A Neutral “Aluminocene” Sandwich Complex: $\eta^1$- versus $\eta^5$- Coordination Modes of a Pentaarylborole with ECp* ($E = Al, Ga$; Cp* = C$_5$Me$_5$)

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Experimental Details

General Information

All manipulations requiring handling under inert conditions were carried out under argon atmosphere using standard Schlenk techniques or an MBraun Glovebox with an Ar atmosphere. Benzene was obtained from an MBraun SPS and stored over molecular sieves, toluene and ether were distilled from sodium and degassed. Hexane and pentane were distilled from Na/K alloy. THF was distilled from potassium. Benzene-<sup>d6</sup> and toluene-<sup>d8</sup> were distilled from potassium, degassed and stored in a glove box.

Elemental analyses were performed by the Analytisches Labor, Institut für Anorganische Chemie, Universität Göttingen.

NMR spectroscopy

NMR spectra were recorded with either a Bruker Avance III 400 NMR spectrometer equipped with a 5 mm BBFO ATM probe head and operating at 400.13 (1<sup>H</sup>), 100.61 (13<sup>C</sup>), 128.38 (19<sup>F</sup>) and 376.45 MHz (19<sup>F</sup>) along with a variable temperature set-up or a Bruker Avance Neo 400 NMR spectrometer with a CryoProbeProdigy BB ATM probe head operating at 400.25 MHz (1<sup>H</sup>) or a Bruker AVIII HD 500 NMR spectrometer with a CryoProbeProdigy ATM probe head and operating at 500.13 (1<sup>H</sup>) and 130.35 MHz (27<sup>Al</sup>). Chemical shifts are reported in δ values in ppm relative to external Me<sub>4</sub>Si and, if not otherwise stated, referenced using the chemical shift of the respective solvent signal. The proton and carbon signals were assigned where possible via a detailed analysis of 1<sup>H</sup>–1<sup>H</sup> COSY, 1<sup>H</sup>–1<sup>H</sup> NOESY, 1<sup>H</sup>–13<sup>C</sup> HSQC, 1<sup>H</sup>–13<sup>C</sup> HMBC NMR spectra.

Young-type teflon-valve borosilicate NMR tubes have been used throughout the study.

Mass spectrometry

Mass spectra were recorded by the Zentrale Analytik within the Faculty of Chemistry, Göttingen applying a Liquid Injection Field Desorption Ionisation-technique on a JEOL accuTOF instrument with an inert-sample application setup under argon atmosphere. The injection capillary was washed several times with dry, distilled and inertly injected toluene before the samples were injected. Samples usually had a concentration of 1 – 2 mmol/L in toluene and were prepared in a glovebox.

Starting materials and reagents

1-(3',5'-Bis-(trifluoromethyl)phenyl)-2,3,4,5-tetrakis(3',5'-di-tert.-butylphenyl)-borole was prepared as previously reported.\[^2\]

Cp*SiMe\(_3\)[\(^{31}\)] Cp*AlBr\(_2\)[\(^{41}\)] (Cp*Al)\(_2\)[\(^{41}\)] and Cp*Ga[\(^{55}\)] were prepared along procedures as reported in the literature. (AlCp*)\(_4\) was recrystallised twice from benzene. GaCp* was distilled and stored at −40°C in a freezer.
Synthesis and Analytical Data

$\eta^5$-[1-(3',5'-Bis-(trifluoromethyl)phenyl)-2,3,4,5-tetakis(3',5'-di-tert.-butylphenyl)-borole]- $\eta^5$-Cp*-Aluminocene

In a glovebox, to a suspension of (AlCp*)₄ (30 mg, 46.3 μmol, 0.25 eq) in benzene (3 mL), an intensely green solution of 1-(3',5'-Bis-(trifluoromethyl)phenyl)-2,3,4,5-tetakis(3',5'-di-tert.-butylphenyl)-borole A (190.3 mg, 0.185 mmol, 1 eq) in dry, degassed benzene (1 mL) was added at ambient temperature and the mixture was stirred for 72h. Over the course of the slow reaction, undissolved (Cp*Al)₄ is continuously dragged into solution and the mixture slowly turns yellow. ¹H-NMR spectroscopic examination reveals clean conversion. The solvent is removed under reduced pressure and the pale-yellow residue is dissolved in toluene (ca. 2-3 mL). The solution is stored at –40°C for two days. Fractions of crystalline yield can be collected and drying under vacuum gives a combined yield of $\eta^5$-[1-(3',5'-Bis-(trifluoromethyl)-phenyl)-2,3,4,5-tetakis(3',5'-di-tert.-butylphenyl)-borole]-$\eta^5$-Cp*-Aluminocene (1) (180 mg, 0.151 mmol, 82%) of a colourless to pale yellow crystalline material. Crystals grow from saturated benzene solutions at ambient temperature or toluene or hexane solutions at –40°C.

NMR: ¹H (400.25 MHz, 298.2K, C₆D₆, C₆D₆-H at 7.15 ppm): 7.93 (br s, 2H, o-H₃), 7.79 (br s, 1H, p-

$\eta^5$-H₃), 7.29 (t, JHH = 1.8 Hz, 2H, p-H₃₂,₃), 7.25 (t, JHH = 1.8 Hz, 2H, p-H₃₄), 6.97 (br s, 4H, o-H₃₂,₃), 6.89 (br s, 4H, o-H₃₂,₃), 2.16 (s, 15H, Cp*-Me), 1.19 (s, 36H, Ar₂,₅-C(Me₃)), 1.16 (s, 36H, Ar₃,₄-C(Me₃)).

¹³C[¹H] (100.61 MHz, 300K, C₆D₆) solvent signal at 128.0 ppm): 149.8 (m-C₃₉), 149.7 (m-C₃₉), 144.2 (broad, ipso-C₃₉), 138.5 (ipso-C₃₉), 135.9 (ipso-C₃₉), 135.7 (br q, JCF = 3 Hz, o-C₃₉), 130.1 (q, JCF = 32 Hz, m-C₃₉), 128.4 (s, putatively borole-C₃₉), 126.6 (o-C₃₉), 126.1 (superimposed with quartet at 124.8 ppm, o-C₃₉₂,₃), 124.8 (q, JCF = 273 Hz, CF₃), 119.2 (p-C₃₉₄,₅), 119.1 (m, p-C₃₉), 118.5 (p-C₃₉₂,₃), 118.0 (br s, putatively borole-C₃₉), 117.7 (Cp*-C₃₉), 117.7 (Cp*-C₃₉), 34.8 (Ar₂,₅-C(Me₃)), 34.7 (Ar₃,₄-C(Me₃)), 31.58 (Ar₃,₄-C(Me₃)), 31.55 (Ar₂,₅-C(Me₃)), 11.5 (Cp*-C₃₉).

¹¹B (128.38 MHz, 298.3K, C₆D₆): 24.6 (broad, $\omega_{1/2} = \text{ca.} 1050$ Hz); (128.38 MHz, 198.2 K, toluene-d₆): 17.3 (broad, $\omega_{1/2} = \text{ca.} 500$ Hz).

¹⁹F[¹H] (376.45 MHz, 298.4K, C₆D₆): –62.45.

²⁷Al (130.35 MHz, 298.2K, C₆D₆): –86.2 (broad, $\omega_{1/2} = \text{ca.} 2650$ Hz).

Elemental Analysis: C₇₈H₉₀BF₆Al calcd C 78.63, H 8.63; observed C 78.68, H 8.63.

LIFDI-MS: calcd exact mass: 1190.78 m/z; observed m/z: 1189.7 (20%), 1190.7 (100%), 1191.7 (80%), 1192.7 (30%), 1193.7 (10%).
**Crystallographic details**

Crystals grow from concentrated benzene solutions at ambient temperature or toluene or hexane solutions at −40°C. Numerous attempts to change the crystallisation conditions have been made.

Crystals from benzene, toluene and hexane have been examined on a diffractometer. All crystals did not reveal reflections at higher resolutions than ca. 1.2 Å. Closer examination of the structures revealed that the crystals tend to be twinned and systematically reveal in all cases a disorder of the whole molecule which accounts for the poor resolutions. The data clearly allow the identification of the key structural fragment of an aluminium atom that is located in the center between the borole- and Cp-rings and thus confirms the \( \eta^5 \)-coordination mode. Modelling of the severe disorder lead to a rather poor data-to-parameter ratio.

Opposed to ambient atmosphere the crystals suspended in oil rapidly lose any crystallinity and crystal examination and picking was only efficiently possible using an XTEMP-setup.

For further detail of the refinement and modelling of the structure please see below (Crystallographic Section).

Crystal crop from benzene:

![Crystal crop from benzene](image1)

Crystal crop from toluene:

![Crystal crop from toluene](image2)
|                      | 1 from Toluene                  | 1 from Benzene                  | 1 from Hexane                  |
|----------------------|--------------------------------|--------------------------------|--------------------------------|
| CCDC number          | 1935771                        | not deposited                   | not deposited                   |
| empirical formula     | C₇₈H₁₀₂AlBF₆ + solvent         | C₇₈H₁₀₂AlBF₆ + solvent         | C₇₈H₁₀₂AlBF₆ + solvent         |
| formula weight        | 1191.38                        | 1191.38                         | 1191.38                         |
| T / K                | 100(2)                         | 100(2)                          | 100(2)                          |
| λ / Å                | 0.71073                        | 0.71073                         | 0.71073                         |
| crystal system        | monoclinic                     | monoclinic                      | monoclinic                      |
| space group           | P₂₁/n                          | P₂₁/n                           | P₂₁/n                           |
| a / Å                | 14.770(4)                      | 14.763(2)                       | 14.665(2)                       |
| b / Å                | 17.075(5)                      | 7.123(2)                        | 16.908(2)                       |
| c / Å                | 34.408(10)                     | 33.817(3)                       | 33.643(3)                       |
| β / °                | 97.27(2)                       | 97.82(2)                        | 102.37(2)                       |
| V / Å³               | 8608(4)                        | 8469(2)                         | 8148(2)                         |
| Z                    | 4                              | 4                               | 4                               |
| ρ / Mg m⁻³           | 0.919                          | 0.934                           | 0.971                           |
| μ / mm⁻¹             | 0.070                          | 0.071                           | 0.074                           |
| F(000)               | 2568                           | 2568                            | 2568                            |
| crystal size / mm⁻³  | 0.415 x 0.309 x 0.100          | 0.416 x 0.121 x 0.100           | 0.305 x 0.143 x 0.061           |
| θ range / °          | 1.193 to 18.122                | 1.216 to 15.897                 | 1.239 to 18.012                 |
| index ranges         | -12 ≤ h ≤ 12                   | -11 ≤ k ≤ 11                    | -8 ≤ k ≤ 12                     |
|                      | -14 ≤ k ≤ 14                   | 0 ≤ l ≤ 13                      | -14 ≤ k ≤ 14                    |
|                      | -29 ≤ l ≤ 30                   | 0 ≤ l ≤ 26                      | -29 ≤ l ≤ 29                    |
| refl. Collected      | 75486                          | 63300                           | 13076                           |
| indep. reflections/ Rint | 5992 / 0.0692               | 4052 / 0.0458                   | 5609 / 0.0419                   |
| completeness to θmax | 99.4 %                         | 99.7 %                          | 99.8 %                          |
| data/restraints/parameters | 5992 / 8425 / 1276       | 4052 / 8469 / 1276              | 5609 / 8645 / 1276              |
| GooF                 | 1.044                          | 1.077                           | 1.355                           |
| final R indices [I>2sigma(I)] | 0.0830 / 0.2047          | 0.0959 / 0.2246                 | 0.1096 / 0.3132                 |
| R indices (all data) | 0.1024 / 0.2193                | 0.1023 / 0.2283                 | 0.1520 / 0.3463                 |
| largest diff. peak and hole / eÅ⁻³ | 0.399 / -0.264          | 0.241 / -0.188                  | 0.470 and -0.421                |
| absorption correction | multiscan                      | multiscan                       | multiscan                       |
| twin fractions       | -                              | 0.918 / 0.082                   | -                               |
| SQUEEZE: Vsolv / Å³  | 1856                           | 1734                            | 1374                            |
| SQUEEZE: Vsolv / Vcell | 22 %                          | 20 %                            | 17 %                            |
| SQUEEZE: number of e⁻ | 544                            | 466                             | 312                             |
11B-NMR spectrum (background suppressed) of 1-[3',5'-CF3][2](C8H3)][2.3.4.5-[3',5'-tBu2](C8H3)][borole x AlCp* in C6D6
(standard borosilicate nmr tube)
11B-NMR spectrum (background suppressed) of 1-[3',5'-(CF3)2(C6H3)],2,3,4,5-[3',5'-iBu2(C6H3)]-borole x AlCp* in toluene-d8 at -75°C (standard borosilicate nmr tube)

27Al NMR spectrum of 1-[3',5'- (CF3)2(C6H3)],2,3,4,5-[3',5'-iBu2(C6H3)]-borole x GaCp* in C6D6

27Al NMR spectrum of 1-[3',5'- (CF3)2(C6H3)],2,3,4,5-[3',5'-iBu2(C6H3)]-borole x AlCp* in C6D6

standard borosilicate nmr tubes
VT-1H-NMR stackplot of Aluminium-complex 1 in toluene-d6, Referenced to toluene-d6 at 2.08 ppm.

30°C

15°C

5°C

-5°C

-15°C

-25°C

-35°C

-45°C

-55°C

-65°C

-75°C

ppm
VT-$^1$H-NMR stackplot of Aluminium-complex 1 in toluene-$d_8$. Referenced to toluene-$d_8$ at 2.08 ppm.
Plots of the LIFDI-MS spectra
In a glovebox, to an intensely green solution of \(1-\{(3',5'\text{-Bis(trifluoromethyl)}\text{phenyl})-2,3,4,5\text{-tetrakis(3',5'\text{-di-tert.\}}\text{-butylphenyl})\text{-borole}\} \) (158.2 mg, 0.154 mmol, 1 eq) in dry, degassed benzene (2 mL) was added a solution of \(\text{GaCp}^*\) (31.5 mg, 0.153 mmol, 1 eq) in benzene (1 mL) at ambient temperature. Once and the mixture immediately changed from green to a bright orange-red. \(^1H\)-NMR spectroscopic examination reveals clean conversion. The solvent is removed under reduced pressure and the orange residue is dried for several hours to give the product 2 in virtually quantitative yield (188 mg, 0.152 mmol, 99%) as an orange solid. The compound is very soluble in hydrocarbons. Crystals were grown by concentrating benzene solutions through slow evaporation of the solvent at ambient temperature. Small fractions of crystalline material can also be obtained from storage of very concentrated solutions in pentane at \(-40^\circ\text{C}\).

NMR:

\(^1H\) (400.13 MHz, 298.2K, \(\text{C}_6\text{D}_6\) at 7.15 ppm): 7.86 (br s, 2H, \(\alpha\text{-H}_{\text{ar1}}\)), 7.64 (br s, 1H, \(\rho\text{-H}_{\text{ar1}}\)), 7.23 (t, \(4J_{HH}=1.9\text{ Hz}, 2H, \rho\text{-H}_{\text{ar3,4}}\)), 7.17 (t, \(4J_{HH}=1.8\text{ Hz}, 2H, \rho\text{-H}_{\text{ar2,5}}\)), 7.11 (d, \(4J_{HH}=1.8\text{ Hz}, 4H, \rho\text{-H}_{\text{ar2,5}}\)), 6.97 (d, \(4J_{HH}=1.9\text{ Hz}, 4H, \rho\text{-H}_{\text{ar3,4}}\)), 1.89 (s, 15H, \(\text{Cp}^*\text{-Me}\)), 1.17 (s, 36H, \(\text{Ar}_{3,4}\text{-C(Me)3}\)), 1.12 (s, 36H, \(\text{Ar}_{2,5}\text{-C(Me)3}\)).

\(^13C\{^1H\} (100.62 MHz, 298.7K, \(\text{C}_6\text{D}_6\), solvent signal at 128.0 ppm): 151.2 (borole \(\text{C}_{3,4}\)), 150.7 (broad, \(ipso\text{-C}_{\text{ar1}}\)), 150.2 (\(m\text{-C}_{\text{ar3,4}}\)), 149.7 (\(m\text{-C}_{\text{ar2,5}}\)), 149.6 (borole \(\text{C}_{2,5}\)), 140.1 (\(ipso\text{-C}_{\text{ar2,5}}\)), 140.0 (\(ipso\text{-C}_{\text{ar3,4}}\)), 135.8 (br q, \(\alpha\text{-C}_{\text{ar1}}\)), 130.4 (q, \(JC=32\text{ Hz}, m\text{-C}_{\text{ar1}}\)), 125.1 (\(\alpha\text{-C}_{\text{ar3,4}}\)), 124.6 (\(\alpha\text{-C}_{\text{ar2,5}}\)), 124.5 (q, \(JC=273\text{ Hz}, CF_3\)), 119.4 (m, \(\rho\text{-C}_{\text{ar1}}\)), 119.34 (\(\rho\text{-C}_{\text{ar3,4}}\)), 119.29 (\(\rho\text{-C}_{\text{ar2,5}}\)), 114.3 (\(\text{Cp}^*\text{-CMe}\)), 34.7 (\(\text{Ar}_{3,4}\text{-C(Me3)}\)), 34.6 (\(\text{Ar}_{2,5}\text{-C(Me3)}\)), 31.7 (\(\text{Ar}_{3,4}\text{-C(Me3)}\)), 31.5 (\(\text{Ar}_{2,5}\text{-C(Me3)}\)), 9.6 (\(\text{Cp}^*\text{-CMe}\)).

\(^11B\) (128.38 MHz, 298.2K, \(\text{C}_6\text{D}_6\)): 7.3 (broad, \(\omega_{z/2}=ca.\ 1550\text{ Hz}\)); (128.38 MHz, 223.1 K, toluene-\(d_8\)): −0.4 (broad; due to superimposition with background no meaningful linewidth assignment possible).

\(^19F\{^1H\} (376.45 MHz, 298.3 K, \(\text{C}_6\text{D}_6\)): −62.46.

Elemental Analysis: \(C_{78}H_{102}BF_9\text{Ga}\) calcd C 75.91, H 8.33; observed C 75.60, H 8.50.

LIFDI-MS: calcd exact mass: 1232.72 m/z; observed only m/z patterns of the free borole (minor) and [borole × \(H_2O\)] (major).
Crystallographic details

Crystals suitable for X-ray analysis grow from benzene solutions carefully concentrated at ambient temperature by evaporation and storage of the very concentrated liquid for a few days.

Opposed to ambient atmosphere the crystals suspended in oil rapidly lose colour and crystallinity, and crystal examination and picking was performed using an XTEMP-setup.

Crystal crop from benzene:
Tabulated crystallographic data for 2.

| Compound | 2 |
|----------|---|
| CCDC number | 1935772 |
| Empirical formula | C_{78}H_{102}BGaF_{6} \times (C_{6}H_{6}) |
| Formula weight | 1312.23 |
| T [K] | 100(2) |
| Λ [Å] | 0.71073 (Mo, Kα) |
| Crystal system | orthorhombic |
| Space group | Pbca |
| a [Å] | 17.4388(13) |
| b [Å] | 29.760(2) |
| c [Å] | 29.925(3) |
| α [°] | 90 |
| β [°] | 90 |
| γ [°] | 90 |
| V [Å³] | 15531(2) |
| Z | 8 |
| ρ [Mg m\(^{-3}\)] | 1.122 |
| μ [mm\(^{-1}\)] | 0.41 |
| F(000) | 5616 |
| Crystal size [mm\(^3\)] | 0.36 \times 0.13 \times 0.11 |
| Theta range [°] | 1.4 – 27.9 |
| Index ranges | | |
| –21 ≤ h ≤ 22 |
| –30 ≤ k ≤ 39 |
| –35 ≤ l ≤ 39 |
| Refl. collected | 76338 |
| Indep. refl. / [R(int)] | 18542/0.058 |
| Completeness to θ\(_{max}\) | 99.8% |
| Data/restraints/parameter | 18542/1003/912 |
| GooF | 1.01 |
| Final R indices |
| [I > 2σ(I)] | R1 / wR2 |
| 0.045 / 0.114 |
| R indices (all data) |
| R1 / wR2 |
| 0.080/0.099 |
| Largest diff. peak & hole [eÅ\(^{-3}\)] | 0.52/–0.36 |
| Absorption correction | multiscan |
Plots of the NMR spectra

1H-NMR-spectrum of 1-(3',5'-((CF3)2(C6H3))-2,3,4,5-(3',5'-tBu2(C6H3))-borole x GaCp* in C6D6
# referenced to C6D5H at 7.15 ppm

**Figure 1: NMR spectrum of 1-(3',5'-((CF3)2(C6H3))-2,3,4,5-(3',5'-tBu2(C6H3))-borole x GaCp* in C6D6**

*pentane

1H-NMR-spectrum of 1-(3',5'-((CF3)2(C6H3))-2,3,4,5-(3',5'-tBu2(C6H3))-borole x 1.1 eq GaCp*
# referenced to (C6D5)CD2H at 2.08 ppm

**Figure 2: NMR spectrum of 1-(3',5'-((CF3)2(C6H3))-2,3,4,5-(3',5'-tBu2(C6H3))-borole x 1.1 eq GaCp**
1H-NMR-spectrum of 1-[3',5'-(CF₃)₂(C₆H₃)]2-2,3,4,5-[3',5'-iBu₂(C₆H₃)]-borole x GaCp⁺ in toluene-d₈ at -50°C. *# referenced to (CD₃)CD₂H at 2.08 ppm

* putatively free GaCp⁺

13C(1H)-NMR-spectrum of 1-[3',5'-CF₃(C₆H₃)]2-2,3,4,5-[3',5'-iBu₂(C₆H₃)]-borole x GaCp⁺ in C₆D₆
*# referenced to C₆D₆ at 128.0 ppm

q: indicates quartet signals from fluorine coupling

pentane
19F{1H}-NMR-spectrum of 1-[3',5'-((CF3)2)(C6H3)]-2,3,4,5-(3',5'-iBu2)(C6H3))-borole x GaCp* in C6D6

11B-NMR spectrum (background suppressed) of 1-[3',5'-((CF3)2)(C6H3)]-2,3,4,5-(3',5'-iBu2)(C6H3))-borole x GaCp* in C6D6
$^{11}B$-NMR spectrum (background suppressed) of 1-hexyl-2,3,4,5-tetraakis(2,6-diisopropylphenyl)-1,4-borole x GaCp in toluene-d8 at -50°C.
VT-\textsuperscript{1}H-NMR stackplot of Gallium-complex 2 in toluene-d\textsubscript{6}. Referenced to toluene-d\textsubscript{6} at 2.08 ppm.

- 20°C
- 10°C
- 0°C
- -10°C
- -20°C
- -30°C
- -40°C
- -50°C
- -60°C
- -70°C

\begin{tabular}{c}
| ppm |
|-----|
| 8.6 |
| 8.4 |
| 8.2 |
| 8.0 |
| 7.8 |
| 7.6 |
| 7.4 |
| 7.2 |
| 7.0 |
| 6.8 |
| 6.6 |
\end{tabular}
VT-$^1$H-NMR stackplot of Gallium-complex 2 in toluene-d$_4$, Referenced to toluene-d$_4$ at 2.08 ppm.

20°C

10°C

0°C

-10°C

-20°C

-30°C

-40°C

-50°C

-60°C

-70°C

ppm
Plots of the LIFDI-MS spectra

Control Experiment (Free Borole in Toluene)

No signals (e.g. GaCp* derivatives) were detected in the lower mass region 0 - 800 m/z
Crystallographic Details
Data Acquisition and Processing

X-ray data for 1, and 2 were collected on Bruker APEX II CCD diffractometers with either Mo Kα radiation from a IµS or spinning anode source. The data were integrated using SAINT implemented in Brukers APEX3 programme suite. SADABS or TWINABS were used for multi-scan absorption correction. Structure solution was performed with SHELXT and refined using SHELXL along the graphical user interphase of ShelXle. In some cases DSR has been applied to treat disordered solvent molecules. All hydrogen atoms were placed with a riding model. Further details on the individual data sets are tabulated in the analytical section of each compound. All structures were deposited with the CCSD.

Crystallographic and Refinement Details 1

Crystals of compound 1 were obtained from three different solvents (toluene, benzene and hexane) from concentrate solutions at ambient or low temperature (~40°C). The crystals are stable under argon atmosphere but lose their crystallinity under ambient conditions in inert oil within minutes. Crystals were therefore mounted with an XTEMP device.

As the crystals of 1 from benzene were twinned, the two reciprocal lattices were sorted using RLATT from within the Bruker Apex 3 2018.7-2 GUI. All three datasets were integrated using SAINT 8.38A.

All three structures showed disorder within the solvent molecules in solvent accessible voids and within the majority (the entire borole sub unit) of the structure itself, which in consequence results in very poor intensity of reflections with a resolution higher than about 1.2 Å. To fit the solvent molecules with as little parameters as possible, the solvent molecules within the moieties were fitted using the SQUEEZE model, as implemented in PLATON.

The disorder of the Ph* and XylF groups were treated differently. The Ph* moiety was modelled using a modified mesityl group as included in the DSR programme with all the non tert-butyl methyl group positions being refined as a rigid-body. The positions of the bound methyl groups were refined freely (see figure on the right).

Within the five membered borole unit, C₃ and C₅ positions were restrained to have similar 1,2 and 1,3 distances. The resulting target symmetry of the restraints would be equivalent to a mirror plane through the boron atom and the opposing carbon-carbon bond. All C-C distances from the borole ring to the outer substituents were refined to be equivalent as well. All tert-butyl groups were restrained to have similar 1,2 and 1,3 distances. Equivalent restraints were applied to the trifluoromethyl groups.

Atomic displacement parameters of atoms within the disordered borole moiety were refined to be have similar Uij components to their neighbours (SIMU). Additionally, rigid body restraints for the atomic displacement parameters were applied to these atoms (RIGU).

With the very similar electron density pattern of a (C-Ph*) vs a (B-XylF) moiety, the quasi five-fold symmetry, as well as the disorder, pose the question, whether there are additional orientations. All putative combinations of boron positions for the two disorders were evaluated, with the reported structures showing a significantly lower R-value than the alternatives. The difference can, in large part, be attributed to the fit of the CF₃ groups. The model should therefore represent the two main positions of the borole moiety. However, due to the nature of the disorder and the limited resolution, additional minor occupation where the ring overlaps but is rotated differently, cannot be ruled out.

Despite the considerable efforts the resulting data-to-parameter ratio was still low for all three structures. This is an inherent result from the structure itself, as already mentioned before. However, the derived features are similar between all three structures and consistent with all other experimental and especially theoretical results.
Tabulated values for the key structural features of the “Aluminocene” 1 from various data sets. Please note, that there are differences of the Al–B distances in Disorder 1 and Disorder 2. This may indicate that the exact assignment/modelling of (C-Ph*) vs.(B-Xyl)-units may be incomplete.

### 1 from Toluene

|                        | Disorder 1 | Disorder 2 | Disorder 1 | Disorder 2 | Disorder 1 | Disorder 2 |
|------------------------|------------|------------|------------|------------|------------|------------|
| occupation / %         | 49.0(2)    | 51.0(2)    | 59.4(3)    | 40.6(3)    | 63.7(2)    | 36.3(2)    |
| d(Al - B) / Å          | 2.31(2)    | 2.13(2)    | 2.24(2)    | 2.08(6)    | 2.25(2)    | 2.15(2)    |
| d(Al - Cₐ,1) / Å       | 2.25(2)    | 2.00(2)    | 2.20(2)    | 2.01(3)    | 2.12(2)    | 2.25(2)    |
| d(Al - Cₛ,2) / Å       | 2.10(2)    | 2.22(2)    | 2.11(3)    | 2.27(4)    | 2.23(2)    | 2.02(2)    |
| d(Al - Cₛ,1) / Å       | 2.19(2)    | 2.17(2)    | 2.15(3)    | 2.20(5)    | 2.18(2)    | 2.30(2)    |
| d(Al - Cₛ,2) / Å       | 2.12(2)    | 2.32(2)    | 2.12(2)    | 2.35(3)    | 2.20(2)    | 2.15(2)    |
| d(B - Cₐ,1) / Å        | 1.54(2)    | 1.53(2)    | 1.54(2)    | 1.55(4)    | 1.54(2)    | 1.53(2)    |
| d(B - Cₛ,1) / Å        | 1.53(2)    | 1.54(2)    | 1.54(2)    | 1.56(4)    | 1.55(2)    | 1.56(2)    |
| d(Cₛ,1 - Cₛ,2) / Å     | 1.46(2)    | 1.47(2)    | 1.45(2)    | 1.48(3)    | 1.46(2)    | 1.46(2)    |
| d(Cₛ,1 - Cₛ,2) / Å     | 1.47(2)    | 1.47(2)    | 1.45(2)    | 1.48(3)    | 1.45(2)    | 1.46(2)    |
| d(Cₛ,2 - Cₛ,2) / Å     | 1.42(2)    | 1.41(2)    | 1.42(2)    | 1.42(4)    | 1.44(2)    | 1.43(2)    |

Depictions of the disordered borole subunit within the molecule 1. Part 1 (Blue), Part 2 (orange). The second fragment is a borole unit rotated by ca. 36° with an inversion of the paddlewheel tilt of the aryl groups. This major disorder, along with further disorder within the t-Bu groups causes the low resolution of the obtainable data.

### Refinement Details 2

The structure contains one molecule of lattice benzene, which is disordered modelled using SIMU, RIGU and SAME commands. Two tert.-butyl groups and a CF₃ group are disordered and each modelled over two positions using SIMU, RIGU and SAME commands.
Computational Details

Structure Optimisation, Frequency Calculation and Thermochemical Approximations

For thermochemical approximations, structures were optimised with Gaussian09.D01\cite{14} applying the BP86 functional\cite{15} and Grimmes D3 dispersion correction\cite{16} with def2-SVP\cite{17} basis sets on all elements. Frequency calculations were performed on these structures and absence of imaginary frequencies confirmed true local minima on the potential energy surface. Thermochemical corrections stem from these calculations. Single point energies were calculated on these structures using a def2-TZVP basis set on all atoms.

| Gaussian09 Thermochemistry BP86-D3/def2-TZVP | kcal/mol |
|---------------------------------------------|----------|
| Hartree ---| E0   | E0+ZVPE | H\(^N\) | G\(^N\) | dE\(\Delta\) | dE0+ZVPE | dH\^* | dG\^* |
| AlCp\(^*\) | -632.722537 | -632.508421 | -632.493222 | 632.54852 |
| GaCp\(^*\) | -2315.39782 | -2315.18444 | -2315.16894 | -2315.2255 |
| A  | -3268.97933 | -3267.62881 | -3267.54704 | -3267.74717 |
| 1  | -3901.79893 | -3900.23013 | -3900.13451 | -3900.35853 |
| 2  | -5584.42566 | -5582.85951 | -5582.76234 | -5582.99003 |
| A + AlCp\(^*\) ➔ 1 | -0.09707216 | -0.09296516 | -0.09425416 | -0.06203816 | -60.91 | -58.30 | -59.15 | -39.43 |
| A + GaCp\(^*\) ➔ 2 | -0.04850441 | -0.04625641 | -0.04635541 | -0.02036841 | -30.44 | -29.03 | -29.09 | -12.75 |

[a] Thermochemical corrections stem from BP86-D3-def-SVP optimisation and frequency calculations.
Summary GIAO-NMR computations

Computational examination was performed using ORCA (version 4.1).\textsuperscript{[18]} For numerical accuracy, a gridsize of “5” and a final step gridsize of “6” is applied. GIAO-NMR spectroscopic properties were calculated as implemented as the default in ORCA4.1 applying RIJK-PBE\textsuperscript{[19]} functional on structures previously optimised using the RI-BP86-D3BJ-def2TZVP/i model chemistry.\textsuperscript{[15, 17, 20]} Input structures were based on X-ray structures of 2 and A. For NMR calculations of the reference set of small molecules, def2-TZVPP basis sets were chosen for B, Al and Ga and def2-TZVP for all other elements. For the rather large molecules 1 and 2, def2-TZVPP basis sets were chosen for B, Al and Ga, while a def2-TZVP basis was chosen for the core carbon atoms (namely borole C$_\alpha$ and C$_\beta$ positions, the ipso-C$_{ipso}$ atom as well as the inner cyclopentadienyl carbon atoms). A def2-SVP basis set was applied for all other atoms.

The reported $^{11}$B-NMR chemical shifts are referenced against the $\sigma_{iso}$ values obtained for Et$_2$O-BF$_3$ with $\delta_{ref} = 0$ ppm.

The reported $^{27}$Al-NMR chemical shifts are referenced against the $\sigma_{iso}$ values obtained for [Al(H$_2$O)$_6$]$^{3+}$ with $\delta_{ref} = 0$ ppm.

The reported $^{13}$C-NMR chemical shifts are internally referenced against the averaged $\sigma_{iso}$ values of the five cyclopentadienyl signals with $\delta_{ref} = \delta_{calc}$ ppm.

\begin{table}[h!]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
& $\sigma_{iso,calc}$ & $\delta_{iso,calc}$ & $\delta_{exp}$ \\
\hline
$^{27}$Al-NMR & & & \\
[Al(H$_2$O)$_6$]$^{3+}$ & 579.3 (ref) & 0 (ref) & 0 (ref) \\
[AlCl$_6$] & 458.8 & 120.5 & 115.2 \textsuperscript{[21]} \\
[Cp*$_2$Al]$^+$ & 691.8 & $-112.5$ & $-102.9$ \textsuperscript{[21]} \\
$tBu$_3$Al & 299.5 & 279.8 & 255 \textsuperscript{[22]} \\
\hline
$^{11}$B-NMR & $\sigma_{iso,calc}$ & $\delta_{iso,calc}$ & $\delta_{exp}$ \\
BF$_3$(OEt)$_2$ & 101.2 (ref) & 0 (ref) & 0 (ref) \\
[Cp*$_2$B]$^+$ & 151.7 & $-50.5$ & $-41.3$ \textsuperscript{[22]} \\
[Cp*$_2$BMe] & 27.8 & 73.4 & 81.9 \textsuperscript{[22]} \\
\hline
1 & 669.3 & $-90$ & $-86.2$ \\
2 & 102.1 & $-0.9$ & $-0.4$ \textsuperscript{[223]} \\
\hline
\end{tabular}
\caption{Experimental and calculated $\sigma_{iso}$ and $\delta_{calc}$ values for selected compounds.}
\end{table}

\begin{table}[h!]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline
& & $^{13}$C-NMR & & & & & $^{13}$C-NMR & & & \\
& & Cp* CMe & C$_\alpha$ & C$_\beta$ & ipso- & Cp* CMe & C$_\alpha$ & C$_\beta$ & ipso- & \\
& & & & & C$_{ipso}$ & & & & C$_{ipso}$ & \\
& & $\sigma_{iso,calc}$ & & & & & $\sigma_{iso,calc}$ & & & \\
\hline
1 & 63.6 & 181.3\textsuperscript{[20]} (62.7, 62.8, 60.3, 66.5, 65.8) & 64.6 (62.1) & 55.2 (55.17, 55.29) & 36.5 & 66.8 & 181.3\textsuperscript{[20]} (66.8, 65.9, 67.3, 64.6, 69.6) & 31.2 (32.4, 29.9) & 29.4 (32.9, 25.8) & 29.5 \\
2 & 117.7 (ref) & 117.9 & 126.1 & 144.8 & 114.3 (ref) & 149.9 & 151.7 & 151.6 \\
\hline
\end{tabular}
\caption{Experimental and calculated $\sigma_{iso,calc}$ values for selected compounds.}
\end{table}

For NMR calculations of the reference set of small molecules, def2-TZVPP basis sets were chosen for B, Al and Ga and def2-TZVP for all other elements. For the rather large molecules 1 and 2, def2-TZVPP basis sets were chosen for B, Al and Ga, while a def2-TZVP basis was chosen for the core carbon atoms (namely borole C$_\alpha$ and C$_\beta$ positions, the ipso-C$_{ipso}$ atom as well as the inner cyclopentadienyl carbon atoms). A def2-SVP basis set was applied for all other atoms.

The reported $^{11}$B-NMR chemical shifts are referenced against the $\sigma_{iso}$ values obtained for Et$_2$O-BF$_3$ with $\delta_{ref} = 0$ ppm.

The reported $^{27}$Al-NMR chemical shifts are referenced against the $\sigma_{iso}$ values obtained for [Al(H$_2$O)$_6$]$^{3+}$ with $\delta_{ref} = 0$ ppm.

The reported $^{13}$C-NMR chemical shifts are internally referenced against the averaged $\sigma_{iso}$ values of the five cyclopentadienyl signals with $\delta_{ref} = \delta_{calc}$ ppm.

\begin{table}[h!]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|}
\hline
& & $^{13}$C-NMR & & & & & $^{13}$C-NMR & & & \\
& & Cp* CMe & C$_\alpha$ & C$_\beta$ & ipso- & Cp* CMe & C$_\alpha$ & C$_\beta$ & ipso- & \\
& & & & & C$_{ipso}$ & & & & C$_{ipso}$ & \\
& & $\sigma_{iso,calc}$ & & & & & $\sigma_{iso,calc}$ & & & \\
\hline
1 & 63.6 & 181.3\textsuperscript{[20]} (62.7, 62.8, 60.3, 66.5, 65.8) & 64.6 (62.1) & 55.2 (55.17, 55.29) & 36.5 & 66.8 & 181.3\textsuperscript{[20]} (66.8, 65.9, 67.3, 64.6, 69.6) & 31.2 (32.4, 29.9) & 29.4 (32.9, 25.8) & 29.5 \\
2 & 117.7 (ref) & 117.9 & 126.1 & 144.8 & 114.3 (ref) & 149.9 & 151.7 & 151.6 \\
\hline
\end{tabular}
\caption{Experimental and calculated $\sigma_{iso,calc}$ values for selected compounds.}
\end{table}

[a] The external reference $^{13}$C $\sigma_{iso,calc}$ value for SiMe$_4$ was calculated to be 186.9 ppm.
Figure SI Plots of $\delta_{\text{exp}}$ vs $\delta_{\text{calc}}$ to allow for an estimation of the reliability of the model chemistry to describe the NMR-chemical shift.
**Frontier Orbital Depictions**

Selected canonical frontier orbitals from BP86 calculations (vide supra) are shown. All drawn at an isosurface value of 0.04 a.u. using the programme ChemCraft for visualisation. All hydrogen atoms are omitted for the sake of clarity.

Compound 1 \( \eta^5\-\{(\text{PhC})_4\text{BXyl}\}, \eta^5\-\text{Cp}^*\-\text{Al(III)} \)

![LUMO+2, HOMO, HOMO-1](image)

Compound 2 \( \eta^1\-\{(\text{PhC})_4\text{BXyl}\}, \eta^5\-\text{Cp}^*\-\text{Ga(I)} \)

![LUMO, HOMO](image)

**Topology Analyses**

Topology analyses and Bader Charge-analyses were carried out using the Multiwfn programme or AIMAll on the RIBP86-D3BJ-def2TZVP wave function files obtained from ORCA.

![AIMAll plots for molecular excerpts of the topological analysis of compound 1 (left) and 2 (right)](image)

*Figure S1* AIMAll plots for molecular excerpts of the topological analysis of compound 1 (left) and 2 (right). In both cases a contour plot of the Laplacian of the electron density \( \nabla^2 \rho(r) \) through the molecule’s central plane \( \{E-\text{B-}[\text{C}_5\text{F}_3\text{C}_5\text{H}_{3\text{prim}}]\} \) is also depicted. Bond critical points are depicted in green, ring critical points are depicted in red and cage critical points are depicted in blue. Blue lines indicate positive Laplacian (area of charge depletion), maroon dotted lines indicate negative Laplacian (area of charge concentration).
To shed further light onto the structure analysis of the aluminium sandwich complex further analyses were carried out. The results from topology analyses did not differ between wavefunctions obtained from BP86 or PBE0 functional calculations and no qualitative change between def-SVP basis sets and def2-TZVPP basis sets were observed. In all cases same CP and bonding path were found giving the same molecular graphs. We further investigated the parent all hydro substituted $\eta^5,\eta^5$-($\mathrm{C}_4\mathrm{BH}_5$),$\mathrm{C}_5\mathrm{H}_5$ Al complex. Structures have been optimised using both BP86 and PBE0 functional and def2-TZVPP basis sets. No imaginary frequencies were found confirming minimum structures. The geometries obtained are summarised in the following Figure.

**Figure S1** Structural features of the optimised geometries for parent borole/Cp “aluminocenes”.

Some features of the QTAIM analyses for both calculations are depicted below. The isodensity surfaces show that electron density around the boron atom is significantly reduced when compared to the densities at $C_\alpha$ but also $C_\beta$.

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**Figure S1** Structural features of the optimised geometries for parent borole/Cp “aluminocenes”.

Some features of the QTAIM analyses for both calculations are depicted below. The isodensity surfaces show that electron density around the boron atom is significantly reduced when compared to the densities at $C_\alpha$ but also $C_\beta$.
Figure S1 AIMAll plots for (C₄BH₅)Al(C₅H₅) from PBE0-def2TZVPP (left) and BP86-def2TZVPP calculations. BCP (green), RCP (red) and CCP (blue).

Bader charges for model complex (C₄BH₅)Al(C₅H₅)

|        | BP86  | PBE0  |
|--------|-------|-------|
| Al1    | 2.2460| 2.3647|
| Borole | B2    | 1.6350| 1.7559|
|        | C3    | -1.0462| -1.0989|
|        | C4    | -0.2460| -0.2645|
|        | C5    | -0.2455| -0.2631|
|        | C6    | -1.0455| -1.0998|
|        | H7    | -0.6122| -0.6447|
|        | H8    | 0.0146 | 0.0122 |
|        | H9    | 0.0201 | 0.0190 |
|        | H10   | 0.0200 | 0.0193 |
|        | H11   | 0.0143 | 0.0116 |
|        | sum   | -1.4914| -1.5531|
| Cp     | C12   | -0.2179| -0.2417|
|        | C13   | -0.1622| -0.1869|
|        | C14   | -0.1766| -0.1846|
|        | C15   | -0.2533| -0.2360|
|        | C16   | -0.2826| -0.2740|
|        | H17   | 0.0596 | 0.0613 |
|        | H18   | 0.0583 | 0.0613 |
|        | H19   | 0.0583 | 0.0614 |
|        | H20   | 0.0610 | 0.0622 |
|        | H21   | 0.0634 | 0.0637 |
| Cp     | sum   | -0.7919| -0.8133|
| Total  | sum   | -0.0373| -0.0017|

NBO and NRT Analyses

NBO and NRT analyses were performed using NBO7 on a [C₄BH₅]²⁺ structure optimised using ORCA BP86-D3BJ and def2-TZVPP basis set.²⁸
Using ORCA4.1 RI-BP86-D3BJ-def2TZVP/j model chemistry

Optimised Structure of compound 1

Using ORCA4.1 RI

XYZ-coordinates of optimised molecules

C  8.163665000  14.559286000  21.705280000
H  8.933650000  14.486616000  22.797110000
H  7.119711000  14.756768000  23.848930000
C  7.939396000  10.364285000  18.361313000
C  8.857187000  11.252515000  19.406085000
H  9.510403000  7.816246000  20.894390000
H  9.339610000  10.364285000  20.427762000
H  9.411704000  8.956364000  20.091157000
F  10.059950000  9.5504014000  20.636599000
H  9.397189000  7.817408000  21.757801000
H  7.805500000  11.873660000  21.655945000
H  7.804200000  12.207290000  21.543400000
H  3.110911000  10.691110000  15.458095000
H  5.968420000  11.570935000  14.705225000
H  12.752610000  3.048866000  21.408500000
H  5.842060000  10.548713000  15.510780000
H  6.167420000  10.160260000  16.675041000
H  5.797630000  9.303665000  20.786606000
H  4.176212000  10.095432000  21.919673000
H  1.714605000  13.232240000  15.084517000
H  7.715465000  13.289890000  14.180616000
F  8.566878000  14.129460000  14.830580000
C  7.697740000  14.059776000  13.622011000
C  7.805115000  14.474600000  19.100747000
C  5.589280000  14.473460000  18.271319000
C  6.350732000  13.628260000  18.745074000
C  6.781300000  17.265104000  17.285219000
C  5.269420000  17.585842000  16.975926000
H  6.001636000  14.182385000  17.172471000
C  6.918400000  15.562090000  16.602129000
C  6.707724000  17.150640000  18.229900000
H  7.526440000  17.004916000  17.184480000
H  6.955290000  17.480070000  19.804022000
H  7.388130000  16.726661000  18.493154000
H  8.915536000  15.518620000  19.638152000
C  11.287260000  16.604200000  19.933060000
C  10.635850000  14.083250000  20.094365000
C  11.283570000  15.544810000  20.655924000
C  10.635850000  15.111010000  21.999486000
H  10.428824000  17.494987000  21.079415000
H  12.241850000  12.227830000  21.037831000
F  12.241850000  17.494987000  21.079415000
H  12.241850000  17.494987000  21.079415000
H  12.241850000  17.494987000  21.079415000
H  12.241850000  17.494987000  21.079415000
| Atom | x (Å) | y (Å) | z (Å) |
|------|-------|-------|-------|
| C    | 12.764559 | 8.825600 | 19.043780 |
| H    | 13.742540 | 8.347040 | 18.892170 |
| H    | 12.095390 | 8.037870 | 19.353209 |
| H    | 12.869530 | 9.117610 | 19.902651 |
| C    | 12.764559 | 8.825600 | 19.043780 |
| H    | 13.742540 | 8.347040 | 18.892170 |
| H    | 12.095390 | 8.037870 | 19.353209 |
| H    | 12.869530 | 9.117610 | 19.902651 |

Optimised Structure of (C\(_4\)BH\(_5\))Al(C\(_5\)H\(_5\)) (PBE0-def2TZVPP)

| Atom | x (Å) | y (Å) | z (Å) |
|------|-------|-------|-------|
| C    | 9.536778  | 10.026770 | 20.644800 |
| C    | 9.298470  | 12.947411 | 18.497036 |
| H    | 10.154652 | 10.043267 | 21.533093 |
| H    | 9.406129  | 7.833405  | 20.338824 |
| C    | 11.351094 | 8.959050  | 20.002398 |
| H    | 11.335230 | 11.743284 | 16.374383 |
| H    | 12.407433 | 9.583030  | 18.643545 |
| C    | 9.136480  | 8.259740  | 20.002398 |
| H    | 10.293815 | 10.034740 | 18.617609 |
| B    | 8.246239  | 10.669300 | 18.698756 |
| C    | 9.100340  | 11.160290 | 19.886710 |
| C    | 12.082790 | 10.931940 | 20.698533 |
| H    | 8.053319  | 8.354040  | 18.137440 |
| C    | 11.827546 | 8.788939  | 17.692980 |
| H    | 8.111104  | 8.959050  | 16.693746 |
| C    | 11.631101 | 10.883430 | 16.954392 |
| C    | 12.820790 | 10.931940 | 20.698533 |
| C    | 12.407433 | 9.583030  | 18.643545 |
| C    | 9.298470  | 10.026770 | 20.644800 |
| H    | 10.154652 | 10.043267 | 21.533093 |
| H    | 9.406129  | 7.833405  | 20.338824 |

Optimised Structure of (C\(_4\)BH\(_5\))Al(C\(_5\)H\(_5\)) (BP86-def2TZVPP)

| Atom | x (Å) | y (Å) | z (Å) |
|------|-------|-------|-------|
| C    | 9.136480  | 8.259740  | 20.002398 |
| H    | 10.293815 | 10.034740 | 18.617609 |
| B    | 8.246239  | 10.669300 | 18.698756 |
| C    | 9.100340  | 11.160290 | 19.886710 |
| C    | 12.082790 | 10.931940 | 20.698533 |
| H    | 8.053319  | 8.354040  | 18.137440 |
| C    | 11.827546 | 8.788939  | 17.692980 |
| H    | 8.111104  | 8.959050  | 16.693746 |
| C    | 11.631101 | 10.883430 | 16.954392 |
| C    | 12.820790 | 10.931940 | 20.698533 |
| C    | 12.407433 | 9.583030  | 18.643545 |
| H    | 10.140118 | 10.643370 | 21.474796 |
| H    | 9.081225  | 12.313720 | 19.701370 |
| H    | 10.140118 | 10.643370 | 21.474796 |
| H    | 9.650956  | 10.129750 | 20.820370 |
| H    | 8.239770  | 7.981784  | 18.582760 |
| C    | 11.696840 | 8.743647  | 17.363027 |
| C    | 11.388520 | 9.842710  | 16.514910 |
| C    | 11.783200 | 11.037270 | 17.170620 |
| C    | 12.346780 | 10.689310 | 18.432860 |
| C    | 12.306110 | 9.259140  | 18.554920 |
| H    | 11.487050 | 7.698168  | 17.163180 |
| H    | 10.861450 | 9.786180  | 15.576300 |
| H    | 11.621250 | 12.047520 | 16.808616 |
| H    | 12.732402 | 11.377650 | 19.178298 |
| H    | 12.661940 | 8.677293  | 19.390240 |

Optimised Structure of (C\(_4\)BH\(_5\))\(_2\) (BP86-def2TZVPP)

| Atom | x (Å) | y (Å) | z (Å) |
|------|-------|-------|-------|
| B    | 8.246239 | 10.669300 | 18.698756 |
| C    | 9.136480  | 8.259740  | 20.002398 |
| H    | 10.154652 | 10.043267 | 21.533093 |
| H    | 9.406129  | 7.833405  | 20.338824 |
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