Supplementary Information

Reduction of hydroxy-functionalised carbaboranyl carboxylic acids to tertiary alcohols by organolithium reagents

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Experimental Section

General considerations

All reactions were carried out under a nitrogen atmosphere using anhydrous solvents. The latter were purified using an MBRAUN solvent purification system MB SPS-800 Series. The chemicals were used as purchased. Thin-layer chromatography (TLC) was performed on pre-coated glass plates (0.25 mm, silica gel 60 F_{254}). The visualisation of the compounds on TLC plates was achieved by treatment with a solution of $PdCl_2$ (1% in MeOH) and gentle heating. Column chromatography was carried out with silica gel (0.035–0.070 mm, 60 Å). All NMR spectra were recorded on a Bruker AVANCE DRX 400 spectrometer. The chemical shifts of ^{1}H, ^{11}B and ^{13}C NMR spectra are reported in parts per million at 400.13, 128.38, and 100.63 MHz, respectively, with tetramethylsilane as internal standard and referencing to the unified scale.[1] FTIR spectra were recorded on a Perkin-Elmer system 2000 FTIR spectrometer, scanning between 400 and 4000 cm^{-1}, by using KBr disks. Mass spectra were recorded on an FTICR MS Bruker-Daltonics ESI mass spectrometer (APEX II, 7 T). Elemental analyses were carried out in a Heraeus VARIO EL oven. The melting points were measured in sealed tubes.

X-Ray crystallography

Data for compound **1b** were collected on an Oxford Diffraction CCD Gemini-S diffractometer (Agilent Technologies) using MoK_α radiation ($\lambda = 71.073$ pm) and ω-scan rotation. Data reduction was performed with CrysAlis Pro[2] including the programme SCALE3 ABSPACK for empirical absorption correction. The structure was solved with direct methods (SIR-92)[3] and the refinement of all non-hydrogen atoms was performed with SHELX97.[4] Excluding carbon-bonded hydrogen atoms, all H atoms were located on difference Fourier maps calculated at the final stage of the structure refinement. CCDC 961910 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html.

Materials

1-Hydroxy-1,2-dicarba-*closo*-dodecaboranyl-2-carboxylic acid (**1a**, **4a**),[5] 1-hydroxy-1,2-dicarba-*closo*-dodecaborane (**1c**, **4c**)[6] and 1,2-dicarba-*closo*-dodecaboranyl-1-carboxylic acid (**2a**)[7] were prepared according to the literature.

Carbaboranyl carboxylic acids (**1a**, **2a**, **3a**, **4a**) were prepared *in-situ* by deprotonation of the cluster with *n*-butyllithium followed by reaction with gaseous CO_2. Then the respective organolithium reagent was added. A detailed description of the procedure is exemplarily given for the synthesis of **1b**.

5-(1-Hydroxy-1,2-dicarba-*closo*-dodecaboranyl)-nonan-5-ol (1b)

Compound **1b** was prepared from **1c** *via in-situ* formation of **1a** followed by reduction with *n*-butyllithium. 1-Hydroxy-1,2-dicarba-*closo*-dodecaborane (**1c**) (0.112 g, 0.70 mmol) was dissolved in anhydrous Et_2O (15 mL) and the solution was cooled to 0 °C. *n*-Butyllithium (1.1 mL, 1.58 M in *n*-hexane, 2.5 eq.) was added and the cloudy solution was stirred for 90 min at 0 °C. A white precipitate formed, which was filtered off, washed with anhydrous Et_2O and re-suspended in anhydrous Et_2O (40 mL). CO_2 was passed through the solution for 10 min at 0 °C while the precipitate dissolved. N_2 was passed through the solution for 10 min at 0 °C to remove any dissolved CO_2; then *n*-butyllithium (1.1 mL, 1.58 M in *n*-hexane, 2.5 eq.) was added. The solution was stirred for 1 h at room temperature. The solvent was removed under reduced pressure to yield a white solid. Aqueous HCl (30 mL, 1 M) was added and the solution was stirred for 1 h at room temperature. The solution was extracted with *n*-hexane and the combined organic layers were washed with water, dried over $MgSO_4$ and all volatile material was removed under reduced pressure. Product **1b** crystallised as colourless crystals (0.08 g, 38%) from the obtained oil over a period of two weeks. The crystals were isolated by filtration, washed with *n*-hexane and dried in vacuum. Mp: 101 °C. Elemental analysis in % found: C 43.8, H 10.1; calculated for $C_{11}H_{30}B_{10}O_2$: C 43.7, H 10.0. IR: ν_{max}/cm^{-1} 3484 (s, OH), 2961 (s, CH), 2651–2596 (s, BH), 1460 (m), 1233 (m). ^{1}H NMR ($CDCl_3$): δ 0.95 (6H, t, $^{3}J_{HH} = 7.2$ Hz, C$\mathbf{H_3}$), 1.50 to 3.53 (10H, br, $C_2B_{10}\mathbf{H_{10}}$), 1.39 (8H, m, C$\mathbf{H_2}$), 1.82 (2H, m, C(OH)(C$\mathbf{H_2}$)), 1.95 (2H, m, C(OH)(C$\mathbf{H_2}$)). The chemical shift of the signal of the acidic OH proton was found to be concentration dependent. ^{11}B NMR ($CDCl_3$): δ –13.0 (4B, m), –11.2 (4B, m), –4.8 (2B, d, $^{1}J_{BH} = 150.0$ Hz). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 13.9 (s, C-CH_2-CH_2-CH_2-**C**H_3), 22.8 (s, C-CH_2-CH_2-

CH_2-CH_3), 25.9 (s, C-CH_2-**C**H_2-CH_2-CH_3), 40.6 (s, C-**C**H_2-CH_2-CH_2-CH_3), 80.1 (s, $C_{cluster}$-**C**), 84.0 (s, **C**$_{cluster}$-C), 104.5 (s, **C**$_{cluster}$-O). MS (ESI(–), acetone): *m/z* 301.2 ([M–H]$^-$).

1-Methoxy-1,2-dicarba-*closo*-dodecaborane (3c)

1-Hydroxy-1,2-dicarba-*closo*-dodecaborane (**1c**) (0.10 g, 0.62 mmol) was dissolved in CH_3CN (50 mL). Na_2CO_3 (1.0 g) was suspended in the solution and CH_3I (0.5 mL) was added at room temperature in several portions until TLC of the reaction mixture indicated complete conversion of the starting material. The solution was concentrated under reduced pressure to a volume of 5 mL, water (50 mL) was added and then extracted with Et_2O. The combined organic layers were washed with NaOH (1 M), dried over $MgSO_4$ and the solvent was removed under reduced pressure to yield compound **3c** as a colourless powder (0.11 g, quantitative). Mp: 95–96 °C. IR: ν_{max}/cm^{-1} 3453 (s, OH), 3067 (m), 2949 (m, CH), 2601 (s, BH), 1636 (m), 1456 (m), 1243 (s, CO), 1129 (m), 1071 (m), 1015 (m), 721 (m). ^{1}H NMR ($CDCl_3$): δ 1.41 to 3.22 (10H, br, C_2B_{10}**H$_{10}$**), 3.56 (3H, s, OC**H$_3$**), 3.91 (1H, s, C**H**). ^{11}B NMR ($CDCl_3$): δ –15.0 (2B, d, $^1J_{BH}$ = 163.1 Hz), –13.7 (2B, m), –12.8 (2B, m), –12.0 (3B, m), –4.6 (1B, d, $^1J_{BH}$ = 150.8 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 61.7 (s, O**C**H_3), 63.3 (s, **C**$_{cluster}$-O), 104.0 (s, **C**$_{cluster}$-O). MS (ESI(–), acetone): *m/z* 173.2 ([M–H]$^-$). HR-MS (ESI(+), MeOH/Na$^+$): *m/z* [M–H+2Na]$^+$ calcd for $C_5H_{17}O_2B_{10}Na_2$: 263.2022, found: 263.2025, the observed isotopic pattern was in agreement with the calculated one.

2-(1-Hydroxy-1,2-dicarba-*closo*-dodecaboranyl)-propan-2-ol (4b)

Compound **4b** was synthesised analogous to compound **1b**. *In-situ* formation of the carboxylic acid **4a** was done in anhydrous Et_2O using 1-hydroxy-1,2-dicarba-*closo*-dodecaborane (**4c**) (0.282 g, 1.76 mmol) and *n*-butyllithium (2.4 mL, 1.58 M in *n*-hexane, 2.15 eq.). Methyllithium (8.0 mL, 0.9 M in Et_2O, 4.1 eq.) was used for the reduction. The colourless oil obtained after work-up was further purified by column chromatography (*n*-hexane/ethyl acetate 5:1 → 0:1) to yield compound **5b** as a pale orange powder (0.08 g, 21%). Mp: 194–197 °C. IR: ν_{max}/cm^{-1} 3430 (s, OH), 2992-2928 (m, CH), 2591 (s, BH), 1199 (m), 1033 (m), 1015 (m). ^{1}H NMR ($CDCl_3$): δ 1.04 to 3.15 (10H, br, C_2B_{10}**H$_{10}$**), 1.67 (6H, s, C**H$_3$**), 2.69 (1H, br, O**H**). The chemical shift of the signal of the acidic OH proton was found to be concentration dependent. ^{11}B NMR ($CDCl_3$): δ –13.1 (4B, m), –11.0 (4B, m), –5.4 (2B, d, $^1J_{BH}$ = 158.8 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 33.1 (C-**C**H_3), 75.9 (s, $C_{cluster}$-**C**), 83.9 (s, **C**$_{cluster}$-C), 106.3 (s, **C**$_{cluster}$-O). MS (ESI(–), acetone): *m/z* 217.1 ([M–H]$^-$).

Notes and references

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