Supplementary Information

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

Wilma Neumann,a Markus Hillera, Peter Löneckea and Evamarie Hey-Hawkins**

a Universität Leipzig, Institut für Anorganische Chemie, Johannisallee 29, 04103 Leipzig, Germany, Fax: +49-341-9739393, Tel: +49-341-9736151, E-mail: hey@uni-leipzig.de

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 PdCl₂ (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 ¹H, ¹¹B and ¹³C 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. 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 MoKα radiation (λ = 71.073 pm) and o-scan rotation. Data reduction was performed with CrysAlis Pro including the programme SCALE3 ABSPACK for empirical absorption correction. The structure was solved with direct methods (SIR-92) and the refinement of all non-hydrogen atoms was performed with SHELX97. 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), 1-hydroxy-1,2-dicarba-closo-dodecaborane (1c, 4c) and 1,2-dicarba-closo-dodecaboranyl-1-carboxylic acid (2a) 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 CO₂. 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 (1e) (0.112 g, 0.70 mmol) was dissolved in anhydrous Et₂O (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 Et₂O and re-suspended in anhydrous Et₂O (40 mL). CO₂ was passed through the solution for 10 min at 0 °C while the precipitate dissolved. N₂ was passed through the solution for 10 min at 0 °C to remove any dissolved CO₂; 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 MgSO₄ 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: C 43.8, H 10.1; calculated for C₁₁H₃₀B₁₀O₂: C 43.7, H 10.0. IR: νmax/cm⁻¹ 3484 (s, OH), 2961 (s, CH), 2651–2596 (s, BH), 1460 (m), 1233 (m). ¹H NMR (CDCl₃): δ 0.95 (6H, t, J_HH = 7.2 Hz, CH₃), 1.50 to 3.53 (10H, br, C₂B₁₀H₁₂), 1.39 (8H, m, CH₂), 1.82 (2H, m, C(OH)(CH₂)), 1.95 (2H, m, C(OH)(CH₂)). The chemical shift of the signal of the acidic OH proton was found to be concentration dependent. ¹¹B NMR (CDCl₃): δ -13.0 (4B, m), -11.2 (4B, m), -4.8 (2B, d, J_HH = 150.0 Hz). ¹³C{¹H} NMR (CDCl₃): δ 13.9 (s, C-CH₂-CH₂-CH₂-CH₂), 22.8 (s, C-CH₂-CH₂-...
CH₂–CH₃), 25.9 (s, C–CH₂–CH₃), 40.6 (s, C–CH₂–CH₂–CH₃), 80.1 (s, C₃cluster–C), 84.0 (s, C₃cluster–C), 104.5 (s, C₃cluster–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 CH₃CN (50 mL). Na₂CO₃ (1.0 g) was suspended in the solution and CH₃I (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 Et₂O. The combined organic layers were washed with NaOH (1 M), dried over MgSO₄ 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: νmax/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), 1071 (m), 1015 (m), 721 (m). ¹H NMR (CDCl₃): δ 1.41 to 3.22 (10H, br, C₁₀B₁₀H₁₀), 3.56 (3H, s, OC₃H₃), 3.91 (1H, s, CH). ¹¹B NMR (CDCl₃): δ –15.0 (2B, d, ¹JBH = 163.1 Hz), –13.7 (2B, m), –12.8 (2B, m), –12.0 (3B, m), –4.6 (1B, d, ¹JBH = 150.8 Hz). ¹³C{¹H} NMR (CDCl₃): δ 61.7 (s, OC₃H₃), 63.3 (s, C₃cluster–O), 104.0 (s, C₃cluster–O). MS (ESI(–), acetone): m/z 173.2 ([M–H]–). HR-MS (ESI(+), MeOH/Na⁺): m/z [M–H+2Na]⁺ calcd for C₅H₁₇O₂B₁₀Na₂: 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 Et₂O 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.). Methylolithium (8.0 mL, 0.9 M in Et₂O, 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: νmax/cm⁻¹ 3430 (s, OH), 2992–2928 (m, CH), 2591 (s, BH), 1199 (m), 1033 (m), 1015 (m). ¹H NMR (CDCl₃): δ 1.04 to 3.15 (10H, br, C₁₀B₁₀H₁₀), 1.67 (6H, s, C₃H₃), 2.69 (1H, br, OH). The chemical shift of the signal of the acidic OH proton was found to be concentration dependent. ¹¹B NMR (CDCl₃): δ –13.1 (4B, m), –11.0 (4B, m), –5.4 (2B, d, ¹JBH = 158.8 Hz). ¹³C{¹H} NMR (CDCl₃): δ 33.1 (C₃H₃), 75.9 (s, C₃cluster–C), 106.3 (s, C₃cluster–O). MS (ESI(–), acetone): m/z 217.1 ([M–H]–).

Notes and references

2 CrysAlis Pro, Agilent Technologies, Version 1.171.35.11.