoborate monoanion **E**<sup>9</sup> and the tricyanoborate dianion  $B(CN)_3^{2-}$  (**1**).<sup>10</sup>



Scheme 1 Selected nucleophilic boron species.

In addition to the reactions found for the nucleophilic boron derivatives depicted in Scheme 1, the high synthetic value of related nucleophilic boron species was demonstrated by reactions of a few other boryl anions that have been described but that could not be isolated. Trapping reactions with various electrophiles have been conducted especially with the carbene-stabilized boryl anion  $NHC-BH_2^-$  ( $NHC = 1,3$ -bis-(2,6-diisopropylphenyl)imidazol-2-ylidene)<sup>11</sup> and the phosphane substituted boryl anion ( $cyclo-C_6H_{11}$ )<sub>3</sub>P-BH<sub>2</sub><sup>-</sup>.<sup>12</sup>

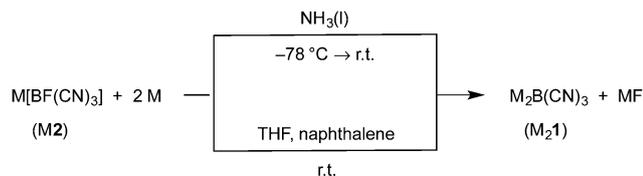
The homoleptic cyanoborate dianion  $B(CN)_3^{2-}$  (**1**),<sup>10</sup> which is isoelectronic to the tricyanmethanide anion  $C(CN)_3^-$ , is the only doubly negatively charged boron-centred base described in the literature.<sup>10</sup> The negative charge of all other related boron-centred bases is fully (**D**) or in part (**A–C** and **E**) compensated by further substituents, e.g. a N-heterocyclic carbene. So far, an alkali metal tetracyanoborate  $M[B(CN)_4]$  ( $M = Li, Na, K$ )<sup>13</sup> is required as starting material for the preparation of  $M_21$  ( $M =$  alkali metal).<sup>10</sup> The  $[B(CN)_4]^-$  anion is either reduced with an alkali metal in liquid ammonia or one of its four cyano groups is removed by the action of a strong base, for example *n*-butyl lithium.<sup>10a</sup> Here we report on (i) alternative syntheses for alkali metal salts of the

<sup>a</sup> Institut für Anorganische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany. E-mail: maik.finze@uni-wuerzburg.de

<sup>b</sup> Merck KGaA, PM-ATI, Frankfurter Straße 250, 64293 Darmstadt, Germany

<sup>c</sup> FB C Anorganische Chemie, Bergische Universität Wuppertal, Gaußstraße 20, 42119 Wuppertal, Germany

† Electronic supplementary information (ESI) available: Experimental and spectroscopic details, <sup>19</sup>F MAS NMR spectrum and IR as well as Raman spectrum of K<sub>2</sub>1·KF. CCDC 1039991 (K4·0.5THF), 1039992 (K6), 1031561 and 1039993 (K5), 1039994 (K3·0.5(CH<sub>3</sub>)<sub>3</sub>CO). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5cc00555h



(M = K, Na; Na<sub>2</sub>·1·NaF was not isolated but used for the preparation of salts of the [BH(CN)<sub>3</sub>]<sup>-</sup> anion (3))

Scheme 2 Synthesis of M<sub>2</sub>·1·MF (M = K, Na).

tricyanoborate anion B(CN)<sub>3</sub><sup>2-</sup> (M<sub>2</sub>·1, M = Na, K) and (ii) on reactions of K<sub>2</sub>·1 with selected electrophiles that demonstrate the nucleophilic nature of the boron atom of 1.

In the course of our studies on the chemical and electrochemical stabilities of tricyanofluoroborates, which are valuable materials for electrochemical applications,<sup>14</sup> we have developed new and easy syntheses for K<sub>2</sub>B(CN)<sub>3</sub> (K<sub>2</sub>·1). These new syntheses are especially attractive because the alkali metal tricyanofluoroborates K[BF(CN)<sub>3</sub>] and Na[BF(CN)<sub>3</sub>] (K2 and Na2)<sup>15</sup> have become easily accessible on large scale (> 100 g).<sup>16</sup> Reaction of K2 with elemental potassium either in liquid ammonia or in THF in the presence of catalytic amounts of naphthalene gives K<sub>2</sub>·1 in yields of up to 89%, which contains one equivalent of KF as byproduct (Scheme 2). So far, it was not possible to separate the KF. However, it was not found to affect subsequent reactions with electrophiles. Similar to the reaction of K[BF(CN)<sub>3</sub>] (K2) in NH<sub>3</sub> and THF, Na<sub>2</sub> is reduced with either sodium in liquid ammonia or sodium naphthalide in THF. A comparative study on the reaction of K2 with potassium, sodium and lithium naphthalide in THF showed that the rate of reduction strongly decreases in the order K > Na > Li. Attempted electrochemical reduction of 2 under the conditions of cyclic voltammetry and in the presence of the weakly coordinating counteranion [nBu<sub>4</sub>N]<sup>+</sup> failed. Hence, the electrochemical stability of [nBu<sub>4</sub>N]·2 exceeds the one of THF.

The reduction of the [BF(CN)<sub>3</sub>]<sup>-</sup> anion (2) leads to a population of its LUMO (Fig. 1) with electrons. Since this molecular orbital is B–F antibonding the formation of the homoleptic cyanoborate

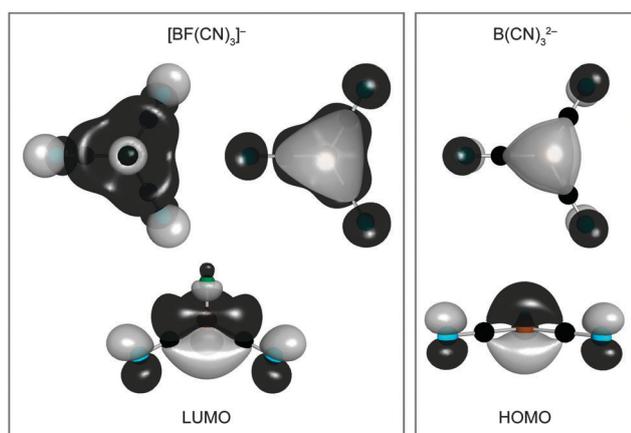


Fig. 1 Different contour plots of the LUMO of the [BF(CN)<sub>3</sub>]<sup>-</sup> anion (2) and of the HOMO of the B(CN)<sub>3</sub><sup>2-</sup> anion (1) [calculated at the PBE0/def2-TZVPP level of theory].

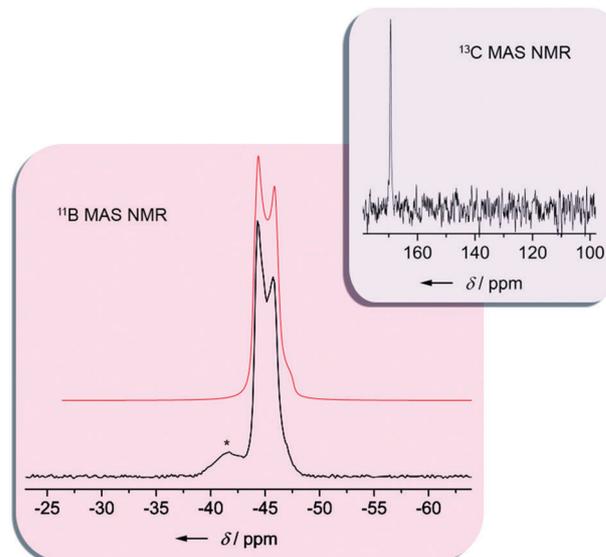


Fig. 2 <sup>11</sup>B MAS NMR spectrum and simulated NMR spectrum (red) as well as <sup>13</sup>C MAS NMR spectrum of K<sub>2</sub>B(CN)<sub>3</sub>·KF (K<sub>2</sub>·1·KF) derived from the reaction of K[BF(CN)<sub>3</sub>] (K2) with elemental K in ammonia (\* unknown impurity, most probably as a result of the sample preparation).

anion B(CN)<sub>3</sub><sup>2-</sup> (1) is rationalized. The similarity of the LUMO of 2 to the HOMO of 1 is evident from the respective contour plots in Fig. 1.

The mixed potassium salt K<sub>2</sub>B(CN)<sub>3</sub>·KF (K<sub>2</sub>·1·KF) was characterized by elemental analysis, solid state NMR spectroscopy and vibrational spectroscopy. The line shape of the <sup>11</sup>B MAS NMR spectrum reveals a second-order quadrupole MAS powder pattern as expected for an anion with a trigonal-planar arrangement at the quadrupolar nucleus. Simulation of the spectrum as depicted in Fig. 2 resulted in an isotropic chemical shift  $\delta_{\text{iso}}$  of -43.4 ppm, a quadrupolar coupling constant  $C_{\text{quad}}$  of 1.01 MHz and a quadrupolar asymmetry parameter  $\eta_{\text{quad}}$  of 0.19. This relatively small quadrupolar asymmetry parameter also reflects the almost trigonal-planar geometry of the anion in the solid state. The <sup>13</sup>C MAS NMR spectrum shows a single signal for the cyano groups at 169.4 ppm. The isotropic <sup>11</sup>B and <sup>13</sup>C chemical shifts observed for solid K<sub>2</sub>·1·KF are close to  $\delta(^{11}\text{B})$  and  $\delta(^{13}\text{C})$  reported for K<sub>2</sub>B(CN)<sub>3</sub> (K<sub>2</sub>·1) dissolved in liquid ND<sub>3</sub> of -45.3 and 158.5 ppm, respectively.<sup>10a</sup> The signal of the fluoride anion of the mixed salt K<sub>2</sub>·1·KF was observed at -133.7 ppm (Fig. S1, ESI<sup>†</sup>), which is in good agreement to  $\delta_{\text{iso}}(^{19}\text{F})$  reported for neat KF of -136 ppm.<sup>17</sup> The IR and Raman spectrum of K<sub>2</sub>·1·KF that are shown in Fig. S2 (ESI<sup>†</sup>) are almost identical to the spectra reported for K<sub>2</sub>·1, earlier.<sup>10a</sup>

The nucleophilic character of the tricyanoborate dianion B(CN)<sub>3</sub><sup>2-</sup> (1) at its boron atom was demonstrated by reactions with (a) water to yield K[BH(CN)<sub>3</sub>] (K3),<sup>10</sup> (b) ethyl iodide to give K[EtB(CN)<sub>3</sub>] (K4), (c) allyl chloride and allyl bromide to result in K[CH<sub>2</sub>=CHCH<sub>2</sub>B(CN)<sub>3</sub>] (K5) and (d) hexafluorobenzene to give K[C<sub>6</sub>F<sub>5</sub>B(CN)<sub>3</sub>] (K6). Salts of the anions 4–6 have been obtained from the corresponding trifluoroborates earlier.<sup>18</sup> However, the synthetic method described in this publication does not rely on the availability of the respective trifluoroborates. The reactions

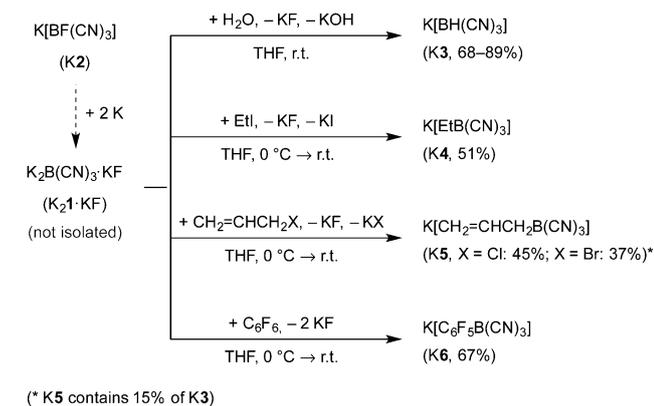
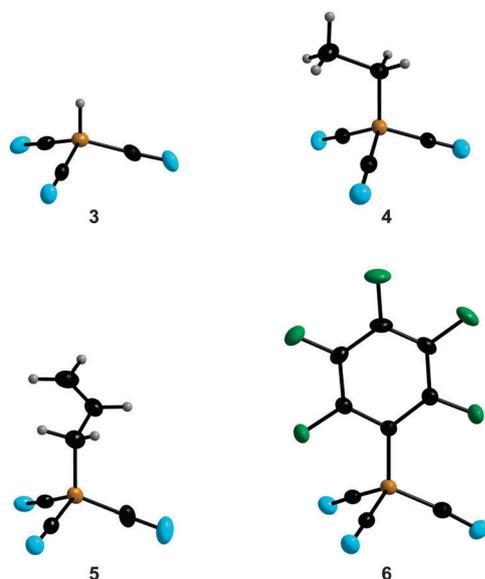
Scheme 3 Reactions of K<sub>2</sub>1·KF with selected electrophiles.

Fig. 3 The anions  $[\text{BH}(\text{CN})_3]^-$  (**3**),  $[\text{EtB}(\text{CN})_3]^-$  (**4**),  $[\text{CH}_2=\text{CHCH}_2\text{B}(\text{CN})_3]^-$  (**5**) and  $[\text{C}_6\text{F}_5\text{B}(\text{CN})_3]^-$  (**6**) in the crystals of their  $\text{K}^+$  salts [ellipsoids are drawn at the 50% probability level except for H atoms, which are depicted with arbitrary radii]. Selected bond lengths [Å] and angles [°] of **3–6** (range of bond lengths and angles where applicable): **3**: B–CN 1.588(2)–1.592(2), C≡N 1.1411(15)–1.1431(15), B–H 1.107(13), B–C≡N 176.87(12)–177.00(12), NC–B–CN 109.35(9)–110.26(9). **4**: B–CN 1.591(5)–1.610(5), C≡N 1.135(4)–1.145(4), B–CH<sub>2</sub> 1.609(5)–1.623(5), CH<sub>2</sub>–CH<sub>3</sub> 1.521(5)–1.528(5), B–C≡N 177.9(3)–179.1(3), NC–B–CN 107.0(3)–108.3(3). **5**: B–CN 1.600(2)–1.607(3), C≡N 1.143(2)–1.144(2), B–CH<sub>2</sub> 1.630(2), CH<sub>2</sub>–CHCH<sub>2</sub> 1.593(2), CH=CH<sub>2</sub> 1.315(3), B–C≡N 175.50(12)–179.12(14), NC–B–CN 106.61(10)–109.80(10). **6**: B–CN 1.600(3)–1.608(3), C≡N 1.141(2)–1.147(2), B–C<sub>1</sub> 1.626(2), B–C≡N 174.8(2)–178.7(2), NC–B–CN 105.67(14)–107.15(15).

depicted in Scheme 3 are most easily performed as a two-step one pot procedure. In the first step the tricyanofluoroborate K2 is converted and after removal of the solvent the K<sub>2</sub>1·KF is suspended in THF and the respective electrophile is added. However, similar results have been obtained with K<sub>2</sub>1·KF that was isolated and stored in a glove box in an inert atmosphere. Related transformations of boron-centred nucleophiles with electrophiles have been described, e.g. the carbene-stabilized boryl anion  $\text{NHC-BH}_2^-$  (NHC = 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene)

reacts with allyl bromide to give an allyl substituted four-coordinate boron derivative with a similar yield (36%).<sup>11</sup> The analogous reactivity unambiguously proves the nucleophilic character at the boron centre of dianion **1**.

The four potassium salts K3, K4, K5 and K6 were characterized by multi-NMR and vibrational spectroscopy and single crystal X-ray diffraction. Molecular structures of the four anions, which show the almost tetrahedral arrangement at the boron atoms, are depicted in Fig. 3 and experimental details on the crystal structure analyses are given in the ESI.†

New and convenient syntheses for the potassium salt of the unusual boron-centred nucleophile  $\text{B}(\text{CN})_3^{2-}$  (**1**)<sup>10</sup> have been developed *via* reaction of the readily available  $\text{K}[\text{BF}(\text{CN})_3]$  (K2)<sup>16b</sup> with potassium. K<sub>2</sub>1 was found to be a valuable starting material for the preparation of tricyanoborates of the type  $\text{K}[\text{RB}(\text{CN})_3]$  (R = H (K3), Et (K4), CH<sub>2</sub>=CHCH<sub>2</sub> (K5), C<sub>6</sub>F<sub>5</sub> (K6)). Further detailed studies on the chemistry of salts of dianion **1** with selected compounds are in progress.

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