Simple synthesis of anions of *closo*-monocarbon carborane-substituted alcohols

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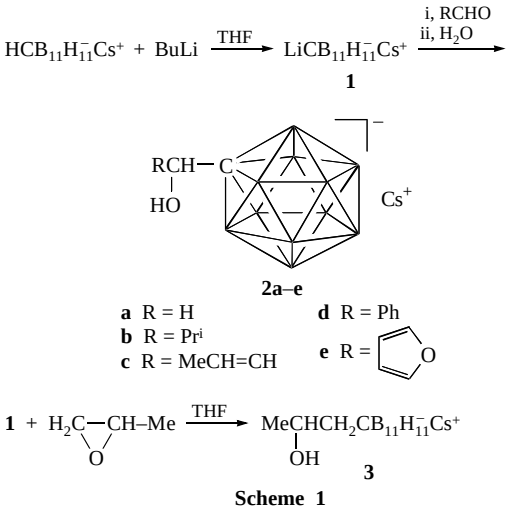
The anions of *closo*-monocarbon carborane-substituted alcohols were synthesised in reactions of the caesium salt of the *closo*-1-lithium monocarbon carborane anion with aldehydes and propylene oxide.

The synthesis of the *closo*-monocarbon carborane anion $HCB_{11}H_{11}^-$, which is isoelectronic to the *closo*-carborane $C_2B_{10}H_{12}$, was reported by Knoth.[1] He also demonstrated that $HCB_{11}H_{11}^-$ is readily metallated with BuLi analogously to $C_2B_{10}H_{12}$ in $LiCB_{11}H_{11}^-$ and assumed the existence of the chemistry of C-derivatives of *closo*-monocarbon carborane anions, which is analogous to the chemistry of neutral $C_2B_{10}H_{12}$ derivatives. This hypothesis was confirmed only in studies[2,3] of reactions of $LiCB_{11}H_{11}^-$ with CO_2 and S_2 and with EtBr, Ph_3SiCl, CF_3Br, Ph_2PCl and $PhCH_2Cl$, resulting in the anions of C-substituted monocarbon carboranes. However, unlike these reagents, in the reaction of $LiCB_{11}H_{11}^-$ with C_6F_5Br in THF, perfluoroarylation proceeded at boron atoms in the 12- and 7-positions rather than at the carbon atom.[3] No explanation for such a 'dual' reactivity of $LiCB_{11}H_{11}^-$ was given; in addition, it was never observed for neutral *closo*-$LiCB_{10}H_{10}CH$. We studied the reactions of the caesium salt of $LiCB_{11}H_{11}^-$ **1** with other electrophilic reagents (aldehydes and propylene oxide). We found that only previously unknown C-substituted anions of *closo*-monocarbon carborane alcohols are readily formed in this case according to Scheme 1.†



Scheme 1

Previously,[2,3] C-substituted *closo*-monocarbon carborane anions were synthesised using only the trimethylammonium salt of *closo*-monocarbon carborane. The reaction of this salt with 2 mol of BuLi in THF resulted in the soluble lithium salt of *closo*-1-lithium monocarbon carborane $LiCB_{11}H_{11}^-Li^+$. However, this procedure is inconvenient because (i) 2 mol of BuLi is required to obtain $LiCB_{11}H_{11}^-Li^+$ and (ii) Me_3N should be removed from the reaction mixture after the addition of 1 mol of BuLi and before the addition the second mole of BuLi.

The reaction suggested can be considered as a general method for preparation of primary and secondary alcohols of *closo*-monocarbon carborane-substituted anions from aldehydes. Unlike the published data,[2,3] the readily available caesium salt of monocarbon carborane ($HCB_{11}H_{11}^-Cs^+$)[4] is readily metallated with one mole of BuLi in THF. Though the caesium salt of *closo*-1-lithium monocarbon carborane is poorly soluble in THF, it easily reacts with aldehydes and propylene oxide to give lithium alcoholates readily soluble in THF. In most cases, treatment of the reaction mixture with water results in crystalline caesium salts of *closo*-monocarbon carborane-substituted alcohols, which are formed in high yields. If the caesium salt of the reaction product is obtained as viscous oil (**2c**), its treatment with Me_4NBr results in the corresponding crystalline tetramethylammonium salt of the *closo*-monocarbon carborane-substituted alcohol. The simple preparation method and high yields of the *closo*-monocarbon carborane alcohols open new possibilities for the use as initial compounds for the synthesis of other functionalised *closo*-monocarbon carborane anions.‡

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† *General procedure for the synthesis of alcohols* **2a**–**e** *and* **3**. A benzene solution of BuLi (5.25 mmol, 1.18 M) was added to a solution of $HCB_{11}H_{11}^-Cs^+$ (5 mmol) in 15 ml of THF under argon at 10–15 °C with stirring. Compound **1** was immediately formed as a white precipitate. After addition of BuLi, the reaction mixture was stirred for 0.5 h at 20 °C, and a solution of the corresponding aldehyde or propylene oxide (5.25 mmol) in THF (4 ml) was added. The precipitate was dissolved at a temperatrure of no higher than 30 °C. After cessation of the exothermic reaction, the reaction mixture was additionally stirred for 4–5 h at 20 °C. THF was removed *in vacuo*, water (4 ml) was added to the residue, and the precipitated crystals were filtered off.

‡ All new compounds exhibited satisfactory elemental analysis data, and their structures were confirmed by NMR and IR spectroscopy. ^{1}H NMR spectra were mearsured on a Bruker AMX 400 instrument (400.13 MHz) in $(CD_3)_2CO$, standard TMS. IR spectra were mearsured in KBr pellets on a UR-20 spectrometer.

[1-Hydroxymethyl-closo-*monocarbon carborane]caesium* **2a**: yield 72%. ^{1}H NMR, δ: 3.25 (t, 1H, OH, ^3J 6.8 Hz), 3.58 (d, 2H, CH_2, ^3J 6.8 Hz). IR (ν/cm^{-1}): 3461 (OH), 2532 (BH). Found (%): C, 7.96; H, 4.56; B, 38.47. Calc. for $C_2H_{14}B_{11}CsO$ (%): C, 7.84; H, 4.57; B, 38.85.

[1-(1'-Hydroxy-2'-methyl)propyl]-closo-*monocarbon carborane]caesium* **2b**: yield 78%. ^{1}H NMR, δ: 0.83 (d, 3H, Me, ^3J 6.8 Hz), 0.87 (d, 3H, Me, ^3J 6.8 Hz), 1.91 (m, 1H, C*H*Me$_2$, ^3J 6.8 Hz, ^3J 6.8 Hz, ^3J 1.6 Hz), 2.56 (d, 1H, OH, ^3J 5.2 Hz), 3.56 (dd, 1H, C*H*OH, ^3J 5.2 Hz, ^3J 1.6 Hz). IR (ν/cm^{-1}): 3459 (OH), 2534 (BH). Found (%): C, 17.51; H, 5.86; B, 33.98. Calc. for $C_5H_{20}B_{11}CsO$ (%): C, 17.25; H, 5.75; B, 34.16.

[1-(1'-Hydroxybut-2'-enyl)-closo-*monocarbon carborane]tetramethylammonium*: yield 81%. ^{1}H NMR, δ: 1.60 (d, 3H, Me, ^3J 4.4 Hz), 2.88 (d, 1H, OH, ^3J 3.6 Hz), 3.42 (s, 12H, Me_4N), 4.03 (m, 1H, CH), 5.34, 5.39 (m, 2H, CH=CH, ^3J 14.4 Hz). IR (ν/cm^{-1}): 3457 (OH), 2533 (BH), 1585 (C=C). Found (%): C, 37.49; H, 10.35; N, 4.95. Calc. for $C_9H_{30}B_{11}NO$ (%): C, 37.66; H, 10.46; N, 4.88.

{1-[1'-Hydroxy(phenyl)methyl]-closo-*monocarbon carborane}caesium* **2d**: yield 77%. ^{1}H NMR, δ: 3.62 (d, 1H, OH, ^3J 3.6 Hz), 4.80 (d, 1H, CH, ^3J 3.6 Hz), 7.14–7.26 (m, 5H, Ph). IR (ν/cm^{-1}): 3458 (OH), 2532 (BH). Found (%): C, 25.06; H, 4.90. Calc. for $C_8H_{18}B_{11}CsO$ (%): C, 25.14; H, 4.71.

{1-[1'-Hydroxy(2-furyl)methyl]-closo-*monocarbon carborane}caesium* **2e**: yield 68%. ^{1}H NMR, δ: 3.71 (br. s, 1H, OH), 4.77 (s, 1H, CH), 6.10 (dd, 1H, H_β, ^3J 3.2 Hz, ^4J 1.2 Hz), 6.76 (dd, 1H, $H_{\beta'}$, ^3J 3.2 Hz, ^3J 2.0 Hz), 7.33 (dd, 1H, $H_{\alpha'}$, ^3J 2.0 Hz, ^4J 1.2 Hz). Found (%): C, 19.80; H, 4.48; B, 31.71. Calc. for $C_6H_{16}B_{11}CsO_2$ (%): C, 19.36; H, 4.30; B, 31.92.

[1-(2'-Hydroxypropyl)-closo-*monocarbon carborane]caesium* **3**: yield 78%. ^{1}H NMR, δ: 1.51 (d, 3H, Me, ^3J 6.0 Hz), 1.87 (dd, 1H, C*H*H, ^2J 14.8 Hz, ^3J 4.4 Hz), 1.94 (dd, 1H, CH*H*, ^2J 14.8 Hz, ^3J 6.8 Hz), 2.92 (d, 1H, OH, ^3J 3.6 Hz), 3.72 (m, 1H, CH, ^3J 6.8 Hz, ^3J 6.0 Hz, ^3J 4.4 Hz, ^3J 3.6 Hz). IR (ν/cm^{-1}): 3556 (OH), 2537 (BH). Found (%): C, 14.35; H, 5.31; B, 35.38. Calc. for $C_4H_{18}B_{11}CsO$ (%): C, 14.58; H, 5.39; B, 35.59.

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