Electronic Supplementary Information

An Exceptionally High Boron Content Supramolecular Cuboctahedron

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1. Synthetic procedures and characterization

General considerations: 1,7-dicarba-closo-dodecaborane (m-carborane) was purchased from Katchem (Czech Republic) and used as received. Diethyl 5-iodoisophthalate was prepared according to previously published literature procedures. All other solvents and chemicals were obtained from Aldrich Chemical Co. (Milwaukee, USA). Deuterated solvents were purchased from Cambridge Isotope Laboratories and used as received. For all air-sensitive manipulations either a Vacuum Atmospheres Nexus II N2-filled glove box or Schlenk techniques were employed. Analytical thin layer chromatography (TLC) was performed using plastic plates pre-coated with silica gel (0.25 mm, 60 Å pore size) with a fluorescent indicator (254 nm). Visualization was accomplished with UV light and/or palladium chloride (PdCl2) in hydrochloric acid (0.6 M in EtOH) as a stain. All NMR spectra were recorded Bruker Avance 400 MHz equipped with a broadband probe at 300 K. 1H and 1H{11B} NMR spectra were referenced internally to residual protons in the deuterated solvents (dichloromethane-d2 = δ 5.32; acetone-d6 = δ 2.05). 13C{1H} NMR spectra were referenced internally to carbons in the deuterated solvents (dichloromethane-d2 = δ 53.84; acetone-d6 = δ 29.84). 11B and 11B{1H} NMR spectra were referenced to a neat BF3·Et2O standard at 0.0 ppm. Electrospray ionization (ESI) mass spectra were recorded on an Agilent 6120 LC–TOF instrument in positive ion mode. Elemental analyses (C, H, N) were performed by Quantitative Technologies (Intertek), Whitehouse, NJ.

Compound 1

Compound 1 was prepared following a procedure analogous to that reported by Schörbel et al.2 To a solution of m-carborane (1.00 g, 6.9 mmol) in diethyl ether (25 mL) was added n-BuLi (1.6 M solution in hexane, 4.3 mL, 6.9 mmol) at 0 °C. After 1.5 hours of stirring at room temperature,
a slurry of CuCl (0.69 g, 6.9 mmol) in 20 mL THF was added at −30 °C under nitrogen. The mixture was allowed to stir for 1 hour at room temperature and then refluxed for 30 minutes. After the solvent was removed under reduced pressure, N-methylpyrrolidone (25 mL), diethyl 5-iodoisophthalate (2.72 g, 7.8 mmol), and PdCl₂(PPh₃)₂ (276 mg, 0.39 mmol) were added. The mixture was stirred at 100 °C for 48 hours, cooled and poured into 30 mL of brine. Additional NaCl (1 g) was added and the mixture was filtered and the filtrate was then discarded. The retentate was stirred in acetone and then filtered. The filtrate was then collected, solvent removed and the mixture was purified by column chromatography using a solvent gradient of 2:1–2:3 hexanes/DCM: 1.22 g (48 %). ¹H{¹¹B} NMR (400 MHz, CD₂Cl₂) δ 1.41 (t, 6 H, alkyl), 2.23 (s, 2 H, BH), 2.32 (s, 3 H, BH), 2.55 (s, 2 H, BH), 2.71 (s, 1 H, BH), 3.05 (s, 2 H, BH), 3.24 (s, 1 H, CH), 4.40 (q, 4 H, CH₂). ¹³C{¹H} NMR (100.6 MHz, CD₂Cl₂) δ 14.53 (CH₃), 56.22 (C(carboraneH), 62.11 (CH₂), 77.34 (C(carboraneCar)), 130.91 (Car), 132.00 (Car), 133.04 (Car), 136.51 (Car), 165.28 (C(ester)); ¹¹B NMR (128.4 MHz, CD₂Cl₂) δ −15.54 (d, ¹J_B-H = 187 Hz), −13.70 (d, ¹J_B-H = 170 Hz), −10.91 (d, ¹J_B-H = 156 Hz), −8.90 (d), −4.63 (d, ¹J_B-H = 160 Hz). HRMS (ESI+): m/z calcd for 1: 367.2678. Found: 367.2715. Anal. Calcd for 1: C 46.14, H 6.64. Found: C 46.13, H 6.57.

**Compound 2**

To a solution of 1 (1.12 g, 3.07 mmol) in EtOH (65 mL) was added a LiOH (4.8 g, 200 mmol) in H₂O (65 mL). After 2 days of stirring H₂O (100 mL) was added and the mixture was filtered. The filtrate was then acidified to pH 1 with conc. HCl producing a white precipitate. This was then filtered and washed with copious amounts of water and dried under dynamic vacuum overnight to obtain 2 in quantitative yield. ¹H{¹¹B} NMR (400 MHz, Acetone-d₆) δ 2.21 (s, 2 H, BH), 2.31 (s, 3 H, BH), 2.53 (s, 2 H, BH), 2.69 (s, 1 H, BH), 3.06 (s, 2 H, BH), 3.82 (s, 1 H, CH),
8.33 (s, 2 H, aromatic), 8.63 (s, 1 H, aromatic); $^{13}\text{C}^{\{1\text{H}\}}$ NMR (100.6 MHz, Acetone-$d_6$) δ 57.18 (C$_{\text{carborane}}$H), 77.67 (C$_{\text{carborane}}$C$_{\text{ar}}$), 131.69 (C$_{\text{ar}}$), 132.48 (C$_{\text{ar}}$), 133.34 (C$_{\text{ar}}$), 136.80 (C$_{\text{ar}}$), 166.05 (C$_{\text{acid}}$); $^{11}\text{B}$ NMR (128.4 MHz, Acetone-$d_6$) δ –14.58 (d), –12.82 (d, $^{1}J_{\text{B-H}} = 171$ Hz), –10.18 (d, $^{1}J_{\text{B-H}} = 154$ Hz), –8.10 (d), –4.06 (d, $^{1}J_{\text{B-H}} = 161$ Hz). HRMS (ESI+): $m/z$ calcd for 2: 311.2052. Found: 311.2071. Anal. Calcd for 2: C 38.95, H 5.23. Found: C 38.64, H 5.10.

**Compound 3**

To a solution of Cu$_2$(OAc)$_4$·2H$_2$O (86.1 mg, 0.23 mmol) in DMF (17 mL) was added 2 (138.8 mg, 0.45 mmol) in DMF (17 mL). The resulting blue solution was fractioned out into 17 × 2 mL portions and allowed to stand for 4 d at rt, after which the supernatant was removed and replaced with MeOH. The MeOH was replaced once a day for three days. The methanolic supernatant was removed and the residual solvent removed by heating under dynamic vacuum: 70.3 mg (42%). Anal. Calcd for 3·30 H$_2$O: C 30.61, H 4.24. Found: C 30.68, H 4.23. The water found in elemental analysis is most likely due to exposure of the material to ambient moisture during sample preparation.
NMR Spectra for Compounds 1 and 2

^1H Compound 1
3. Crystallographic Structure Determination and Refinement Details.

Single crystals of 3 were mounted in inert oil and transferred to the cold gas stream of a Bruker Kappa APEX CCD area detector equipped with a CuKα microsource with Quazar optics. TWINABS-2012/1 (Bruker, 2012) was used for absorption correction. For twin component 1: \( wR2(\text{int}) \) was 0.0574 before and 0.0464 after correction. For twin component 2: \( wR2(\text{int}) \) was 0.0661 before and 0.0493 after correction. The ratio of minimum to maximum transmission is 0.85. All B–B and B–C distances in the carborane moieties were refined with similar distance restraints (SADI). The location of the carbon atom not attached to the phenyl ring was determined by examining the displacement parameters of the atoms in the carborane. The elongated displacement parameters of all B and C atoms indicate that these moieties are rotating about the C(Ph)–C bonds. The solvent masking procedure as implemented in Olex2 was used to remove the electronic contribution of non-coordinated solvent molecules from the refinement. As the exact solvent content is not known, only the atoms used in the refinement model are reported in the formula here. Total solvent accessible volume / cell = 43982.1 Å\(^3\) [63.1%], total electron count / cell = 9643.9.\(^3\)-6

**Table S1** Crystal data and structural refinement for 3; for atomic coordinates, equivalent isotropic displacement parameters, bond lengths, angles, and anisotropic displacement parameters please see the CIF (CCDC code 942360)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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<tr>
<td>Empirical formula</td>
<td>( \text{C}<em>{258}\text{H}</em>{414}\text{B}<em>{240}\text{Cu}</em>{24}\text{N}<em>{6}\text{O}</em>{120} )</td>
</tr>
<tr>
<td>Formula weight</td>
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</tr>
<tr>
<td>Temperature (K)</td>
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<tr>
<td>Crystal system</td>
<td>trigonal</td>
</tr>
<tr>
<td>Space group</td>
<td>( \text{R}\overline{3} )</td>
</tr>
<tr>
<td>( a, b, c ) (Å)</td>
<td>31.498(4), 31.498(4), 81.077(12)</td>
</tr>
</tbody>
</table>
a (°), β (°), γ (°) 90, 90, 120
Volume (Å³) 69662(24)
Z 3
Calculated Density (mg/mm³) 0.689
Absorption coefficient (mm⁻¹) 0.871
F(000) 14580
Crystal size (mm³) 0.117 × 0.091 × 0.056
2θ range for data collection 7.82 to 117.86°
Index ranges –34 ≤ h ≤ 17, 0 ≤ k ≤ 34, 0 ≤ l ≤ 90
Reflections collected 103596
Independent reflections 22202 [R(int) = 0.0534]
Data/restraints/parameters 22202/5193/976
Goodness-of-fit on F² 1.119
Final R indices [I > 2σ (I)] R₁ = 0.0870, wR₂ = 0.2878
Final R indices [all data] R₁ = 0.1088, wR₂ = 0.3009
Largest diff. peak and hole (e Å⁻³) 0.913/−0.358
4. Powder X-ray Diffraction (PXRD)

![Graph Image]

**Figure S1.** Powder X-ray diffraction (PXRD) patterns of 3: pattern simulated from single-crystal structure in black, experimental pattern for the as-synthesized sample in red.
5. Thermogravimetric Analysis (TGA)

![TGA Curve](image)

**Figure S2.** TGA curve of 3 (activated). The first step in the TGA is most likely due to residual moisture of the sample.

6. Gas Adsorption

The activation of 3: an as-synthesized sample of 3 was soaked in methanol for 3 days, refreshing the methanol once per day. The methanol from the final soak was decanted and replaced with supercritical CO$_2$. Before adsorption measurement, the sample was further activated by heating under vacuum. Finally, 73.9 mg sample was used in gas adsorption measurement. Isotherms of N$_2$ at 77 K are shown below (Fig S3).
Figure S3. Adsorption and desorption isotherms of N\textsubscript{2} on activated 3.

7. References


3. APEX2 V2.1–4 (Bruker, 2007)
