Supporting Information

Completing the series of boron-nucleophilic cyanoborates: Boryl anions of type NHC–B(CN)$_2^-$

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**Synthetic details and procedures**

General Remarks: All procedures involving air- or moisture-sensitive compounds were performed in a glove box (MBraun 200B) under dry argon atmosphere or using Schlenk techniques. Solvents were purified using a Solvent Purification System (Braun) and stored over molecular sieve (3-4 Å). All commercially available compounds (TCI, aber, Sigma Aldrich) were used without further purification if not otherwise stated. The compounds B(SEt)_3[^1], Me_3SiCN[^2], 1,3-dimethyl-benzimidazolium-iodide (BAC·HI)^[^3], B (IMes)^[^4] and A [IMe(Me)_2]^[^5] were prepared according to literature methods. Abbreviations used:

![Structures](image)

NMR spectra were recorded on Bruker Avance II-300, Avance III-HD, Avance III-400 and Bruker DRX-40 instruments. The chemical shifts (δ) are reported in parts per million (ppm).
The residual solvent peaks (THF-d$_7$, $\delta = 3.58$ ppm; benzene-d$_5$, $\delta = 7.16$ ppm; CHCl$_3$, $\delta = 7.26$ ppm; toluene-d$_8$, $\delta = 2.08$ ppm; CHDCl$_2$, $\delta = 5.32$ ppm) are used for referencing of the $^1$H spectra. The $^{13}$C spectra are internally calibrated by using the $^{13}$C resonances of the solvent peaks (THF-d$_8$, $\delta = 67.21$ ppm; CDCl$_3$, $\delta = 77.16$ ppm; benzene-d$_5$, $\delta = 128.06$ ppm; toluene-d$_8$, $\delta = 20.43$ ppm; CD$_2$Cl$_2$, $\delta = 53.84$ ppm). For $^{19}$F and $^{11}$B NMR an external calibration with CFCl$_3$ and BF$_3$·Et$_2$O was used. Coupling constants are stated in Hertz (Hz), multiplicities are defined as s (singlet), br s (broad singlet), d (doublet), t (triplet), q (quartet), br q (broad quartet), quin (quintet) or m (multiplet).

In general, $^{13}$C-NMR NMR signals of boron bound carbon atoms are broad due to the quadrupolar environment of $^{10}$B and $^{11}$B nuclei and could only be detected for the compounds as stated. In all other cases the carbon signal is reported as not observed and further increase of the substance concentration led to signal broadening of the remaining 13C-NMR signals due to substance aggregation or elevated viscosity.

Elemental analyses were accomplished by combustion and gas chromatographic analysis using a VarioMICRO Tube and HW detection. Values are reported in %.

The IR spectra were recorded on a Bruker Vertex 70.

The UV/Vis spectra were recorded on a Varian Cary 50 Scan.

GC-MS were recorded on a Finnigan MAT 8400-MSS I, Finnigan MAT 4515 and Finnigan LCQDeca using ES and ESI$^+$/-$ methods using a Finnigan MAT 95 XL Trap.

**X-ray crystallography**

Single crystals were mounted on glass fibres in perfluorinated oil. Intensity measurements (at 100 K) were registered on Oxford Diffraction diffractometers, either Xcalibur E with monochromated Mo $K\alpha$ or Nova A with mirror-focused Cu $K\alpha$ radiation. Absorption corrections were based on multi-scans. The structures were refined anisotropically on $F^2$ using the program SHELXL-97 or SHELXL-14.[6]

Treatment of hydrogen atoms: Hydrogen atoms were added using rigid methyl groups or a riding model.

*Exceptions and special features*: Compound 1B was measured at 130 K because the crystals shatter at 100 K, presumably because of a phase transition. It is achiral and crystallizes only by chance in a chiral (Söhncke) space group (the same is true of 3A). For compound 2B, the methyl hydrogens at C11 were refined in an idealized hexagon of half-occupied sites.
Compound 7A crystallizes as a dichloromethane solvate; both residues display crystallographic mirror symmetry. Compound 7B crystallizes as a pseudomerohedral twin because its β angle is close to 90°; the relative volume of the smaller twin component refined to 0.4131(4). The asymmetric unit contains three molecules related approximately by the translation c/3; however, the separation is not exact. Each molecule displays approximate mirror symmetry (r.m.s deviations 0.08, 0.05, 0.03 Å). The molecule of 7C displays crystallographic mirror symmetry. For K-8B, regions of badly disordered THF were removed with the program SQUEEZE;[13] the quoted composition, formula mass etc. involve an idealized content of 4 THF per asymmetric unit. The compound [K(18-cr-6)-8C crystallizes as an inversion-symmetric dimer. Compound 11 crystallizes with two independent molecules, each with mirror symmetry; the dichloromethane molecule also has mirror symmetry. Compound 14 crystallizes as a dichloromethane solvate.

For those molecules not shown as Figures in the main publication, ellipsoid diagrams are given below (pp. 58 ff.). For all compounds with informative packing diagrams, these are also given.

Complete data have been deposited at the Cambridge Crystallographic Data Centre under the CCDC numbers 1550754 (1B), 1550755 (2B), 1550760 (7B), 1550767 (K-8B), 1550769 (9), 1550740 (1C), 1550756 (2C), 1550774 (7C), 1550768 {[K(18-cr-6)-8C, 1550770 (11), 1550771 (13), 1550772 (14), 1550757 (3A), 1550759 (7A), 1550758 (4) and can be obtained free of charge at http://www.ccdc.cam.ac.uk/.
Synthesis of IMes-substituted compounds.

IMes-B(SEt)$_3$ (1B).

B(SEt)$_3$ (1.28 g, 6.57 mmol) was added to a solution of IMes (2.00 g, 6.57 mmol) in toluene (25 mL). After stirring for 5 min, pentane (40 mL) was added to complete the precipitation of a crystalline solid. After filtration, washing with pentane (40 mL) and drying \textit{in vacuo} the product (2.16 g, 4.34 mmol, 66%) was obtained as colorless crystalline material. Crystals suitable for X-ray crystallography were obtained by slow diffusion of pentane into a solution of the product in THF.

$^1$H NMR (300.1 MHz, C$_6$D$_6$): $\delta$ (ppm) = 6.75 (m, 4 H, Mes-meta-C$_3$H), 5.76 (s, 2 H, NCH), 2.57 (br q, 6 H, BSCH$_2$, $^3$J$_{HH}$ = 7.4 Hz), 2.24 (s, 12 H, Mes-ortho-CH$_3$), 2.10 (s, 6 H, Mes-para-CH$_3$), 1.32 (t, 9 H, BSCH$_2$CH$_3$, $^3$J$_{HH}$ = 7.5 Hz).

$^{13}$C{$^1$H} NMR (75.5 MHz, C$_6$D$_6$): $\delta$ (ppm) = 139.3 (s, Mes-para-C), 136.1 (s,Mes-ipso-C), 135.9 (s, Mes-ortho-C), 129.2 (s, Mes-meta-CH), 123.1 (s, NCH), 24.1 (s, BSCH$_2$CH$_3$), 21.1 (s, Mes-para-CH$_3$), 19.1 (s, 4 C, Mes-ortho-CH$_3$), 17.7 (s, BSCH$_2$CH$_3$), not observed (BCN).

$^{11}$B{$^1$H} NMR (96.3 MHz, C$_6$D$_6$): $\delta$ (ppm) = −2.0 (s, $\omega_{1/2}$ = 3 Hz).

Elemental Analysis. Calcd. for C$_{27}$H$_{40}$BN$_2$S$_3$: C 65.04, H 7.88, N 5.62. Found: C 64.97, H 7.83, N 5.82.

MS: Representative mass spectra could not be recorded.

IR (ATR, cm$^{-1}$): $\tilde{\nu}$ = 3159 (w), 3100 (w), 2976 (m), 2956 (m), 2919 (m), 2861 (m), 1609 (w), 1566 (w), 1483 (m), 1453 (m), 1408 (m), 1376 (m), 1222 (m), 854 (s), 773 (s), 742 (s), 684 (s).
IMes-B(SEt)$_2$CN (2B).

A solution of Me$_3$SiCN (56 mg, 0.57 mmol) in benzene (0.5 mL) was slowly added to IMes-B(SEt)$_3$ (1B, 101 mg, 0.20 mmol) dissolved in toluene (2 mL). The mixture was heated to 45 °C for 24 h, and colorless crystals precipitated. The supernatant solution was removed, the solid residue washed with toluene (0.6 mL) and dried in vacuo (59 mg, 0.13 mmol, 64%). Crystals suitable for X-ray crystallography were obtained by slow diffusion of hexane into a solution of the product in THF.

$^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = 7.05 (s, 2H, NC$_2$H), 7.02-7.03 (m, 4H, Mes-meta-CH), 2.38 (s, 6 H, Mes-para-CH$_3$), 2.25 (q, 6 H, BSCH$_2$, $^3$J$_{HH}$ = 7.5 Hz), 2.20 (s, 12 H, Mes-ortho-CH$_3$), 1.08 (t, 6 H, BSCH$_2$CH$_3$, $^3$J$_{HH}$ = 7.5 Hz).

$^{13}$C{$^1$H} NMR (100 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = 140.7 (s, Mes-para-C), 136.2 (s, Mes-ipso-C), 134.2 (s, Mes-ortho-C), 129.3 (s, Mes-meta-CH), 124.6 (s, BCNCH), 25.2 (s, BSCH$_2$CH$_3$), 21.3 (s, Mes-para-CH$_3$), 18.6 (s, Mes-ortho-CH$_3$), 16.8 (s, BSCH$_2$CH$_3$), not observed (BCN).

$^{11}$B{$^1$H} NMR (96.3 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = -13.7 (s, $\omega_{1/2}$ = 3 Hz).

Elemental Analysis. Calcd. for C$_{26}$H$_{35}$BN$_3$S$_2$: C 67.37, H 7.39, N 9.07. Found: C 67.38, H 7.08, N 8.89.

MS (EI): m/z = 402.2 [M–SEt]$^+$. 

IR (ATR, cm$^{-1}$): $\tilde{\nu}$ = 3171 (w), 3120 (w), 3081 (w), 2976 (w), 2914 (m), 2859 (w), 2736 (w), 2194 (w), 1764 (w), 1731 (w), 1610 (w), 1564 (w), 1485 (m), 1440 (m), 1415 (m), 1372 (w), 1301 (w), 1260 (m), 1230 (m), 1172 (w), 1150 (w), 1091 (w), 1060 (w), 1038 (w), 1017 (w), 984 (w), 967 (w), 931 (w), 901 (w), 879 (m), 864 (m), 850 (m), 784 (s), 768 (m), 750 (m), 737 (m), 696 (s), 672 (m).
IMes-B(CN)$_2$SEt (3B).

Me$_3$SiCN (2.28 g, 23 mmol) dissolved in toluene (15 mL) was added dropwise to a solution of IMes-B(SEt)$_3$ (1B, 5.00 g, 10 mmol) in toluene (50 mL). After addition of B(SEt)$_3$ (150 mg, 0.77 mmol) the reaction mixture was heated to 95 °C for 12 h, whereupon the product precipitated. The hot suspension was filtered and the solid product (2.72 g, 6.35 mmol, 64%) was dried in vacuo. The material was sufficiently pure for further reactions. Analytically pure samples could be obtained by washing the product with hot toluene several times.

$^1$H NMR (400 MHz, CD$_2$Cl$_2$): δ (ppm) = 7.19 (s, 2 H, BCNCH), 7.06-7.08 (m, 4 H, Mes-meta-CH), 2.39 (s, 6 H, Mes-para-CH$_3$), 2.36-2.28 (m, 2 H, BSCH$_2$), 2.17 (s, 12 H, Mes-ortho-CH$_3$), 1.12 (t, 3 H, BSCH$_2$CH$_3$, $^3$J$_{HH}$ = 7.4 Hz).

$^{13}$C{$^1$H} NMR (100 MHz, CD$_2$Cl$_2$): δ (ppm) = 141.5 (s, Mes-para-C), 136.0 (s, Mes-ipso-C), 133.0 (s, Mes-ortho-C), 129.7 (s, Mes-meta-CH), 125.2 (s, NCH), 25.1 (s, SCH$_2$CH$_3$), 21.4 (s, Mes-para-CH$_3$), 18.3 (s, Mes-ortho-CH$_3$), not observed (SCH$_2$CH$_3$), not observed (BCN).

$^{11}$B{$^1$H} NMR (96.3 MHz, CD$_2$Cl$_2$): δ (ppm) = −24.8 (s, $\omega_{\mathbf{B}} = 3$ Hz).

Elemental Analysis. Calcd. for C$_{25}$H$_{29}$BN$_4$S: C 70.09, H 6.82, N 13.08, S 7.48. Found: C 69.75, H 6.88, N 12.64, S 7.23.

MS (EI): m/z = 428.2 [M]$^+$, 367.2 [M−SEt]$^+$.

IR (ATR, cm$^{-1}$): $\tilde{\nu}$ = 3165 (w), 3133 (w), 3100 (w), 2972 (w), 2925 (w), 2857 (w), 2732 (w), 2200 (w), 2124 (w), 1723 (w), 1610(w), 1561 (w), 1485 (m), 1440 (m), 1375 (w), 1322 (w), 1290 (w), 1262 (w), 1236 (m), 1177 (w), 1160 (w), 1112 (w), 1067 (w), 1038 (w), 1001 (w), 977 (w), 951 (w), 933 (m), 918 (w), 897 (m), 867 (m), 849 (m), 815 (w), 793 (m), 767 (m), 742 (m), 711 (s), 674 (w), 618 (w).
**Me₃Si-N≡C-B(CN)₂SEt (4).**

B(SEt)₃ (490 mg, 2.53 mmol) was added to a solution of Me₃SiCN (910 mg, 9.19 mmol) in toluene (3 mL). After 30 min a crystalline precipitate had formed. The supernatant solution was decanted and the remaining solids were washed with toluene. After drying *in vacuo* the product (230 mg, 1.03 mmol, 41%) was obtained as colorless crystals.

**¹H NMR (300 MHz, CD₂Cl₂):**  δ (ppm) = 2.60 (q, 2 H, SCH₂CH₃,  ³J_HH = 7 Hz), 1.33 (t, 3 H, SCH₂CH₃,  ³J_HH = 7 Hz), 0.62 [s, 9 H, Si(CH₃)₃].

**¹³C{¹H} NMR (75 MHz, CD₂Cl₂):** δ (ppm) = 24.6 (s, SCH₂CH₃), 16.9 (s, BSCH₂CH₃), −0.8 [s, Si(CH₃)₃].

**¹¹B{¹H} NMR (96.3 MHz, CD₂Cl₂):** δ (ppm) = −28.1 (s, ω₂ = 14 Hz).

Elemental Analysis. Calcd. for C₈H₁₄BN₃SSi: C 43.05, H 6.32, N 18.83, S 14.37. Found: C 42.74, H 6.13, N 18.39, S 13.91.

**MS (EI):** m/z = 124.0 [B(CN)₂SEt]⁺.

**IR (ATR, cm⁻¹):** ν = 2976 (w), 2930 (w), 2871 (w), 2615 (w), 2316 (w), 2271 (m), 2223 (w), 2034 (w), 1975 (w), 1892 (w), 1671 (w), 1494 (w), 1457 (w), 1438 (w), 1375 (w), 1254 (m), 1061 (w), 984 (w), 951 (w), 904 (w), 864 (s), 843 (s), 795 (m), 774 (s), 677 (w), 634 (m).
IMes-B(CN)$_2$Br (6B).

Br$_2$ (56 mg, 0.35 mmol) was added to a solution of IMes-B(CN)$_2$SEt (3B, 150 mg, 0.35 mmol) in CH$_2$Cl$_2$ (20 mL). After stirring for 90 s, the pale brown solution was evacuated to dryness. The remaining solid was recrystallized twice by slow diffusion of pentane into a solution of the solid in CHCl$_3$. The product was obtained as a pale pink powder (104 mg, 0.23 mmol, 67%).

In an alternative approach IMes-B(CN)$_2$H (368 mg, 1.00 mmol) was dissolved in CH$_2$Cl$_2$ (20 mL). Br$_2$ (160 mg, 1.00 mmol) was added and the red solution was stirred for 5 min. All volatile components were removed in vacuo. The remaining solid was recrystallized by slow diffusion of pentane into a solution of the solid in CHCl$_3$. The product was obtained as a colorless powder (344 mg, 0.77 mmol, 77%).

Samples obtained from both procedures gave identical $^1$H and $^{11}$B NMR spectra.

$^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = 7.26 (s, 2 H, NC$_{mes}$H), 7.08 (m, 4 H, Mes-meta-C$_{mes}$H), 2.39 (s, 6 H, Mes-para-C$_{mes}$H$_3$), 2.16 (s, 12 H, Mes-ortho-C$_{mes}$H$_3$).

$^{13}$C{$^1$H} NMR (150 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = 141.9 (s, Mes-para-C), 135.8 (s, Mes-ipso-C), 132.4 (s, Mes-ortho-C), 129.9 (s, Mes-meta-C), 125.5 (s, NCH), 21.4 (s, Mes-para-C$_3$H), 18.3 (s, Mes-ortho-C$_3$H), not observed (BCN).

$^{11}$B{$^1$H} NMR (128.5 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = $-29.3$ (s, $\omega_\frac{1}{2} = 38$ Hz).

Elemental Analysis. Calcd. for C$_{23}$H$_{24}$BrN$_4$: C 61.78, H 5.41, N 12.53. Found: C 61.74, H 5.35, N 12.23.

MS (EI): m/z = 446.1 [M]$^+$, 420.1 [M–CN]$^+$. 

IR (ATR, cm$^{-1}$): $\tilde{\nu}$ = 3160 (w), 3135 (w), 2920 (w), 2854 (w), 2211 (w), 1748 (w), 1633 (w), 1609 (w), 1561 (w), 1483 (m), 1454 (m), 1414 (w), 1380 (m), 1323 (w), 1290 (w), 1233 (m), 1261 (w), 1184 (w), 1134 (m), 1178 (w), 1163 (w), 1094 (w), 1035 (w), 980 (m), 947 (w), 932 (w), 896 (w), 874 (m), 857 (m), 778 (s), 681 (s).
IMes-B(CN)$_2$I (7B).

Methyl iodide (9.10 g, 64 mmol) was added to a solution of IMes-B(CN)$_2$SEt (3B, 2.75 g, 6.4 mmol) in CH$_2$Cl$_2$ (120 mL). After stirring for 3 d the mixture was washed with brine (3 × 100 mL). The organic phase was dried over MgSO$_4$, and the solvent was removed in vacuo. The solid residue was recrystallized by slow diffusion of pentane into a highly concentrated solution in CH$_2$Cl$_2$. After 5 d the supernatant solution was removed, the colorless crystals (1.5 g, 3 mmol, 47%) were washed with CH$_2$Cl$_2$ (3×5 mL) and dried in vacuo. A second crop obtained from the yellow solution increased the yield to 68%.

$^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = 7.26 (s, 2 H, NCH), 7.08 (br s, 4 H, Mes-meta-C$_H$), 2.40 (s, 6 H, Mes-para-C$_H_3$), 2.19 (s, 12 H, Mes-ortho-C$_H_3$).

$^{13}$C{$^1$H} NMR (100 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = 142.0 (s, Mes-para-C), 135.7 (s, Mes-ipso-C), 132.4 (s, Mes-ortho-C), 130.1 (s, Mes-meta-C), 125.7 (s, NCH), 21.4 (s, Mes-para-C$_H_3$), 18.9 (s, Mes-ortho-C$_H_3$), not observed (BCN).

$^{11}$B{$^1$H} NMR (96.3 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = −41.7 (s, $\omega_{\beta} = 46$ Hz).

Elemental Analysis. Calcd. for C$_{23}$H$_{25}$BIN$_4$: C 55.90, H 4.90, N 11.34. Found: C 55.67, H 4.81, N 11.32.

MS (EI): m/z = 494.0 [M]$^+$, 367.2 [M−I]$^+$.

IR (ATR, cm$^{-1}$): $\tilde{\nu}$ = 3164 (w), 3138 (w), 2921 (w), 2858 (w), 2733 (w), 2207 (w), 1803 (w), 1766 (w), 1611 (w), 1561 (w), 1484 (m), 1449 (m), 1410 (w), 1378 (m), 1322 (w), 1291 (w), 1233 (m), 1184 (w), 1167 (m), 1095 (w), 1036 (w), 990 (w), 956 (m), 930 (w), 897 (w), 876 (s), 864 (s), 775 (s), 727 (m), 703 (w), 683 (w), 666 (m), 648 (s).
**K[IMes-B(CN)$_2$] (K-8B).**

IMes-B(CN)$_2$I (7B, 1.4 g, 2.8 mmol) was added to a suspension of KC$_8$ (2.28 g, 16.8 mmol) in THF (30 mL). After stirring for 20 min at r.t. the mixture was filtered. The solution was dried *in vacuo* to obtain the product as a deep-red solid (966 mg, 2.38 mmol, 85% yield). Crystals suitable for X-ray crystallography were obtained by slow diffusion of pentane into a solution of the product in THF.

$^1$H NMR (300 MHz, THF-$d_8$): $\delta$ (ppm) = 6.76 (br s, 4 H, Mes-meta-CH), 6.1 (br s, NCH), 2.20 (br s, 6 H, Mes-para-CH$_3$), 2.15 (br s, 12 H, Mes-ortho-CH$_3$).

$^{13}$C{$^1$H} NMR (75 MHz, THF-$d_8$): $\delta$ (ppm) = 138.5 (s, Mes-para-C), 137.7 (s, Mes-ipso-C), 136.1 (s, Mes-ortho-C), 128.8(s, Mes-meta-CH), 115.7 (s, NCH), 21.2 (s, Mes-para-CH$_3$), 18.8 (s, Mes-ortho-CH$_3$), not observed (BCN).

$^{11}$B{$^{11}$H} NMR (96.3 MHz, THF-$d_8$): $\delta$ (ppm) = $-28.3$ (s, $\omega_{1/2} = 107$ Hz).

MS: Representative mass spectra could not be recorded.

**Figure 1:** Molecular structure of (K-8B)$_9$ (nonameric unit) as found in the asymmetric unit. THF solvent molecules were treated with SQUEEZE for clarity. Hydrogen atoms omitted.
Experimental IR spectrum of $\text{[K(18-cr-6)]-8B}$, THF solution, cm$^{-1}$: $\nu = 2123$ (s), 2090 (s).

Calculated IR spectrum of 8B, cm$^{-1}$: $\nu = 2140$ (s), 2055 (m).

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Figure 2: Experimental IR spectrum of $\text{[K(18-cr-6)]-8B}$.

Figure 3: Calculated IR spectrum of anion 8B.
Experimental UV-Vis (THF):

\[ \lambda_{\text{max}} = 361 \text{ nm, } \varepsilon = 9.96 \cdot 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}, \text{ shoulder } \lambda_{\text{max}} = 480 \text{ nm, } \varepsilon = 5.52 \cdot 10^3 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}. \]

Figure 4: Experimental UV-Vis spectrum of K-8B.

TD-DFT analysis diagnostic UV-VIS transitions:

Intense charge transfer within the B–C carbene bond, partly delocalized \((f_{\text{osc}} = 0.507, \lambda = 295 \text{ nm})\) HOMO \(\rightarrow\) LUMO+4 transition (60%).

Figure 5: Computed difference electron density of N-UV-transition 19 in anion 8B (blue: donor orbitals, red: acceptor orbitals).

Moderately intense charge transfer from the boron-centred lone pair into the symmetrical \(\pi\)-orbital of the mesityl groups \((f_{\text{osc}} = 0.028, \lambda = 478 \text{ nm})\) HOMO \(\rightarrow\) LUMO+1 transition (98%).

Figure 6: Computed difference electron density of Vis-transition 5 in anion 8B (blue: donor orbitals, red: acceptor orbitals).
IMes-B(CN)$_2$Me (9).

Methyl iodide (0.05 mL, 0.80 mmol) was added dropwise to a solution of K-8B (300 mg, 0.74 mmol) in THF (15 mL). A colorless precipitate formed immediately. After stirring for 10 min at r.t. the precipitate was removed by filtration. The filtrate was evaporated to dryness in vacuo and the solid recrystallized by slow diffusion of pentane into a solution of crude product in CHCl$_3$ (42 mg, 0.12 mmol, 15%).

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ (ppm) = 7.13 (s, 2 H, NCH), 7.05 (s, 4 H, Mes-meta-CH), 2.37 (s, 6 H, Mes-para-CH$_3$), 2.14 (s, 12 H, Mes-ortho-CH$_3$), -0.27 (s, 3 H, BCH$_3$).

$^{13}$C {$^1$H} NMR (150 MHz, CDCl$_3$): $\delta$ (ppm) = 141.0 (s, Mes-para-C), 135.2 (s, Mes-ortho-C), 132.9 (s, Mes-ipso-C), 129.6 (s, Mes-meta-C), 124.2 (s, NCH), 21.3 (s, Mes-para-CH$_3$), 17.8 (s, Mes-ortho-CH$_3$), not observed (BCN).

$^{11}$B {$^1$H} NMR (96.3 MHz, CDCl$_3$): $\delta$ (ppm) = -27.6 (s, $\omega_{1/2}$ = 44 Hz).

Elemental Analysis. Calcd. for C$_{23}$H$_{25}$BIN$_4$: C 75.40, H 7.12, N 14.65. Found: C 75.12, H 7.13, N 14.36.

MS: Representative mass spectra could not be recorded.

IR (ATR, cm$^{-1}$): $\nu = 3163$ (w), 2980 (s), 2919 (m), 2201 (w), 1654 (w), 1610 (w), 1565 (w), 1486 (s), 1448 (s), 1381 (m), 1315 (w), 1235 (s), 1156 (s), 1006 (s), 965 (s), 930 (s), 854 (s), 770 (m), 723 (s).
IMes-B(CN)\(_2\)Au(PMe\(_2\)Ph) (10).

AuCl(PMe\(_2\)Ph) (187 mg, 0.51 mmol) in THF (4 mL) was added to a solution of K-8B (207 mg, 0.51 mmol) in THF (20 mL). After stirring for 2 h, the mixture was filtered, and the filtrate was evaporated to dryness in vacuo. The product was obtained as a red solid (190 mg, 0.27 mmol, 53%). Analytically pure samples were obtained by repeated (three times) slow diffusion of pentane into a solution of the crude product in THF to afford a colorless crystalline material.

\(^1\)H NMR (300 MHz, THF-d\(_8\)): \(\delta\) (ppm) = 7.68-7.61 (m, 2 H, Ph-CH), 7.43-7.39 (m, 3 H, Ph-CH), 7.10 (s, 2 H, NCH), 6.88-6.87 (m, 4 H, Mes-meta-CH), 2.26 (s, 6 H, Mes-para-CH\(_3\)), 2.18 (s, 12 H, Mes-ortho-CH\(_3\)), 1.55 (d, \(^2\)J\(_{PH}\) = 8 Hz, 6 H, PCH\(_3\)).

\(^13\)C\(^{\{1\}H}\) NMR (75 MHz, THF-d\(_8\)): \(\delta\) (ppm) = 139.7 (s, Mes-para-C), 136.5 (s, Mes-ortho-C), 134.8 (s, Mes-ipso-C), 132.5 (d, \(^2\)J\(_{PC}\) = 13 Hz, Ph-ortho-CH), 130.8 (s, Ph-para-CH), 129.6 (s, Mes-meta-C), 129.3 (d, \(^2\)J\(_{PC}\) = 10 Hz, Ph-meta-CH), 122.7 (s, NCH), 21.1 (s, Mes-para-CH\(_3\)), 18.9 (s, Mes-ortho-CH\(_3\)), 14.7 (d, \(^1\)J\(_{PC}\) = 24 Hz, P-CH\(_3\)), not observed (BCN), not observed (Ph-ipso-C).

\(^11\)B\(^{\{1\}H}\) NMR (96.3 MHz, THF-d\(_8\)): \(\delta\) (ppm) = −29.7 [d, \(^2\)J\(^{11\}B}\)\(^{11\}B\) = 65 Hz, \(\omega_{11}\) = 116 Hz].

\(^{31}\)P\(^{\{1\}H}\) NMR (121.5 MHz, THF-d\(_8\)): \(\delta\) (ppm) = 27.7 [d, \(^2\)J\(^{31\}P}\)\(^{11\}B\) = 70 Hz].

Elemental Analysis. Calcd. for C\(_{33}\)H\(_{35}\)AuBN\(_4\)P: C 53.01, H 5.02, N 7.98. Found: C 53.45, H 5.34, N 7.26.

MS: Representative mass spectra could not be recorded.

IR (ATR, cm\(^{-1}\)): \(\tilde{v}\) = 3154 (w), 2971 (w), 2912 (w), 2856 (w), 2164 (m), 1610 (w), 1562 (w), 1486 (m), 1435 (m), 1408 (m), 1375 (w), 1310 (m), 1232 (s), 1183 (w), 1150 (w), 1105 (m), 1063 (m), 1032 (w), 982 (s), 953 (m), 908 (s), 848 (m), 807 (w), 695 (m), 649 (w).
Synthesis of BAC-substituted compounds  

**BAC-B(SEt)₃ (1C).**

A solution of NaHMDS (6.62 g, 36.1 mmol) in THF (30 mL) was slowly added to a cooled (−78 °C) suspension of 1,3-dimethyl-1H-benzimidazolium iodide (9.89 g, 36.1 mmol) and THF (40 mL). After stirring for 5 min at −78 °C a solution of B(SEt)₃ (7.01 g, 36.1 mmol) in THF (20 mL) was added dropwise. The yellow solution was warmed to room temperature and stirred for 3 d. The solution was filtered to remove precipitated salts, and the filtrate was evaporated to dryness *in vacuo*. The residue was dissolved in toluene (100 mL). The opaque solution was filtered and evaporated to dryness. The remaining solid was washed with pentane (50 mL) to afford a colorless powder (9.19 g, 26.9 mmol, 75%). Crystals suitable for X-ray crystallography were obtained by slow diffusion of hexane into a solution of the product in toluene.

**1H NMR** (600 MHz, toluene-d₈): δ(ppm) = 6.89-6.87 (m, 2 H, ar-H), 6.62-6.60 (m, 2 H, ar-H), 4.10 (s, 6H, NCH₃), 2.77-2.73 (m, 6H, SCH₂CH₃), 1.31 (t, 3JHH=7.5 Hz, 9H, SCH₂CH₃).

**13C {¹H} NMR** (150 MHz, toluene-d₈): δ(ppm) = 133.5 (s, ar-CN), 124.7 (s, ar-CH), 111.3 (s, ar-CH), 34.3 (s, NCH₃), 23.8 (s, SCH₂CH₃), 17.7 (s, SCH₂CH₃), not observed (BCN).

**11B {¹H} NMR** (128.5 MHz, toluene-d₈): δ(ppm) = −1.2 (s, ω₁/₂= 3 Hz).

Elemental Analysis. Calcd. for C₁₅H₂₅BN₂S₃: C 52.93, H 7.40, N 8.23, S 28.26. Found: C 52.59, H 7.26, N 8.39, S 28.32.

**MS (EI):** m/z = 279.1 [M−SEt]⁺.

**IR (ATR, cm⁻¹):** ν = 3060 (w), 2961 (w), 2928 (w), 2916 (w), 1485 (m), 1453 (m), 1439 (m), 1382 (m), 1350 (w), 1326 (w), 1255 (m), 1194 (w), 1139 (w), 1053 (w), 1020 (w), 975 (w), 926 (w), 833 (s), 818 (s), 728 (s), 667 (m), 602 (m).
BAC-B(SEt)$_2$CN (2C).

BAC-B(SEt)$_3$ (1C, 2 g, 5.86 mmol) was dissolved in toluene (20 mL) and Me$_3$SiCN (581 mg, 5.86 mmol) in toluene (5 mL) was added dropwise. After stirring the mixture for 24 h at 45 °C the solvent was evaporated to dryness. The solid residue was dissolved in CH$_2$Cl$_2$ and purified by silica pad filtration. The product (1.41 g, 5.0 mmol, 86%) was obtained as a pale yellow solid after drying in vacuo. Crystals suitable for X-ray crystallography were obtained by slow diffusion of pentane into a solution of the product in CH$_2$Cl$_2$.

$^1$H NMR (400 MHz, C$_6$D$_6$): $\delta$(ppm) = 6.93-6.89 (m, 2 H, ar-H), 6.56-6.52 (m, 2 H, ar-H), 3.87 (s, 6 H, NCH$_3$), 3.03-2.94 (m, 2H, SCH$_2$CH$_3$), 2.91-2.82 (m, 2 H, SCH$_2$CH$_3$)$_3$, 1.35 (t, $^3J_{HH}$ = 7 Hz, 6 H, SCH$_2$CH$_3$).

$^{13}$C{$_^1$H} NMR (100 MHz, C$_6$D$_6$): $\delta$(ppm) = 132.7 (s, ar-CN), 124.8 (s, ar-CH), 111.2 (s, ar-CH), 33.6 (s, NCH$_3$), 24.4 (s, SCH$_2$CH$_3$), 17.3 (s, SCH$_2$CH$_3$), not observed (BCN).

$^{11}$B{$_^1$H} NMR (96.3 MHz, C$_6$D$_6$): $\delta$(ppm) = −13.72 (s, $\omega_{1/2}$= 3 Hz).

Elemental Analysis. Calcd. for C$_{14}$H$_{20}$BN$_3$S$_2$: C 55.08, H 6.60, N 13.77, S 21.00. Found: C 54.81, H 6.62, N 14.00, S 21.00.

MS (EI): m/z = 305.1 [M]$^+$, 244.1 [M−SEt]$^+$.

IR (ATR, cm$^{-1}$): $\nu$ = 3040 (w), 2982 (m), 2970 (m), 2922 (m), 2188 (w), 1480 (m), 1466 (s), 1429 (w), 1390 (s), 1372 (m), 1263 (m).
**BAC-B(CN)₂SEt (3C).**

Me₃SiCN (3.54 g, 35.7 mmol) was added to a solution of BAC-B(SEt)₃ (1C, 5.3 g, 15.6 mmol) in toluene (80 mL). Subsequently B(SEt)₃ (100 mg, 0.52 mmol) was added. The mixture was stirred for 12 h at 95 °C. The product precipitated as a yellow solid and was separated from the supernatant solution by filtration. The remaining solid was washed with pentane and dried *in vacuo* to afford the product (3.26 g, 12.1 mmol, 77%).

¹H NMR (400 MHz, CD₂Cl₂) δ(ppm) = 7.66-7.60 (m, 4 H, Ar-H), 4.30 (s, 6 H, NCH₃), 2.72-2.65 (m, 2 H, SCH₂CH₃), 1.33 (t, 3J_HH= 7.4 Hz, 2 H, SCH₂CH₃).

¹³C{¹H} NMR (100 MHz, CD₂Cl₂) (ppm) = 133.6 (s, ar-C), 128.0 (q, ¹J_BC = 70 Hz, BCN), 126.8 (s, ar-CH), 112.4 (s, ar-CH), 34.4 (s, NCH₃), 24.6 (s, SCH₂CH₃), 16.9 (s, SCH₂CH₃), not observed (carbene-BCN).

¹¹B{¹H} NMR (128.5 MHz, CD₂Cl₂): δ(ppm) = −24.7 (s, ωᵣ= 2 Hz).

Elemental Analysis. Calcd. for C₁₃H₁₅BN₄S: C 57.80, H 5.60, N 20.74, S 11.87. Found: C 57.65, H 5.55, N 20.49, S 11.67.

MS (EI): m/z: 270.1 [M]+, 209.1 [M−SEt]+.

IR (ATR, cm⁻¹): v = 2979 (w), 2202 (w), 2127 (w), 1493 (w), 1471 (s), 1395 (m), 1383 (m), 1350 (w), 1262 (m), 1253 (m), 1133 (w), 1065 (w), 1018 (m), 1008 (m), 940 (m), 912 (s), 829 (w), 808 (m), 763 (s), 758 (s), 692 (m), 665 (m).
BAC-B(CN)₂I (7C).
Methyl iodide (2.8 mL, 45.0 mmol) was added to a solution of BAC-B(CN)₂SEt (3C, 2.0 g, 7.4 mmol) in chloroform (40 mL). The resulting yellow mixture was stirred for 5 h at 70 °C. After cooling to r.t. the suspension was filtered and the residual pale yellow solid dried *in vacuo* (1.84 g, 5.5 mmol, 74%). Crystals suitable for X-ray crystallography were obtained by slow diffusion of pentane into a solution of the product in CH₂Cl₂.

\(^1\)H NMR (600 MHz, CD₂Cl₂) \(\delta(ppm) = 7.69-7.64 (m, 4 H, ar-H), 4.24 (s, 6 H, NCH₃)\).

\(^{13}\)C\{\(^1\)H\} NMR (150 MHz, CD₂Cl₂) \(\delta(ppm) = 133.6 (s, ar-CN), 127.2 (s, ar-CH), 112.5 (s, ar-CH), 34.6 (s, NCH₃), not observed (BCN)\).

\(^{11}\)B\{\(^1\)H\} NMR (96.3 MHz, CD₂Cl₂): \(\delta(ppm) = -41.2 (s, \omega_B = 30 Hz)\).

Elemental Analysis. Calcd. for C₁₁H₁₀BIN₄: C 39.33, H 3.00, N 16.68. Found: C 39.02, H 3.05, N 16.50.

MS (EI): m/z: 335.9 [M⁺], 209.9 [M-I⁺].

IR (ATR, cm⁻¹): \(v = 1473 (m), 1394 (w), 1354 (w), 1255 (w), 1207 (w), 1134 (w), 1020 (m), 1009 (w), 989 (w), 959 (w), 942 (w), 919 (m), 803 (w), 792 (w), 753 (s), 734 (w), 720 (m), 669 (w), 663 (w), 651 (w), 605 (w), v (CN) not observed."
**K[BAC-B(CN)] (K-8C).**

BAC-B(CN)I (7C, 250 mg, 0.7 mmol) was added to a solution of KC₈ (604 mg, 4.5 mmol) in DME (evaporated to dryness *in vacuo*). The product was obtained as a bright-orange solid (139 mg, 0.56 mmol, 80%).

18-crown-6 was added to increase the solubility of K-8C and to access further analysis. Crystals suitable for X-ray crystallography were obtained by slow diffusion of pentane into a mixture of 18-crown-6 and K-8C in THF to afford single crystals of [K(18-cr-6)][BAC-B(CN)]₂, [K(18-cr-6)]-8C.

**¹H NMR (300 MHz, THF-d8)**  δ(ppm) = 6.35-6.32 (m, 2 H, ar-H), 6.12-6.09 (m, 2 H, ar-H), 3.55 (s, 60 H, 18-crown-6 CH₂).

**¹³C{¹H} NMR (75 MHz, THF-d8)**  δ(ppm) = 139.5 (s, ar-CN), 117.8 (s, ar-CH), 101.0 (s, ar-CH), 70.9 (s, 18-cr-6 CH₂), 32.3 (s, NCH₃), not observed (BCN).

**¹¹B{¹H} NMR (96.3 MHz, THF-d8):**  δ(ppm) = −24.1 (s, ωᵥ = 20 Hz).

**MS:** Representative mass spectra could not be recorded.
Experimental IR of $[K(18\text{-cr-6})\cdot 8C]$, THF solution, cm$^{-1}$: $\nu = 2134$ (s), 2115 (m).

![Experimental IR spectrum of $[K(18\text{-cr-6})\cdot 8C]$.](image1)

**Figure 7:** Experimental IR spectrum of $[K(18\text{-cr-6})\cdot 8C]$.

Calculated IR spectrum of $8C$, cm$^{-1}$: $\nu = 2110$ (s), 2085 (m).

![Calculated IR spectrum of anion $8C$.](image2)

**Figure 8:** Calculated IR spectrum of anion $8C$. 
BAC-B(CN)$_2$Me (11).

Methyl iodide (0.2 mL, 3.2 mmol) was added to a suspension of K-8C (400 mg, 1.6 mmol) in THF (5 mL). After 10 min the reaction mixture was dried *in vacuo*, the residue was suspended in H$_2$O and the solution extracted three times with CH$_2$Cl$_2$. The combined organic phases were dried over Na$_2$SO$_4$ and the solvent was removed *in vacuo*. The residue was dissolved in CH$_2$Cl$_2$ and filtered through Celite®545. After evaporation of the filtrate to dryness BAC-B(CN)$_2$Me (233 mg, 1.04 mmol, 65%) was obtained. Crystals suitable for X-ray crystallography were obtained by slow diffusion of pentane into a solution of the product in CH$_2$Cl$_2$.

$^1$H NMR (600 MHz, CD$_2$Cl$_2$) $\delta$(ppm) = 7.64-7.62 (m, 2 H, ar-$H$), 7.59-7.58 (m, 2 H, ar-$H$), 4.20 (s, 6 H, NCH$_3$), 0.37 (s, 3 H, BCH$_3$).

$^{13}$C{$^1$H} NMR (150 MHz, CD$_2$Cl$_2$) $\delta$(ppm) = 133.5 (s, ar-CN), 126.3 (s, ar-CH), 112.1 (s, ar-CH), 34.0 (s, BCH$_3$), not observed (BCN).

$^{11}$B{$^1$H} NMR (96.3 MHz, CD$_2$Cl$_2$): $\delta$(ppm) = −27.4 (s, $\omega_{\beta} = 18$ Hz).

MS (EI): m/z: 224.1 [M]$^+$, 209.1 [M–CH$_3$]$^+$.

IR (ATR, cm$^{-1}$): $\nu$ = 3067 (w), 3040 (w), 2950 (w), 2903 (w), 2202 (w), 1473 (m), 1400 (w), 1354 (w), 1301 (w), 1261 (w), 1203 (w), 1140 (w), 1041 (w), 1016 (m), 1005 (m), 989 (m), 946 (w), 863 (w), 818 (m), 761 (s), 757 (s), 624 (w).

Elemental Analysis. Calcd. for C$_{12}$H$_{13}$BN$_4$ · 0.11 CH$_2$Cl$_2$ C 62.33, H 5.67, N 24.02. Found: C 62.49, H 5.72, N 23.68.
BAC-B(CN)$_2$SiMe$_3$ (12).

An excess of Me$_3$SiCl (0.1 mL, 0.8 mmol) was added to a suspension of K-8C (60 mg, 0.2 mmol) in THF (5 mL) and the mixture was stirred for 15 min. After removing the solvent *in vacuo*, the residue was dissolved in CH$_2$Cl$_2$, filtrated through Celite® 545, and the filtrate was evaporated to dryness *in vacuo*. The residue was recrystallized by slow diffusion of pentane into a solution of the solid in CH$_2$Cl$_2$ to afford the product (31 mg, 0.1 mmol, 54%).

$^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$(ppm) = 7.58-7.52 (m, 4 H, ar-H), 4.12 (s, 6 H, NCH$_3$), 0.14 [s, 9 H, Si(CH$_3$)$_3$].

$^{13}$C{$^1$H} NMR (100 MHz, CD$_2$Cl$_2$) $\delta$(ppm) = 133.7 (s, ar-CN), 125.8 (s, ar-CH), 111.5 (s, ar-CH), 34.2 (s, NCH$_3$), -1.0 [s, Si(CH$_3$)$_3$], not observed (BCN).

$^{11}$B{$^1$H} NMR (96.3 MHz, CD$_2$Cl$_2$): $\delta$(ppm) = $-$33.3 (s, $\omega_{1/2}$ = 27 Hz).

Elemental Analysis. Calcd. for C$_{14}$H$_{19}$BN$_4$Si: C 59.58, H 6.79, N 19.85. Found: C 59.62, H 6.90, N 19.68.

MS (EI): m/z: 282.1 [M]$^+$, 267.1 [M–Me]$^+$, 209.1 [M–Si(Me)$_3$]$^+$.

IR (ATR, cm$^{-1}$): $\nu$ = 2948 (w), 2892 (w), 2192 (m), 1965 (w), 1496 (w), 1471 (m), 1421 (w), 1395 (w), 1349 (w), 1259 (w), 1239 (m), 1203 (w), 1168 (w), 1127 (w), 1022 (m), 1017 (m), 955 (w), 929 (m), 830 (s), 751 (s), 737 (s), 690 (m), 683 (m), 665 (m), 624 (m), 612 (m).
**BAC-B(CN)$_2$SnMe$_3$ (13).**

Me$_3$SnCl (233 mg, 1.2 mmol) was added to a suspension of K-8C (290 mg, 1.2 mmol) in THF (10 mL) and the mixture was stirred for 15 min. The solvent was removed *in vacuo*, the solid residue dissolved in CH$_2$Cl$_2$ (25 mL) and filtered. Crystallization by slow diffusion of pentane into the solution of CH$_2$Cl$_2$ afforded the product (224 mg, 0.6 mmol, 50%). Crystals suitable for X-ray crystallography were obtained by slow diffusion of pentane into a solution of the product in CH$_2$Cl$_2$.

$^1$H NMR (600 MHz, CD$_2$Cl$_2$) $\delta$(ppm) = 7.54-7.50 (m, 4 H, ar-H), 4.06 (s, 6 H, NCH$_3$), 0.15 [s, 9 H, Sn(CH$_3$)$_3$].

$^{13}$C{$^1$H} NMR (150 MHz, CD$_2$Cl$_2$) $\delta$(ppm) = 133.6 (s, ar-CN), 129.5 (q, $^1$J$_{BC}$ = 71 Hz, BCN), 125.7 (s, ar-CH), 111.3 (s, ar-CH), 33.9 (s, NCH$_3$), -9.1 [s, Sn(CH$_3$)$_3$], not observed (carbene-BCN).

$^{11}$B{$^1$H} NMR (96.3 MHz, CD$_2$Cl$_2$): $\delta$(ppm) = -35.9 [satellites: d, $^1$J$(^{117}$Sn-$^{11}$B) = 325 Hz; d, $^1$J$(^{119}$Sn-$^{11}$B) = 338 Hz, $\omega_{1/2}$ = 6 Hz].

Elemental Analysis. Calcd. for C$_{14}$H$_{19}$BN$_4$Sn: C 45.10, H 5.14, N 15.03. Found: C 45.17, H 5.18, N 14.74.

MS (EI): m/z: 374.1 [M]$^+$, 209.1 [M−Sn(CH$_3$)$_3$]$^+$.  

IR (ATR, cm$^{-1}$): $\nu$ = 2971 (w), 2909 (w), 2188 (m), 1604 (w), 1493 (w), 1471 (m), 1421 (w), 1397 (w), 1346 (w), 1261 (w), 1204 (w), 1193 (w), 1168 (w), 1126 (w), 1023 (m), 1017 (m), 962 (w), 938 (m), 802 (w), 753 (s), 724 (m), 650 (w), 612 (w).
ClP(tBu)₂ (0.13 mL, 0.69 mmol) was added to a solution of **K-8C** (230 mg, 0.93 mmol) in DME (20 mL). After stirring for 1 h the mixture was filtered and evaporated to dryness. The remaining solids were washed with pentane (4×5 mL) and dried *in vacuo* (132 mg, 0.37 mmol, 40%). Crystals suitable for X-ray crystallography were obtained by slow diffusion of pentane in a solution of the product in CH₂Cl₂.

**1H NMR** (400 MHz, THF-d₈) δ(ppm) = 7.83-7.55 (m, 4 H, ar-H), 4.45 (s, 6 H, NCH₃), 1.26 [d, 3Jₚₜₜ = 11 Hz, 18 H, C(CH₃)₃].

**13C{¹H} NMR** (150 MHz, THF-d₈) δ(ppm) = 134.3 (s, ar-CN), 129.8 (q, 1JBC = 70 Hz, BCN), 126.3 (s, ar-CH), 112.7 (s, ar-CH), 34.6 (d, 2JPC = 14 Hz, NCH₃), 33.0 (d, 2JPC = 26.3 Hz, C(CH₃)₃), 32.1 [d, 2JPC = 13 Hz, C(CH₃)₃], not observed (carbene-BCN).

**11B{¹H} NMR** (128.5 MHz, THF-d₈): δ(ppm) = −29.6 [d, 1Jₕₕ = 24 Hz, ωₜₜ = 9 Hz].

**31P{¹H} NMR** (162.1 MHz, THF-d₈): δ(ppm) = 5.96 [q, 1Jₕₕ = 24 Hz].

**Elemental Analysis.** Calcd. for C₁₉H₂₈BN₄P: C 64.42, H 7.97, N 15.82. Found: C 64.47, H 7.86, N 15.94.

**MS (ESI, positive mode):** 377.2 [M+Na]+.

**IR (ATR, cm⁻¹):** v = 3061 (w), 2918 (w), 2892 (w), 2858 (w), 2197 (w), 1604 (w), 1470 (s), 1390 (m), 1361 (m), 1309 (m), 1259 (w), 1231 (w), 1200 (w), 1171 (w), 1221 (w), 1059 (w), 1016 (s), 983 (w), 947 (w), 882 (w), 853 (w), 806 (m), 747 (s), 662 (w), 645 (w).
Synthesis of IMe(Me)$_2$-substituted compounds

IMe(Me)$_2$-B(SEt)$_3$, (1A).

B(SEt)$_3$ (1.56 g, 8.1 mmol) was added dropwise to a solution of IMe(Me)$_2$ (1 g, 8.1 mmol) in toluene. After stirring the pale yellow solution for 5 min the solvent was removed in vacuo. The residue was washed with pentane (40 mL), and after evaporating to dryness in vacuo the product was obtained as a colorless powder (2.57 g, 8.0 mmol, 99%).

$^1$H NMR (400 MHz, C$_6$D$_6$) $\delta$ (ppm) = 3.85 (s, 6 H, NCH$_3$), 2.92-2.86 (m, 6 H, SCH$_2$), 1.43 (t, $^3$$J_{HH}$ = 7.5 Hz, 9 H, SCH$_2$CH$_3$), 1.11 (s, 6 H, NCCCH$_3$).

$^{13}$C{$^1$H} NMR (100 MHz, C$_6$D$_6$) $\delta$ (ppm) = 125.0 (s, NCC), 34.4 (s, NCH$_3$), 23.9 (s, SCH$_2$), 17.8 (s, SCH$_2$CH$_3$), 8.2 (s, NCCH$_3$), not observed (BCN).

$^{11}$B{$^1$H} NMR (96.3 MHz, C$_6$D$_6$): $\delta$ (ppm) = -1.1 (s, $\omega_{B} = 5$ Hz).

Elemental Analysis. Calcd. for C$_{13}$H$_{27}$BN$_2$S$_3$: C 49.05, H 8.55, N 8.80, S 30.21. Found: C 49.37, H 8.64, N 9.21, S 29.71.

MS (EI): m/z = 289.1 [M-Et]$^+$, 257.1 [M-SEt]$^+$.

IR (ATR cm$^{-1}$): $\nu$ = 2957 (m), 2923 (m), 2859 (m), 1657 (m), 1438 (s), 1404 (w), 1384 (s), 1370 (m), 1258 (m).
IME(Me)$_2$-B(CN)(SEt)$_2$ (2A).

Me$_3$SiCN (164 mg, 1.65 mmol) dissolved in toluene (2 mL) was added dropwise to a solution of IMe(Me)$_2$-B(SEt)$_3$ (500 mg, 1.57 mmol) in toluene (5 mL). The pale yellow solution was left for 24 h at 45 °C, and the solvent was removed in vacuo. After washing with pentane (40 mL) the product was obtained as a colorless powder (442 mg, 1.55 mmol, 99%).

$^1$H NMR (400 MHz, C$_6$D$_6$) δ(ppm) = 3.60 (s, 6 H, NCH$_3$), 3.04-2.84 (m, 4 H, SCH$_2$CH$_3$), 1.40 (t, $^3$J$_{HH}$ = 8 Hz, 6 H, SCH$_2$CH$_3$), 1.11 (s, 6 H, NCCN$_3$).

$^{13}$C{$_^1$H} NMR (100 MHz, C$_6$D$_6$) δ(ppm) = 125.7 (s, NCCN), 34.0 (s, NCH$_3$), 24.6 (s, SCH$_2$), 17.4 (s, SCH$_2$CH$_3$), 7.7 (s, NCCN)$_3$, not observed (BCN).

$^{11}$B{$_^1$H} NMR (96.3 MHz, C$_6$D$_6$): δ(ppm) = -13.6 (s, $\omega_{\beta}$ = 7 Hz).

Elemental Analysis. Calcd. for C$_{12}$H$_{22}$BN$_3$S$_2$: C 50.88, H 7.83, N 14.83, S 22.64. Found: C 50.68, H 7.77, N 15.10, S 22.20.

MS (EI): m/z = 283.1 [M]$^+$, 222 [M-SEt]$^+$.

IR (ATR cm$^{-1}$): ν = 2970 (m), 2923 (m), 2868 (m), 2181 (w), 1655 (m), 1471 (m), 1442 (s), 1413 (w), 1393 (s), 1371 (m), 1260 (s), 1227 (w).
IMe(Me)$_2$-B(CN)$_2$SEt (3A).

Me$_3$SiCN (954 mg, 9.61 mmol) dissolved in toluene (2 mL) was added dropwise to a solution of IMe(Me)$_2$-B(SEt)$_3$ (1.33 g, 4.18 mmol) in toluene (10 mL). Subsequently B(SEt)$_3$ (30 mg, 0.15 mmol) was added. After stirring the pale yellow solution for 12 h at 95 °C and removal of the solvent in vacuo a yellow solid was obtained. The residue was dissolved in a minimum amount of CH$_2$Cl$_2$ and passed through a pad of silica gel. Evaporating to dryness in vacuo afforded the product as a colorless crystalline material (853 mg, 3.43 mmol, 82%).

$^1$H NMR (400 MHz, C$_6$D$_6$) δ(ppm) = 3.30 (s, 6 H, NCH$_3$), 3.08-3.02 (m, 2 H, SCH$_2$CH$_3$), 1.49 (t, $^3$$J_{HH}$ = 7 Hz, 3 H, SCH$_2$CH$_3$), 0.94 (s, 6 H, NCCH$_3$).

$^{13}$C{$^1$H} NMR (100 MHz, C$_6$D$_6$) δ(ppm) = 126.1 (s, NCCN), 33.5 (s, NCH$_3$), 24.7 (s, SCH$_2$), 17.1 (s, SCH$_2$CH$_3$), 7.8 (s, NCCH$_3$), not observed (BCN).

$^{11}$B{$^1$H} NMR (96.3 MHz, C$_6$D$_6$): δ(ppm) = -24.4 (s, $\omega_{B}$ = 6 Hz).

Elemental Analysis. Calcd. for C$_{11}$H$_{17}$BN$_4$S: C 53.24, H 6.91, N 22.58, S 12.92. Found: C 53.13, H 6.85, N 22.65, S 12.18.

MS (EI): m/z = 248.1 [M]$^+$, 187.1 [M-SEt]$^+$.

IR (ATR cm$^{-1}$): ν = 2961 (m), 2924 (m), 2869 (m), 2204 (w), 1653 (m), 1487 (m), 1446 (s), 1422 (m), 1403 (m), 1374 (m), 1263 (m), 1232 (w), 916(s), 895(s), 797(s), 681(s).
**IMe(Me)$_2$-B(CN)$_2$I (7A).**

IMe(Me)$_2$-B(CN)$_2$(SEt) (3.20 g, 12.89 mmol) was dissolved in toluene (70 mL) and methyl iodide (3.85 g, 27.09 mmol) was added. The mixture was stirred at 45 °C overnight, whereby the colorless product precipitated. Filtration, washing with pentane (40 mL) and drying *in vacuo* afforded a colorless crystalline material (2.39 mg, 7.61 mmol, 59%).

$^1$H NMR (300 MHz, CD$_2$Cl$_2$) $\delta$(ppm) = 3.83 (s, 6 H, NCH$_3$), 2.20 (s, 6 H, NCCH$_3$).

$^{13}$C{$^1$H} NMR (100 MHz, CD$_2$Cl$_2$) $\delta$(ppm) = 128.3 (s, NCCN), 34.6 (s, NCH$_3$), 9.3 (s, NCCH$_3$), not observed (BCN).

$^{11}$B{$^1$H} NMR (96.3 MHz, CD$_2$Cl$_2$): $\delta$(ppm) = -41.6 (s, $\omega_{1/2}$ = 47 Hz).

Elemental Analysis. Calcd. for C$_9$H$_{12}$BIN$_4$: C 34.43, H 3.85, N 17.85. Found: C 34.69, H 3.95, N 17.67.

MS (EI): m/z = 313.9 [M]$^+$.  

IR (ATR cm$^{-1}$): $\nu$ = 2959 (m), 2929 (w), 2210 (w), 1643 (s), 1482 (s), 1441 (s), 1403 (m), 1062 (m), 990 (s), 898 (s), 749 (s), 642 (s).
**General procedure for the reactions 2A-C → 3A-C.**

In a typical reaction a portion of 2A-C (5.00 mmol) was dissolved in toluene (50 mL) and Me₃SiCN (645 mg, 6.50 mmol) and B(SEt)₃ (30 mg, 0.15 mmol) were added. The solution was maintained at 95 °C for 24 h. The work-up of compounds 3A-C was performed as mentioned above and afforded samples giving comparable yield and identical ¹H and ¹¹B NMR spectra as stated (vide supra).

**Alternative preparation of K-8B and K-8C by reduction with K in liquid NH₃.**

In a typical reaction a portion of potassium (234 mg, 6.00 mmol) was dissolved in liquid NH₃ (10 mL) at −60 °C. Compounds 7B or 7C (2.00 mmol) were added as solids to give a rapid change in color from blue to green. After 20 min all volatiles were removed *in vacuo* maintaining a constant temperature of −60 °C. The red (K-8B) or orange (K-8C) residue was dissolved (K-8B: THF, 20 mL; K-8C: DME, 20 mL) and the solution filtered to remove potassium iodide. The solvent was removed *in vacuo*, which afforded samples giving comparable yield and identical ¹H and ¹¹B NMR spectra as stated (vide supra).
NMR Spectra

IMes-substituted compounds

Figure 9: $^1$H NMR spectrum of IMes-B(SeEt)$_3$, 1B (300 MHz, $C_6D_6$, 25 °C).

Figure 10: $^{11}$B($^1$H) NMR spectrum of IMes-B(SeEt)$_3$, 1B (96.3 MHz, $C_6D_6$, 25 °C).
Figure 11: $^1$H NMR spectrum of IMes-B(CN)(SEt)$_2$, 2B (400 MHz, CD$_2$Cl$_2$, 25 °C).

Figure 12: $^{11}$B($^1$H) NMR spectrum of IMes-B(CN)(SEt)$_2$, 2B (96.3 MHz, CD$_2$Cl$_2$, 25 °C).
Figure 13: $^1$H NMR spectrum of IMes-$\text{B(CN)}_2$(SEt), 3B (400 MHz, CD$_2$Cl$_2$, 25 °C).

Figure 14: $^{11}$B($^1$H) NMR spectrum of IMes-$\text{B(CN)}_2$(SEt), 3B (96.3 MHz, CD$_2$Cl$_2$, 25 °C).
Figure 15: $^1$H NMR spectrum of TMS-$\equiv$C-$\equiv$B(CN)$_2$SEt, 4 (300 MHz, CD$_2$Cl$_2$, 25 °C).

Figure 16: $^{11}$B$^{'1}$H) NMR spectrum of TMS-$\equiv$C-$\equiv$B(CN)$_2$SEt, 4 (96.3 MHz, CD$_2$Cl$_2$, 25 °C).
Figure 17: $^1H$ NMR spectrum of IMes-B(CN)$_2$Br, 6 (400 MHz, CD$_2$Cl$_2$, 25 °C).

Figure 18: $^{11}$B($^1$H) NMR spectrum of IMes-B(CN)$_2$Br, 6 (128.5 MHz, CD$_2$Cl$_2$, 25 °C).
Figure 19: $^1$H NMR spectrum of IMes-B(CN)$_2$I, 7B (400 MHz, CD$_2$Cl$_2$, 25 °C).

Figure 20: $^{11}$B($^1$H) NMR spectrum of IMes-B(CN)$_2$I, 7B (96.3 MHz, CD$_2$Cl$_2$, 25 °C).
Figure 21: $^1$H NMR spectrum of K[I Mes-B(CN)$_2$], K-8B (300 MHz, THF-d8, 25 °C).

Figure 22: $^{11}$B($^1$H) NMR spectrum of K[I Mes-B(CN)$_2$], K-8B (96.3 MHz, THF-d8, 25 °C).
Figure 23: $^1$H NMR spectrum of IMes-B(CN)$_2$Me, 9 (600 MHz, CDCl$_3$, 25 °C).

Figure 24: $^{11}$B($^1$H) NMR spectrum of IMes-B(CN)$_2$Me, 9 (96.3 MHz, CDCl$_3$, 25 °C).
Figure 25: $^1$H NMR spectrum of IMes-B(CN)$_2$AuPMe$_2$Ph, 10 (300 MHz, THF-$d_8$, 25 °C).

Figure 26: $^{11}$B($^1$H) NMR spectrum of IMes-B(CN)$_2$AuPMe$_2$Ph, 10 (96.3 MHz, THF-$d_8$, 25 °C).
Figure 27: $^31$P($^1$H) NMR spectrum of IMes-B(CN)$_2$AuPMe$_2$Ph, 10 (121.5 MHz, THF-$d_8$, 25 °C).
BAC-substituted compounds

Figure 28: $^1$H NMR spectrum of BAC-B(SEt)$_3$, 1C (600 MHz, toluene-d8, 25 °C).

Figure 29: $^{11}$B($^1$H) NMR spectrum of BAC-B(SEt)$_3$, 1C (128.5 MHz, toluene-d8, 25 °C).
Figure 30: $^1$H NMR spectrum of BAC-B(SEt)$_2$CN, 2C (400 MHz, $C_6D_6$, 25 °C).

Figure 31: $^{11}$B($^1$H) NMR spectrum of BAC-B(SEt)$_2$CN, 2C (96.3 MHz, $C_6D_6$, 25 °C).
Figure 32: $^1$H NMR spectrum of BAC-B(CN)$_2$SEt, 3C (400 MHz, CD$_2$Cl$_2$, 25 °C).

Figure 33: $^{11}$B($^1$H) NMR spectrum of BAC-B(CN)$_2$SEt, 3C (128.5 MHz, CD$_2$Cl$_2$, 25 °C).
Figure 34: $^1$H NMR spectrum of $\text{BAC-B(CN)}_2$J, 7C (600 MHz, CD$_2$Cl$_2$, 25 °C).

Figure 35: $^{11}$B($^1$H) NMR spectrum of $\text{BAC-B(CN)}_2$J, 7C (96.3 MHz, CD$_2$Cl$_2$, 25 °C).
Figure 36: $^1\text{H}$ NMR spectrum of $[\text{K}(18\text{-cr-6})][\text{BAC-B(CN)}_2]. [\text{K}(18\text{-cr-6})]_{\text{8C}}$ (300 MHz, THF-d$_8$, 25 °C).

Figure 37: $^{11}\text{B}[^1\text{H}]$ NMR spectrum of $[\text{K}(18\text{-cr-6})][\text{BAC-B(CN)}_2]. [\text{K}(18\text{-cr-6})]_{8\text{C}}$ (96.3 MHz, THF-d$_8$, 25 °C).
Figure 38: $^1$H NMR spectrum of BAC-B(CN)$_2$Me, 11 (600 MHz, CD$_2$Cl$_2$, 25 °C).

Figure 39: $^{11}$B($^1$H) NMR spectrum of BAC-B(CN)$_2$Me, 11 (96.3 MHz, CD$_2$Cl$_2$, 25 °C).
Figure 40: $^1\text{H}$ NMR spectrum of BAC-B(CN)$_2$SiMe$_3$, 12 (400 MHz, CD$_2$Cl$_2$, 25 °C).

Figure 41: $^{11}$B($^1\text{H}$) NMR spectrum of BAC-B(CN)$_2$SiMe$_3$, 12 (96.3 MHz, CD$_2$Cl$_2$, 25 °C).
Figure 42: $^1H$ NMR spectrum of BAC-B(CN)$_2$SnMe$_3$, 13 (600 MHz, CD$_2$Cl$_2$, 25 °C).

Figure 43: $^{11}B$($^1H$) NMR spectrum of BAC-B(CN)$_2$SnMe$_3$, 13 (96.3 MHz, CD$_2$Cl$_2$, 25 °C), zoomed signal.
Figure 44: $^1$H NMR spectrum of BAC-B(CN)$_2$P(tBu)$_3$ 14 (400 MHz, THF-d$_8$, 25 °C).

Figure 45: $^{11}$B($^1$H) NMR spectrum of BAC-B(CN)$_2$P(tBu)$_3$, 14 (128.5 MHz, THF-d$_8$, 25 °C).
Figure 46: $^{31}P(^1H)$ NMR spectrum of BAC-B(CN)$_2$P(tBu)$_2$, 14 (162.1 MHz, THF-$d_8$, 25 °C).
IMe(Me)$_2$-substituted compounds

Figure 47: $^1$H NMR spectrum of IMe(Me)$_2$-B(SEt)$_3$. I$_{\lambda}$ (400 MHz, C$_6$D$_6$, 25 °C).

Figure 48: $^{11}$B($^1$H) NMR spectrum of IMe(Me)$_2$-B(SEt)$_3$. I$_{\lambda}$ (96 MHz, C$_6$D$_6$, 25 °C).
Figure 49: $^1$$H$ NMR spectrum of IMe(Me)$_2$-B(SEt)$_2$CN, 2A (400 MHz, CD$_6$D$_6$, 25 °C).

Figure 50: $^{11}$$B$$^1$$H$ NMR spectrum of IMe(Me)$_2$-B((SEt)$_2$CN, 2A (96.3 MHz, CD$_6$D$_6$, 25 °C).
Figure 51: $^1$H NMR spectrum of IMe(Me)$_2$-B(CN)$_2$(SEt), 3A (400.4 MHz, C$_6$D$_6$, 25 °C).

Figure 52: $^{11}$B($^1$H) NMR spectrum of IMe(Me)$_2$-B(CN)$_2$(SEt), 3A (96.3 MHz, C$_6$D$_6$, 25 °C).
Figure 53: $^1$H NMR spectrum of IMe(Me)$_2$-B(CN)$_2$J, 7A (400.4 MHz, CD$_2$Cl$_2$, 25 °C).

Figure 54: $^{11}$B($^1$H) NMR spectrum of IMe(Me)$_2$-B(CN)$_2$J, 7A (96.3 MHz, CD$_2$Cl$_2$, 25 °C).
### X-ray Structure Analysis

Table 1: Selected Crystallographic Data for IMes-based Compounds Measured by X-ray Structure Analysis.

|               | 1B          | 2B          | 7B          | K-8B·4THF    | 9            |
|---------------|-------------|-------------|-------------|--------------|--------------|
| CCDC          | 1550754     | 1550755     | 1550760     | 1550767      | 1550769      |
| Formula       | C$_{27}$H$_{39}$BN$_2$S$_3$ | C$_{25}$H$_{37}$BN$_3$S$_2$ | C$_{23}$H$_{32}$BN$_4$ | C$_{24}$H$_{29}$B$_3$K$_3$N$_9$O$_4$ | C$_{24}$H$_{27}$BN$_4$ |
| M [g mol$^{-1}$] | 498.59      | 463.49      | 494.17      | 4234.35      | 382.31       |
| T/K           | 130(2)      | 100(2)      | 100(2)      | 100(2)       | 100(2)       |
| $\lambda$/Å   | 1.54184     | 1.54184     | 0.71073     | 1.54184      | 1.54184      |
| Crystal system| Orthorhombic | Monoclinic  | Monoclinic  | 4                |
| Space group   | P2$_1$2$_1$2$_1$ | P2$_1$/c    | P2$_1$/n    | P2$_1$/c      | Orthorhombic |
| a/Å           | 12.63216(10) | 8.20315(10) | 16.5750(3)  | 33.0927(5)    | 16.1393(3)   |
| b/Å           | 13.55052(10) | 16.7145(2)  | 17.3066(2)  | 30.3266(4)    | 7.9763(2)    |
| c/Å           | 16.37821(10) | 37.3775(7)  | 23.9859(4)  | 25.1212(4)    | 34.8942(7)   |
| a/$^\circ$    | 90          | 90          | 90          | 90            | 90           |
| $\beta$/°     | 90          | 95.505(2)   | 90.036(2)   | 106.881(2)    | 90           |
| $\gamma$/°    | 90          | 90          | 90          | 90            | 90           |
| Z              | 4           | 8           | 12          | 4             | 8            |
| $D_c$/g cm$^{-3}$ | 1.181       | 1.207       | 1.431       | 1.166         | 1.131        |
| $\mu$/mm$^{-1}$ | 2.533       | 2.017       | 1.412       | 1.898         | 0.518        |
| F(000)        | 1072        | 1984        | 2976        | 9016          | 1632         |
| Cryst. size/mm | 0.22x0.10x0.08 | 0.15x0.10x0.03 | 0.22x0.20x0.18 | 0.22x0.15x0.10 | 0.30x0.18x0.16 |
| Theta range/° | 4.23 to 76.31 | 3.55 to 76.30 | 2.35 to 30.03 | 3.21 to 76.36 | 3.73 to 76.32 |
| Reflections collected | 74082 | 92739 | 398935 | 563295 | 86768 |
| Indep. reflections | 5849 | 10650 | 20085 | 50397 | 4686 |
| R(int)        | 0.0620      | 0.0699      | 0.0571      | 0.0662        | 0.0410       |
| Data / restraints / parameters | 5849 / 0 / 307 | 10650 / 0 / 593 | 20085 / 0 / 803 | 50397 / 0 / 2404 | 4686 / 0 / 269 |
| GooF          | 1.050       | 1.027       | 1.059       | 1.020         | 1.057        |
| R1 (F, >4σ(F)) | 0.0256      | 0.0359      | 0.0292      | 0.0390        | 0.0514       |
| wR2 (F$^2$, all refl.) | 0.0693      | 0.0937      | 0.0627      | 0.1013        | 0.1501       |
| Flack parameter | 0.000(9)  | —           | —           | —             | —            |
| max. $\Delta$$\rho$/Å$^{-3}$ | 0.326/−0.252 | 0.295/−0.291 | 0.538/−0.486 | 0.207/−0.267 | 0.302/−0.237 |
Table 2: Selected Crystallographic Data for BAC-based Compounds Measured by X-ray Structure Analysis.

|          | 1C                  | 2C                  | 7C                  | [K(18-cr-6)-8C]       | 11-½CH₂Cl₂ |
|----------|---------------------|---------------------|---------------------|-----------------------|------------|
| CCDC     | 1550740             | 1550756             | 1550774             | 1550768               | 1550770    |
| Formula  | C₁₅H₂₅BN₂S₃         | C₁₅H₂₅BN₂S₂        | C₁₁H₁₀BN₁₄         | C₄₀H₅₈B₂K₂N₈O₁₂      | C₁₂₂₅H₁₄BCN₄ |
| M [g mol⁻¹] | 340.36             | 305.26             | 335.94             | 1024.90               | 266.54     |
| T/K      | 100(2)              | 100(2)             | 100(2)             | 100(2)                | 100(2)     |
| λ/Å      | 0.71073             | 0.71073            | 0.71073            | 1.54184               | 1.54184    |
| Crystal system | Triclinic       | Monoclinic         | Orthorhombic       | Monoclinic            | Orthorhombic |
| Space group | P 1               | P2₁/c             | Pnmm               | P2₁/c                | Cmc2₁      |
| a/Å      | 8.4435(2)           | 10.4737(2)         | 8.8243(2)          | 9.0098(1)             | 11.3418(3) |
| b/Å      | 8.5770(2)           | 12.0926(2)         | 10.9964(2)         | 22.6206(2)            | 18.4372(5) |
| c/Å      | 12.2867(3)          | 13.1679(3)         | 12.7995(3)         | 13.0457(1)            | 12.9532(3) |
| α/°      | 84.407(2)           | 90                 | 90                 | 90                    | 90         |
| β/°      | 89.589(2)           | 104.764(2)         | 90                 | 100.351(1)            | 90         |
| γ/°      | 82.070(2)           | 90                 | 90                 | 90                    | 90         |
| V/Å³     | 877.08(4)           | 1612.71(5)         | 1242.00(5)         | 2615.54(4)            | 2708.64(12)|
| Z        | 2                   | 4                  | 4                  | 2                     | 8          |
| D₄/g cm⁻³ | 1.289              | 1.257              | 1.797              | 1.301                 | 1.307      |
| μ/mm⁻¹   | 0.417               | 0.323              | 2.560              | 2.148                 | 2.394      |
| F(000)   | 364                 | 648                | 648                | 1088                  | 1112       |
| Cryst. size/mm | 0.40x0.30x0.15 | 0.40x0.30x0.15     | 0.28x0.22x0.18     | 0.18x0.18x0.02        | 0.20x0.12x0.08 |
| θ range/° | 2.41 to 31.09     | 2.23 to 31.38      | 2.44 to 31.08      | 3.908 to 76.170       | 4.58 to 76.21 |
| Reflections collected | 89317            | 120276             | 31556              | 53304                 | 27441      |
| Indep. reflections | 5288             | 5120               | 2021               | 5473                  | 2795       |
| R(int)   | 0.0363              | 0.0458             | 0.0353             | 0.0664                | 0.0400     |
| Data / restraints / parameters | 5288 / 0 / 195   | 5120 / 0 / 185     | 2021 / 0 / 83      | 5473 / 0 / 319        | 2795 / 1 / 184 |
| GooF     | 1.044               | 1.064              | 1.107              | 1.047                 | 1.049      |
| R1 (F, >4σ(F)) | 0.0296           | 0.0364             | 0.0185             | 0.0361                | 0.0327     |
| wR2 (F², all refl.) | 0.0750          | 0.0868             | 0.0456             | 0.0986                | 0.0861     |
| Flack parameter | —                | —                  | —                  | —                     | 0.019(17)  |
| max. Δρ/e Å⁻³ | 0.420/−0.287   | 0.433/−0.313       | 0.489/−0.411       | 0.376/−0.284           | 0.238/−0.401 |
Table 3: Selected Crystallographic Data for BAC-, IMe(Me)$_2$- and TMS-based Compounds Measured by X-ray Structure Analysis.

|                  | 13                  | 14·CH$_2$Cl$_2$   | 3A         | 7A·CH$_2$Cl$_2$ | 4                  |
|------------------|---------------------|-------------------|------------|-----------------|-------------------|
| CCDC             | 1550771             | 1550772           | 1550757    | 1550759         | 1550758           |
| Formula          | C$_{14}$H$_{19}$BN$_3$Sn | C$_{20}$H$_{30}$BCl$_2$N$_3$P | C$_{11}$H$_{13}$BN$_4$S | C$_{10}$H$_{13}$BCl$_2$IN$_4$ | C$_{9}$H$_{12}$BN$_3$SSi |
| M [g mol$^{-1}$] | 372.83              | 439.16            | 248.16     | 398.86          | 223.18            |
| T/K              | 100(2)              | 100(2)            | 100(2)     | 100(2)          | 100(2)            |
| λ/Å              | 0.71073             | 1.54184           | 0.71073    | 0.71073         | 1.54184           |
| Crystal system   | Monoclinic          | Orthorhombic      | Orthorhombic | Orthorhombic   | Monoclinic        |
| Space group      | $P_2_1/c$           | $Pbcn$            | $P_2_12_1$ | $Cmc2_1$       | $P_2_1/c$         |
| a/Å              | 11.0134(1)          | 31.987(2)         | 8.5576(3)  | 10.8977(4)      | 9.5297(2)         |
| b/Å              | 21.1517(2)          | 8.6554(6)         | 9.7069(3)  | 12.4002(4)      | 8.5096(2)         |
| c/Å              | 13.8999(1)          | 16.7007(9)        | 16.4514(6) | 11.6286(2)      | 16.0181(4)        |
| $\alpha/$°      | 90                  | 90                | 90         | 90              | 90                |
| $\beta/$°       | 90.555(1)           | 90                | 90         | 90              | 94.741(2)         |
| $\gamma/$°      | 90                  | 90                | 90         | 90              | 90                |
| V/Å$^3$          | 3237.86(5)          | 4623.7(5)         | 1366.60(8) | 1571.42(8)      | 1294.52(5)        |
| Z                | 8                   | 8                 | 4          | 4               | 4                 |
| $D_v$/g cm$^{-3}$| 1.530               | 1.262             | 1.206      | 1.686           | 1.145             |
| $\mu$/mm$^{-1}$ | 1.573               | 3.272             | 0.221      | 2.366           | 2.852             |
| F(000)           | 1488                | 1856              | 528        | 776             | 472               |
| Cryst. size/mm   | 0.40x0.10x0.10      | 0.15x0.08x0.06    | 0.30x0.25x0.25 | 0.25x0.20x0.12 | 0.16x0.08x0.03    |
| Theta range/°    | 2.420 to 31.094     | 5.29 to 76.23     | 2.44 to 31.08 | 2.49 to 30.96 | 4.66 to 76.22     |
| Reflections      | 91552               | 50662             | 36589      | 20643           | 25988             |
| collected        | 9835                | 4827              | 4129       | 2470            | 2701              |
| Indep. reflections | 0.0416             | 0.0833            | 0.0500     | 0.0367          | 0.0501            |
| R(int)           | 0.0416              | 0.0833            | 0.0500     | 0.0367          | 0.0501            |
| Data / restraints / parameters | 9835 / 0 / 371 | 4827 / 0 / 261 | 4129 / 0 / 159 | 2470 / 1 / 93 | 2701 / 0 / 131 |
| GooF             | 1.102               | 1.032             | 1.062      | 1.062           | 1.060             |
| R1 (F, >4σ(F))   | 0.0263              | 0.0393            | 0.0380     | 0.0169          | 0.0267            |
| wR2 (F$^2$, all refl.) | 0.0520          | 0.0990            | 0.0823     | 0.0359          | 0.0704            |
| Flack parameter  | —                   | —                 | 0.01(6)    | −0.037(13)      | —                 |
| max. $\Delta\rho$/e Å$^{-3}$ | 0.568/−0.640 | 0.381/−0.460 | 0.465/−0.408 | 0.308/−0.342 | 0.305/−0.239 |
Figure 55: ORTEP diagram of IMes-B(SEt)$_3$, 1B. Ellipsoids are drawn at 50% probability levels. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: S1-B1 1.9210(15), S2-B1 1.9363(15), S3-B1 1.9277(15), B1-C1 1.6421(19), N1-C1 1.3633(18), N2-C1 1.3589(18), C1-B1-S1 111.89(9), C1-B1-S2 109.39(7), C1-B1-S3 111.63(7).

Figure 56: Packing diagram of IMes-B(SEt)$_3$, 1B. The molecules are linked in chains parallel to the b axis by the contacts H2⋯S3 2.97 and H3⋯S2 2.85 Å (shown as dashed bonds).
Figure 57: ORTEP diagram of IMes-B(SEt)_2-CN, 2B. Ellipsoids are drawn at 50% probability levels. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: S1-B1 1.9121(17), S2-B1 1.9450(16), B1-C26 1.593, B1-C1 1.632, N1-C1 1.3561(19), N2-C1 1.3586(18), C1-B1-S1 104.89(10), C1-B1-S2 114.77(8), C1-B1-C26 111.92(12). The asymmetric unit contains two independent molecules, of which only one is shown here; a least-squares fit of all non-hydrogen atoms except ethyl C gives an r.m.s. deviation of 0.2 Å.

Figure 58: Packing diagram of IMes-B(SEt)_2-CN, 2B. Each independent molecule is linked in chains parallel to the a axis by the contacts H2···N3 2.44, H3···S2 2.98, H2···N3' 2.42, H3···S2' 2.91 Å (shown as dashed bonds); the chains are crosslinked to form ribbons by the contacts H8···N3' 2.61 and H8···N3 2.69 Å.
Figure 59: ORTEP diagram of IMes-B(CN)$_2$Me, 9. Ellipsoids are drawn at 50% probability levels. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: B1-C1 1.627(2), B1-C22 1.604(2), B1-C23 1.594(2), B1-C24 1.628(2), C22-B1-C1 112.38(11), C23-B1-C1 112.55(12), C24-B1-C1 109.96(12). The molecule displays approximate mirror symmetry (r.m.s. deviation 0.05 Å).

Figure 60: Packing diagram of IMes-B(CN)$_2$Me, 9. The molecules form chains parallel to the b axis via the contacts H2⋯N3 2.42 and H3⋯N4 2.42 Å.
Figure 61: ORTEP diagram of BAC-B(SEt)$_3$, 1C. Ellipsoids are drawn at 50% probability levels. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: S1-B1 1.9324(12), S2-B1 1.9217(12), S3-B1 1.9169(12), B1-C1 1.6419(15), N1-C1 1.3604(13), N2-C1 1.3613(13), C1-B1-S1 111.27(7), C1-B1-S2 106.97(7), C1-B1-S3 112.47(7).

Figure 62: ORTEP diagram of BAC-B(SEt)$_2$CN, 2C. Ellipsoids are drawn at 50% probability levels. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: S1-B1 1.9084(13), S2-B1 1.9250(12), B1-C14 1.5895(16), B1-C1 1.6229(16), N1-C1 1.3562(13), N2-C1 1.3558(13), C1-B1-S1 105.12(7), C1-B1-S2 109.70(6), C1-B1-C14 115.08(9).
Figure 63: Packing diagram of BAC-B(SEt)$_2$-CN, 2C. The molecules are linked to form layers parallel to the bc plane by the contacts H6⋯N3 2.39 Å and H3⋯S2 2.82 Å.

Figure 64: ORTEP diagram of BAC-B(CN)$_2$Me, 11. Ellipsoids are drawn at 50% probability levels. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: B1-C1 1.638(3), B1-C6 1.603(2), B1-C7 1.624(2), C6-B1-C1 111.22(13), C7-B1-C1 111.22(13), C6-B1-C6' 103.84(18), B1-C1' 1.625(3), B1-C6 1.609(2), B1-C7' 1.629(2), C6-B1-C6' 110.88(13), C7-B1-C1' 109.86(19), C6-B1-C6 102.55(18)
Figure 65: Packing diagram of BAC-B(CN)\textsubscript{2}Me, 11. The second independent molecule of 11 (atom names with primes in the coordinate lists) together with the dichloromethane, forms a layer parallel to the ab plane. The contacts are H99(solvent) - N2' 2.70 Å and H4'-N2' 2.61 Å. The first molecule forms a similar plane but without direct contacts to dichloromethane.

Figure 66: ORTEP diagram of BAC-B(CN)\textsubscript{2}SnMe\textsubscript{3}, 13. Ellipsoids are drawn at 50% probability levels. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Sn1-B1 2.324(2), B1-C1 1.586(3), B1-C10 1.572(3), B1-C11 1.573(3), Sn1-B1-C1 106.6(3), C10-B1-C11 116.0(3), C11-B1-C1 115.6(3). This is one of two independent molecules; a least-squares fit of both molecules gave an r.m.s. deviation of 0.11 Å.
Figure 67: Packing diagram of BAC-B(CN)$_2$SnMe$_3$. The molecules are linked by several H···N contacts of 2.35 – 2.73 Å to form a layer structure parallel to the ac plane. However, there are further links in the third dimension between these layers.

Figure 68: ORTEP diagram of BAC-B(CN)$_2$P(tBu)$_2$. Ellipsoids are drawn at 50% probability levels. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: B1-C10 1.586(2), B1-C11 1.601(2), B1-C1 1.628(2), B1-P1 2.0408(19), C10-B1-C1 113.02(14), C11-B1-C1 104.81(13), C1-B1-P1 111.72(11).
Figure 69: Packing diagram of BAC-B(CN)$_2$P(tBu)$_2$. The molecules are linked by several $H \equiv N$ and $H \equiv Cl$ contacts to form a layer structure parallel to the bc plane. However, there are further links in the third dimension between these layers. A $P \equiv H(-Cl)$ contact of 3.02 Å is omitted.

Figure 70: ORTEP diagram of IMe$_2$(Me)$_2$B(CN)$_2$S$\text{Et}$. Ellipsoids are drawn at 50% probability levels. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: S1-B1 1.8250(17), B1-C8 1.597(2), B1-C9 1.600(2), B1-C1 1.611(2), N1-C1 1.3475(17), N2-C1 1.3501(17), C8-B1-C1 113.28(12), C9-B1-C1 111.16(12), C1-B1-S1 106.12(9). The molecule possesses non-crystallographic mirror symmetry with an r.m.s. deviation of 0.20 Å.
Figure 71: Packing diagram of IMe$_2$(Me)$_2$-B(CN)$_2$SEt, 3A. The molecules are linked to form layers parallel to the ac plane by the contacts H5A···N3 2.49 and H5C···N4 2.52 Å.

Figure 72: Packing diagram of Me$_3$Si-N≡C-B(CN)$_2$SEt, 4. The molecules are linked to form thick bands parallel to the bc plane by the contacts H2A···N3 2.66 and H3A···N2 2.55 Å.
Figure 73: Packing diagram of IMe(Me)$_2$-B(CN)$_2$I, 7A (dichloromethane solvate). The molecules are linked to form corrugated layers parallel to the ac plane by the contacts H99A-N2 2.57 and Cl1-Cl2 3.33 Å.

Figure 74: The three independent molecules of IMes-B(CN)$_2$I, 7B, together with one further symmetry-generated molecule (extreme right). The molecules are form a chain parallel to the c axis by the contacts H2'-N3" 2.56, H3'-N4" 2.50, H2-N3'A 2.50, H3-N4'A 2.71, H2"-N3 2.6356, H3"-N4 2.51 Å.
Figure 75: Packing diagram of BAC-Bi(CN)$_3$. The molecules form corrugated chains parallel to the ac plane by the contacts H3$\cdots$N2 2.60 Å. The layers are linked in the third dimension by the contact H5C(methyl)$\cdots$N2 2.57 Å (not shown here).
DFT Calculations

All DFT calculations were performed using ORCA2.9.1.\textsuperscript{[7]} TZVP basis sets\textsuperscript{[8]} were used throughout. Geometric structure optimizations of several boryl anions (see Figure 76) were performed with the GGA functional BP86.\textsuperscript{[9]} Dispersion contributions were approximated using Grimme’s DFT-D3 atom-pair-wise dispersion corrections.\textsuperscript{[10]} Solvent effects were taken into account at the polarizable continuum model level, using COSMO (Conductor-Like Screening Model)\textsuperscript{[11]} implemented in ORCA, with parameters for tetrahydrofuran. Numerical frequency calculations revealed the optimized structures of 8B and 8C to be stationary points on the energy surface. xyz-Data of the optimized structures are given in Tables 5–9. UV/VIS/NIR spectroscopic properties of 8B were extracted from single-point TD-DFT calculations at the BLYP-35\textsuperscript{[12]}-D3/TZVP/COSMO(THF) level of theory in the BP86-optimized atomic positions. Spectral positions and intensities of the computed transitions are given in Table 4.

Table 4: Computed UV-Vis transitions of anion IMes-B(CN)$_2^-$ (8B); transitions with vanishing oscillator strength ($f_{osc} < 10^{-5}$) are neglected.

|   | $\tilde{\nu}$ [cm$^{-1}$] | $\lambda$ [nm] | $f_{osc}$   |
|---|-----------------|---------------|-------------|
| 2 | 19305.5         | 518           | 0.00523     |
| 5 | 20924.2         | 477.9         | 0.02796     |
| 8 | 21625.6         | 462.4         | 9.61838E-4 |
| 9 | 21953.8         | 455.5         | 9.2088E-5  |
|12 | 28257.3         | 353.9         | 0.01404     |
|16 | 27855.9         | 359           | 0.03597     |
|17 | 30487.1         | 328           | 0.04296     |
|19 | 33875.7         | 295.2         | 0.50733     |
|23 | 34271.5         | 291.8         | 7.8436E-5  |
|28 | 35374.6         | 282.7         | 4.4663E-5  |
|30 | 36844.9         | 271.4         | 1.0188E-4  |
|31 | 37317.1         | 268           | 0.00255     |
|33 | 35213.8         | 284           | 0.00237     |
|38 | 38590.9         | 259.1         | 0.00464     |
|39 | 38667.1         | 258.6         | 0.0046      |
|40 | 41347.5         | 241.9         | 0.23018     |
Figure 76. Energies of frontier orbitals in the boryl anion series \( L^-B(CN)_2^- \), \( L = \) carbene or \( CN^- \): (a) truncated anion \( VI \); (b) 8C; (c) hypothetical 8A; (d) 8B; (e) anion VII.

| Bond-Order (BC) | 1.59 | 1.46 | 1.35 | 1.43 | 1.20 |
|-----------------|------|------|------|------|------|
| Mulliken-Charge (B) | -0.14 | -0.22 | -0.33 | -0.39 | -0.57 |

Figure 77. HOMOs within the boryl anion series \( L^-B(CN)_2^- \), \( L = \) carbene or \( CN^- \): (a) truncated anion \( VI \); (b) 8C; (c) hypothetical 8A; (d) 8B; (e) anion VII.
Table 5: Coordinates of boryl anion VI.

|  | B     | C     | N     | N     | N     | C     | C     | H     | C     | C     | C     | C     | H     | H     | H     | H     | C     | H     | H     | H     | H     | H     | H     | H     | H     | H     | H     | H     | H     | H     |
|---|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
|   | 4.733395 | 14.944204 | 11.189277 | 5.907152 | 15.486530 | 13.539550 | 4.001091 | 14.077897 | 13.511682 | 6.393406 | 16.533066 | 9.748827 | 3.156310 | 13.420185 | 9.600004 | 4.804623 | 14.852776 | 12.663406 | 5.502744 | 15.078507 | 14.981678 | 4.871526 | 15.862684 | 15.428299 | 4.672009 | 13.813134 | 14.795165 | 3.926399 | 13.657453 | 15.585885 | 5.957212 | 17.017195 | 13.412605 | 2.707685 | 13.602312 | 13.282523 | 1.789048 | 14.324148 | 12.490218 | 0.481630 | 13.873172 | 12.337068 | -0.211923 | 14.455210 | 11.726271 | 0.047829 | 12.691323 | 12.957215 | 0.951726 | 11.972121 | 13.746708 | 0.637877 | 11.046212 | 14.233344 | 2.265977 | 12.416994 | 13.912647 | 5.687468 | 15.847853 | 10.394212 | 3.819371 | 14.085836 | 10.306115 | -0.976059 | 12.338714 | 12.823978 | 2.961012 | 11.833489 | 14.517822 | 2.116628 | 15.244008 | 12.008687 | 6.671808 | 17.433841 | 14.141363 | 4.967263 | 17.453668 | 13.611468 | 6.273206 | 17.327058 | 12.408410 | 5.306329 | 12.910178 | 14.732948 | 6.376516 | 14.927106 | 15.630394 | 7.283330 | 14.883268 | 13.189886 | 8.065345 | 15.315645 | 13.834602 | 7.281830 | 13.791662 | 13.329656 | 7.541319 | 15.088880 | 12.142491 |
Table 6: Coordinates of boryl anion 8C.

|     |       |       |       |
|-----|-------|-------|-------|
| C   | 3.766663 | 15.250594 | 6.945704 |
| C   | 4.558200  | 15.976901 | 8.980468  |
| C   | 4.727342  | 16.466581 | 10.275755 |
| H   | 3.877348  | 16.783249 | 10.880478 |
| C   | 6.041175  | 16.536342 | 10.782507 |
| H   | 6.200516  | 16.917622 | 11.792137 |
| C   | 7.136326  | 16.118965 | 10.017357 |
| H   | 8.143066  | 16.182926 | 10.433865 |
| C   | 6.967356  | 15.622172 | 8.708749  |
| H   | 7.826197  | 15.311803 | 8.113533  |
| C   | 5.667581  | 15.550121 | 8.206672  |
| C   | 2.103003  | 16.256191 | 8.559121  |
| H   | 1.446921  | 15.423094 | 8.848960  |
| H   | 1.650463  | 16.774707 | 7.703343  |
| H   | 2.188146  | 16.956628 | 9.398872  |
| C   | 5.956097  | 14.450472 | 5.971882  |
| H   | 6.920378  | 14.159641 | 6.403888  |
| H   | 6.131038  | 15.104500 | 5.105940  |
| H   | 5.430866  | 13.549825 | 5.628329  |
| C   | 1.326303  | 14.830665 | 5.983027  |
| C   | 3.343597  | 14.578246 | 4.409335  |
| B   | 2.844484  | 14.898707 | 5.818133  |
| N   | 3.429861  | 15.796528 | 8.196883  |
| N   | 5.164735  | 15.110221 | 6.993024  |
| N   | 0.153796  | 14.731729 | 6.062776  |
| N   | 3.669890  | 14.353354 | 3.298585  |
Table 7: Coordinates of boryl anion 8A.

|   | A          | B          | C          |
|---|------------|------------|------------|
| B | 4.767290   | 14.835205  | 11.342291  |
| N | 5.763524   | 15.447061  | 13.683326  |
| N | 3.882892   | 14.323618  | 13.750863  |
| N | 6.197881   | 16.538634  | 9.800083   |
| N | 3.269140   | 13.070980  | 9.939050   |
| C | 4.803265   | 14.867383  | 12.858851  |
| C | 5.441821   | 15.262025  | 15.038315  |
| C | 6.300788   | 15.769458  | 16.143699  |
| C | 4.268203   | 14.563603  | 15.080334  |
| C | 3.462179   | 14.102964  | 16.244508  |
| C | 7.014756   | 15.987746  | 13.187858  |
| C | 2.610397   | 13.764149  | 13.337781  |
| C | 5.593133   | 15.792220  | 10.490943  |
| C | 3.903930   | 13.844286  | 10.570846  |
| H | 2.149666   | 14.427207  | 12.589011  |
| H | 1.950158   | 13.681244  | 14.208073  |
| H | 2.730424   | 12.770766  | 12.883207  |
| H | 6.871663   | 16.960955  | 12.697367  |
| H | 7.441261   | 15.293640  | 12.446926  |
| H | 7.714857   | 16.108044  | 14.021856  |
| H | 7.303844   | 15.312946  | 16.137209  |
| H | 5.839563   | 15.534692  | 17.111382  |
| H | 6.435884   | 16.861966  | 16.091640  |
| H | 3.326143   | 13.009394  | 16.243595  |
| H | 2.459237   | 14.559301  | 16.265357  |
| H | 3.967059   | 14.377104  | 17.179379  |
Table 8: Coordinates of boryl anion $8B$.

|     |          |          |          |
|-----|----------|----------|----------|
| B   | 4.761874 | 14.877285| 11.340643|
| N   | 5.783265 | 15.414671| 13.686436|
| N   | 3.877692 | 14.328162| 13.741134|
| N   | 6.689524 | 15.945234| 9.773476 |
| N   | 2.794280 | 13.734522| 9.879805 |
| C   | 4.800483 | 14.880851| 12.841456|
| C   | 5.492810 | 15.146214| 15.028306|
| H   | 6.142650 | 15.488032| 15.824649|
| C   | 4.314854 | 14.474478| 15.062290|
| H   | 3.725117 | 14.109443| 15.894270|
| C   | 6.924888 | 16.146142| 13.244264|
| C   | 6.774778 | 17.499480| 12.896295|
| C   | 7.905711 | 18.194274| 12.455198|
| H   | 7.802468 | 19.245042| 12.170547|
| C   | 9.158059 | 17.572432| 12.351569|
| C   | 9.268426 | 16.222659| 12.712830|
| H   | 10.236284| 15.721033| 12.625437|
| C   | 8.161360 | 15.487495| 13.154149|
| C   | 5.421208 | 18.151542| 12.961232|
| H   | 5.485161 | 19.218347| 12.710353|
| H   | 4.971069 | 18.048144| 13.960599|
| H   | 4.734798 | 17.656769| 12.253212|
| C   | 10.349937| 18.331187| 11.822198|
| H   | 11.293748| 17.856443| 12.124350|
| H   | 10.355156| 19.371163| 12.178797|
| H   | 10.332183| 18.364085| 10.720370|
| C   | 8.265549 | 14.020466| 13.478285|
| H   | 8.095307 | 13.824812| 14.548713|
| H   | 9.257257 | 13.631712| 13.211965|
| H   | 7.502918 | 13.452233| 12.925588|
| C   | 2.657296 | 13.690877| 13.369553|
| C   | 1.549964 | 14.483421| 13.021319|
| C   | 0.368247 | 13.834391| 12.647008|
| H   | -0.496232| 14.437796| 12.356587|
| C   | 0.274141 | 12.435894| 12.613896|
| C   | 1.402089 | 11.679572| 12.963054|
| H   | 1.351588 | 10.587711| 12.916907|
| C   | 2.606282 | 12.287333| 13.38567|
| C   | 1.665585 | 15.982036| 13.010875|
| H   | 2.001320 | 16.366292| 13.985924|
| H   | 0.705132 | 16.450490| 12.759397|
| H   | 2.422360 | 16.292975| 12.270986|
| C   | -1.017335| 11.759071| 12.223484|
| H   | -1.682490| 11.642389| 13.095313|
| H   | -0.834047| 10.755840| 11.814014|
| H   | -1.562818| 12.345951| 11.470573|
| C   | 3.835819 | 11.475354| 13.650349|
| H   | 4.126046 | 11.564513| 14.709109|
| H   | 4.690219 | 11.830812| 13.055313|
| H   | 3.668593 | 10.412967| 13.428604|
| C   | 5.872233 | 15.491333| 10.495862|
| C   | 3.633449 | 14.217838| 10.556544|
Table 9: Coordinates of boryl anion VII.

| B    | 4.737921 | 14.878634 | 11.285838 |
|------|----------|-----------|-----------|
| N    | 4.817272 | 14.923721 | 13.989730 |
| N    | 6.256239 | 16.602101 | 9.856613  |
| N    | 3.134897 | 13.111828 | 10.010245 |
| C    | 4.782968 | 14.904206 | 12.802148 |
| C    | 5.588878 | 15.845529 | 10.484502 |
| C    | 3.839076 | 13.887742 | 10.570654 |

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