Boron- versus Nitrogen-Centered Nucleophilic Reactivity of (Cyano)hydroboryl Anions: Synthesis of Cyano(hydro)organoboranes and 2-Aza-1,4-diboratatrienes

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Abstract: Cyclic alkyl(amine)carbene-stabilized (cyano)hydroboryl anions were synthesized by deprotonation of (cyano)hydroborane precursors. While they display boron-centered nucleophilic reactivity towards organohalides, generating fully unsymmetrical substituted cyano(hydro)organoboranes, they show cyano-nitrogen-centered nucleophilic reactivity towards haloboranes, resulting in the formation of hitherto unknown linear 2-aza-1,4-diborabutatrienes.

Introduction

As anionic boron analogues of carbenes, boryl anions ([R₂B]⁻) long remained in the realm of computational curiosities. While the transient formation of [Ph₂B]⁻ upon photolysis of [Ph₂B]⁺ salts had been deduced from trapping reactions as early as 1967,[5,6] these claims were later disputed.[7,8] Although Curran, Fensterbank, Malacria and Lacôte demonstrated in 2010 that Lewis base-stabilized parent boryl anions [L–B]⁻ can indeed be generated in situ by the reduction of L–BH₃, and trapped with electrophiles, these species are too thermodynamically unstable to be isolated.[9–11]

The first isolable boryl anion, compound I (Figure 1), was reported in 2006 by Yamashita and Nozaki, making use of the same features that help stabilize N-heterocyclic carbenes (NHCs).[12] The anionic boron center of I is incorporated within a five-membered ring, electronically stabilized by the two adjacent nitrogen π donors and sterically shielded by the bulky Dip groups ([Dip = 2,6-diisopropylphenyl]), while complexation to the lithium cation provides further thermodynamic stability.[11,12]

Diazaborolyl anions such as I have since been used as powerful Brønsted bases, reducing agents and boron nucleophiles to access a plethora of new boron-element bonds.[13–19]

In the last decade the available repertoire of stable boryl anions has been steadily increasing. In 2010 our group reduced a NHC-stabilized bromoborole to the corresponding aromatic borony anion, II, which reacts as a boron nucleophile towards MeI.[20] Taking further inspiration from NHCs, the electronic properties of which can be fine-tuned by changes in the heterocycle, Kinjo and co-workers designed the 1,2,4,3-triazaborol-3-yl lithium complex IV, which is capable of coupling two CO molecules to a diboraalkene and cyclizing arylinonitriles to 2-boranyindole derivatives.[21] The reactivity of I was further increased by synthesizing the mixed lithium-potassium salt of the diazaborolyl anion dimer, IV, which is capable of deprotonating benzene,[22] or the dimeric potassium salt V, in which both anionic boron centers are “naked” and promote facile C–H activation at a pendant Dip-isopropyl group.[23]

While boryl anions I–V are accessed by reduction of haloboron precursors, Bertrand and co-workers showed that the

![Figure 1. Selection of isolable boryl anions. Dme = dimethoxyethane, thf = tetrahydrofuran, dbc = dibenzo-18-crown-6.](image)
B–H bond of a cyclic alky(amo)carbene (CAAC)-stabilized (dicyano)hydroborane undergoes an "umpolung" due to the electron-withdrawing nature of the cyano ligands, which enables the synthesis of the corresponding boryl anion VI by deprotonation.[24] The negative charge at boron in VI is further stabilized by π backdonation to the π-acidic CAAC ligand. Using the same umpolung principle, Finze and co-workers deprotonated [BH(CN)]₂⁻ to the corresponding dianion [B(CN)]₂⁻,[25] while Hörner and Frank synthesized stable NHC analogues of VI, such as the nonameric potassium salt VII.[24] The latter was shown to react as a boron-centered nucleophile with a variety of organic, main group and transition metal electrophiles.

Our group has shown that a single cyano ligand at boron suffices to induce a B–H bond umpolung, enabling access to the (cyano)hydroboronyl anion dimer 2a by deprotonation of the corresponding (CAAC)₂BH₂(CN) precursor 1a (Scheme 1a, CAAC<sup>Me</sup> = 1-(2,6-disopropylphenyl)-3,3,5,5-tetramethyl-pyrollidin-2-ylidene).[26]

While 2a reacted as a soft boron-centered nucleophile towards soft heavier triorganotetrel chlorides (Scheme 1b), the reaction with triorganosilyl chlorides occurred at the hard terminal cyano-nitrogen, generating a silylisonitrile-stabilized borylene (Scheme 1c), which in solution undergoes subsequent silyl migration to boron (Scheme 1d).

The divergent reactivity of 2a, both as a soft boron- and as a hard nitrogen-centered nucleophile, prompted us to undertake further investigations into the reactivity of (cyano)hydroboryl anions with electrophiles. In this contribution we present the synthesis of monomeric and dimeric CAAC-stabilized (cyano)hydroboryl anions with electrophiles. In this contribution we present the synthesis of monomeric and dimeric CAAC-stabilized (cyano)hydroboryl anions with electrophiles. In this contribution we present the synthesis of monomeric and dimeric CAAC-stabilized (cyano)hydroboryl anions with electrophiles.

Results and Discussion

Synthesis of boryl anion precursors

With the aim of obtaining a monomeric analogue of 2a, the more sterically demanding CAAC<sup>5</sup> ligand (CAAC<sup>5</sup> = 2-(2,6-

![Scheme 1](image1.png)  
**Scheme 1.** Synthesis of boryl anion 2a and its reactivity with group 14 electrophiles.

diisopropyl(phenyl)-3,3-dimethyl-2-azaspiro[4.5]decan-1-ylidene) was employed to synthesize the (cyano)hydroborane precursor 1b. The deprotonation of 1b with nBuLi in THF yielded the boryl anion 2b (Scheme 2a), which displays an <sup>11</sup>B NMR doublet at −13.9 ppm, nearly identical to 2a (δ<sub>B</sub> = −10.8 ppm).[27] Due to its extremely high solubility in nonpolar hydrocarbon solvents only a few crystals of 2b could be obtained, which confirmed the monomeric nature of the species (Figure 2).

Unlike in 2a, the lithium cation in 2b is terminally bound to the cyano substituent and stabilized by three THF molecules. The boron center is trigonal planar (2<sub>1–C1</sub> bond length of 1.450(5) Å) is similar to that of 2a (1.447(3) Å)[27] and denotes a B–C double bond, indicating strong π backdonation from the boryl anion lone pair into the empty π orbital at the CAAC ligand. Due to the high Bronsted basicity of the borylene all attempts to recrystallize 2b in higher yields from hexanes resulted in partial hydrolysis back to 1b and crystallization of the cubane-type cluster 3b (Scheme 2b, Figure 2). Four [(CAAC)<sup>5</sup>](BH₂(CN)Li) units generate the central Li₄N₄ cube of C₄ᵥ symmetry, the opposing lithium apices of which are stabilized by two (CAAC)<sup>5</sup> li(CN)Li units coordinating as nitrogen donors, and two N interactions with adjacent Dip substituents, respectively. The structure of 3b is reminiscent of that of [Ph(NC=N)(NC<sub>3</sub>H<sub>3</sub>)]<sub>4</sub>, which also crystallizes as a tetramer with a cubic Li₄N₄ core and pyridine-stabilized lithium apices.[28]

In order to isolate 2b in high yields and analytical purity its tetramethyltetrahydeniamine (TMEDA) analogue 2b-TMEDA was synthesized by the addition of TMEDA to crude 2b (Scheme 2c), or alternatively by deprotonating 1b in hexanes at −35 °C in the presence of TMEDA (Scheme 1d). 2b-TMEDA (δ<sub>B</sub>= −12.9 ppm, d, δ<sub>B-H</sub>=98.3 Hz) was isolated as a yellow crystalline solid in 62% yield. Its solid-state structure (Figure 2) is dimeric,
similar to that of 2a. The main difference with 2a is that the borylene plane in 2b-TMEDA is not coplanar with the central Li$_2$N$_2$ unit but rotated by ca. 70°, presumably due to steric repulsion between the TMEDA ligands and the CAAC-cyclohexyl moiety.

Reactivities of 2a and 2b as boron-centered nucleophiles

Similarly to $^{[16,17,18,25]}$ the reactions of the boryl anions 2a and 2b towards organohalides (RX = 1-bromobutane, allyl bromide, dichloromethane, acetyl chloride, benzyl chloride) at room temperature resulted in the clean formation of the corresponding colorless cyano(hydro)organoboranes 4a$^a$ and 4b$^b$, respectively, by salt elimination (Scheme 3). The $^{11}$B NMR shifts of each 4a$^a$/4b$^b$ pair are nearly identical (Δδ$_{11B} \approx 1.5$ ppm) and range from $\Delta$-23.6 ppm for R = COMe to $\Delta$-25.1 ppm for R = Br. This boron-centered reactivity reflects that of 2a with heavier group 14 triorganochlorides (Scheme 1b).$^{[27]}

It is noteworthy that unlike 2a and 2b, the diazaborolyl anion I reacts with 1-bromobutane to provide the corresponding bromoborane rather than the butylborane.$^{[27]}$ Marder and Lin showed that the preference of boryl anion I for halogen abstraction from RX over nucleophilic attack at the halide-bound carbon atom increases for the heavier halides, and can be promoted by the stability of the R$^-$ fragment in the transition state of the halogen abstraction step.$^{[26]}

The reaction between 2a or 2b with 1,2-dibromopropane in benzene at room temperature was accompanied by rapid gas evolution as the reaction mixture became colorless. In CD$_3$O, the $^1$H NMR spectra of the two reaction mixtures showed the formation of propene as a by-product ($\delta_{\text{H}}$ = 5.71, 4.99 and 4.93 ppm for the alkene protons), while the $^{13}$B NMR spectra showed a single boron-containing product with a doublet around $\Delta$-25 ppm ($\Delta$δ$_{13B} \approx 100$ Hz), identified by X-ray structural analyses as the CAAC-stabilized bromo(cyano)hydroboranes 4a$^b$ and 4b$^b$, respectively (Scheme 4). In this case the entropically favored elimination of propene is likely to be the driving force of the bromine abstraction versus the nucleophilic attack at carbon.

All 4a$^b$/$4b^b$ boranes crystallized as colorless solids and were characterized by X-ray crystallographic analyses (Figure 3 and Figures S60–S64). In all cases the B1−C1 bond length is ca. 1.62 Å, slightly longer than in the precursors 1a (1.608(3) Å) and 1b (1.597(3) Å), typical for a CAAC−borane donor interaction, while the C1−N1 bond length of ca. 1.30 Å corresponds to a double bond. Furthermore, the substituents at boron are always
arranged so that the N1–C1–B1–H1 torsion angle tends towards 0° (from ca. 0.9° in 4aBu to ca. 20.7° in 4aCOPh), in order to minimize steric repulsion between the Dip substituent and the CN and R substituents. Overall the syntheses presented in Schemes 2 and 3 represent facile routes to fully unsymmetrically substituted boranes, which would otherwise be difficult to access.

Reactions of 2a and 2b as cyano-nitrogen-centered nucleophiles

The reactivity of 2a and 2b towards haloboranes (R2BX) proceeded rather differently. Instead of turning colorless as in the reactions with organohalides the reaction mixtures turned dark red or bright orange for Mes2BF (Mes = 2,4,6-Me3C6H2) or (iPr2N)2BCl, respectively. The 11B NMR spectra of the reaction products, compounds 5a/bR, showed a broad resonance around 36 ppm for 5a/bMes and 22 ppm for 5a/bNiPr2, upfield-shifted from the precursors Mes2BF (δ11B = 53 ppm)\(^{[31]}\) and (iPr2N)2BCl (δ11B = 34 ppm)\(^{[32]}\), as well as a BF doublet around −9 ppm for 5a/bMes and −14 ppm 5a/bNiPr2, in a similar range to those of precursors 2a and 2b (δ11B = −10.8 and −12.9 ppm, respectively). These data suggested nucleophilic attack at the borane by the terminal cyano-nitrogen donor rather than by the boryl anion (Scheme 5), in analogy to the reaction between 2a and triorganosilyl chlorides (Scheme 1c).\(^{[27]}\)

This was confirmed by X-ray structural analyses (Figure 4, Figures S65 and S66), which showed that the geometry around B1 remains trigonal planar (Σ(B1) = 360°) and the BR2 moiety coordinates at the cyano-nitrogen N2. The B1–C1–N2–B2 moiety presents a near-linear arrangement with a B1-C21-N2 angle of ca. 174° and a C21-N2-B2 angle of ca. 170° for 5a/bMes and ca. 160° for 5a/bNiPr2. In the 5a/bMes derivatives the B1–C21, C21–N2 and N2–B2 distances (ca. 1.45, 1.17 and 1.41 Å, respectively) are all within the range of double bonds,\(^{[33–34]}\) while the C1–B1 and N1–C1 bond lengths (ca. 1.51 and 1.34 Å, respectively) suggest only a small amount of π backbonding from the electron-rich boron to the CAAC ligand. In the 5a/bNiPr2 derivatives the electronic structure is slightly different due

Figure 3. Crystallographically derived molecular structures of 4aBu, 4bCH3, 4aCOMe, 4bCH2Cl, 4aCPH and 4bBr. Atomic displacement ellipsoids are set at 50% probability. Ellipsoids of carbon atoms of the ligand periphery and hydrogen atoms omitted for clarity, except for boron-bound hydrides.
to partial π backbonding from the amino substituents to B2 (B2-N3/4 ca. 1.43 Å) the B1–C21, C21–N2 and N2–B2 distances (ca. 1.48, 1.18 and 1.45 Å, respectively) are slightly elongated compared to 5a\textsuperscript{b\textsubscript{Mes}}. Moreover, the C1–B1 and N1–C1 bond lengths (ca. 1.47 and 1.36 Å, respectively) also indicate partial double bonds, suggesting that π electron density in 5a\textsuperscript{b\textsubscript{Mes}} is delocalized over the entire [N1–C1–B1–C21–N2–B2–N3/4] framework. The preference for the addition of the boron electrophiles at the cyano-nitrogen rather than at the borylene center is likely owed to the formation of a strong B–N multiple bond rather than a comparatively weak B–B single bond.

The UV-vis spectra of 5a\textsuperscript{Mes} and 5b\textsuperscript{Mes} in hexane showed absorption maxima at 516 and 520 nm, respectively, accounting for their red color, as well as a secondary absorption band around 380 nm. In contrast, the major absorption bands of 5a\textsuperscript{b\textsubscript{Mes}} (423 nm) and 5b\textsuperscript{b\textsubscript{Mes}} (429 nm) are blueshifted by ca. 100 nm compared to those of 5a\textsuperscript{Mes} and 5b\textsuperscript{Mes}, accounting for their orange color, and overlap with strong secondary absorptions around 400 nm.

Density functional theory (DFT) calculations on 5a\textsuperscript{Mes} and 5a\textsuperscript{b\textsubscript{Mes}} performed at the B3LYP/def2-SVP\textsuperscript{[35]} and PBE0-D3/def2-SVP\textsuperscript{[36–37]} levels of theory (see Supporting Information for details) showed that in both compounds the canonical Kohn-Sham HOMO extends over the [N1–B1–C21–N2–B2–N3/4] π systems, with a strong π-bonding character between B1 and C21, and to a lesser degree B1 and C1 (Figure 4), as suggested by the X-ray crystallographic data. Nodal planes are found in the N1-C1 and C21-N2 bond regions. Additionally, the 5a\textsuperscript{b\textsubscript{Mes}} derivative shows small contributions from the lone pairs at N3 and N4, with nodal planes at B2–N3 and B2–N4. Furthermore, bond orders calculated using natural resonance theory (NRT)\textsuperscript{[16]} analysis (see Figure S67 in the Supporting Information) suggest a better delocalization of the [N1–B1–C21–N2] π system in 5a\textsuperscript{b\textsubscript{Mes}} compared to 5a\textsuperscript{Mes}, as deduced from the crystallographic data. 5a\textsuperscript{b\textsubscript{Mes}} may thus be regarded as the first examples of 2-aza-1,4-diborabutatrienes. Other reported azaborabutatrienes include a 1-aza-2-borabutatriene rhodium complex generated by borylene transfer from a molybdenum aminoborylene complex to a rhodium vinylidene,\textsuperscript{[39]} as well as a couple of aminoborylacte- lenes Et\textsubscript{3}N–C=C–BY\textsubscript{2} (Y = Mes, NMe\textsubscript{2}),\textsuperscript{[40,41]} which show significant contribution from their 1-aza-4-borabutatriene resonance forms, Et\textsubscript{3}N–C=C–BY\textsubscript{2}.

Conclusion

We have shown that CAAC-stabilized (cyano)hydroboryl anions may be isolated as either dimeric or monomeric lithium THF adducts, depending on the steric of the CAAC ligand. The monomeric species, however, is extremely moisture-sensitive and is best generated in situ for further reactivity. The prepared [CAAC]BH(CN)\textsuperscript{−} anions acts as boron-centered nucleophiles towards the majority of organohalides, including alkyl, haloalkyl, and allyl halides as well as acid chlorides, resulting in the formation of fully unsymmetrically substituted cyano(hydro) organoboranes. This reaction constitutes a very promising late-stage method to elaborate the family of boranes with a wide range of organic electrophiles, compounds that would otherwise be difficult to prepare. In contrast, the reaction with 1,2-dibromopropane leads to bromine abstraction and elimination of propene gas, which is likely the driving force of this reaction. The reactions of [CAAC]BH(CN)\textsuperscript{−} with haloboranes result in nucleophilic attack by the terminal cyano nitrogen atom and the formation of a linear B–C=N–B chain. X-ray crystallographic

Figure 4. Left: Crystallographically-derived molecular structures of 5a\textsuperscript{Mes} and 5a\textsuperscript{b\textsubscript{Mes}}. Atomic displacement ellipsoids are set at 50 % probability. Ellipsoids of carbon atoms of the ligand periphery and hydrogen atoms omitted for clarity, except for boron-bound hydrides. Selected bond lengths (Å) and angles (°) for 5a\textsuperscript{b\textsubscript{Mes}}; N1–C1 1.3382(13), C1–B1 1.5117(17), B1–C21 1.4574(15), C21–N2 1.158(3), N2–B2 1.4107(15), B1–C21–N2 174.05(11), C21–N2–B2 169.71(11), Σ₁(B1) = 359.35(10), Σ₁(B2) = 359.97(10); for 5a\textsuperscript{b\textsubscript{Mes}}; N1–C1 1.347(9), C1–B1 1.449(5), B1–C21 1.4801(16), C21–N2 1.1814(14), N2–B2 1.4338(14), B2–N3 1.4158(14), B2–N4 1.4263(14), B1–C21–N2 174.56(11), C21–N2–B2 156.36(10), Σ₁(B1) = 359.68(5), Σ₁(B2) = 360.00(9). Right: Canonical Kohn–Sham molecular orbitals of 5a\textsuperscript{Mes} and 5a\textsuperscript{b\textsubscript{Mes}} at the B3LYP/def2-SVP level of theory.
and DFT analyses of these orange/red compounds show a significant contribution of the cumulenic B=C=N−B resonance form, making these the first examples of azadiborabutatrienes.

**Experimental Section**

**Crystallographic data**: Deposition numbers 2065319, 2065320, 2065321, 2065322, 2065323, 2065325, 2065326, 2065327, 2065328, 2065329, 2065330, 2065331, 2065332, 2065333, 2065334, 2065335, 2065336, and 2065337 contain the supplementary data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**: boron - boryl anion - cumulene - nucleophile

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