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Monocarbaborane anion chemistry. The elusive C-arylated $[PhCB_{11}H_{11}]^-$, $[PhCB_9H_9]^-$ and $[PhCB_8H_8]^-$ anions

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Received (in Cambridge, UK) 27th June 2001, Accepted 1st August 2001
First published as an Advance Article on the web 3rd September 2001

$B_{10}H_{14}$ and PhCHO yield [6-Ph-*nido*-6-$CB_9H_{11}]^-$ (94%), from which the nine-vertex C-phenyl monocarbaborane anion [4-Ph-*closo*-4-$CB_8H_8]^-$ (68%) can be obtained by heating at 200 °C, and from which the twelve- and ten-vertex analogues [1-Ph-*closo*-1-$CB_{11}H_{11}]^-$ (50%) and [4-Ph-*closo*-4-$CB_9H_9]^-$ (25%) can be obtained by heating at 210 °C with $BH_3(NEt_3)$.

There is much contemporary interest in the *closo* monocarbaborane monoanions $[1\text{-}CB_{11}H_{12}]^-$ and $[1\text{-}CB_9H_{10}]^-$, and in their derivatives. This is because their very low basicities, as manifested, for example, in their 'least coordinating anion' properties, enable the investigation and exploitation of species with very high Lewis acidities.[1,2] A considerable focus of current activity derives from the substituent chemistry of these anions, and how their low basicities can be tailored by these substituents for particular purposes. Although C-substitution of $[CB_{11}H_{12}]^-$ and $[CB_9H_{10}]^-$ has engendered a variety of derivatives,[1–3] and, although B-arylation has been achieved,[4] the important target of C-arylation has proved elusive, with no reports in the literature. Here we now report preliminary results on convenient routes to the C-phenylated twelve-vertex [1-Ph-*closo*-1-$CB_{11}H_{11}]^-$ anion **1**, and to its corresponding ten-vertex [1-Ph-*closo*-1-$CB_9H_9]^-$ analogue **2**. We also report the nine-vertex [4-Ph-*closo*-4-$CB_8H_8]^-$ anion **3**, which is the C-phenylated derivative of the very recently established 'missing link' [*closo*-4-$CB_8H_9]^-$ monoanion.[5] All three species are characterised crystallographically (Fig. 1),† and by NMR spectroscopy.‡

The synthesis of this series derives from Brellochs' report of the reaction of PhCHO with $B_{10}H_{14}$ in 5% aqueous ethanolic KOH,[6] which we have found to give the [6-Ph-*nido*-6-$CB_9H_{11}]^-$ anion **4** in 94% yield. The method is essentially the same as that for the synthesis of unsubstituted [*arachno*-6-$CB_9H_{14}]^-$ from HCHO and $B_{10}H_{14}$,[5,6] except that, interestingly, the *nido* rather than the *arachno* ten-vertex species is formed. The reaction may go *via* the [*arachno*-$B_9H_{14}]^-$ anion as intermediate. Thence, solid-state thermolysis of the $[NEt_4]^+$ salt of [6-Ph-*nido*-6-$CB_9H_{11}]^-$ **4** at 200 °C for 4 h, followed by column chromatographic separation (silica gel, 30 cm × 2.5 cm, MeCN–CH_2Cl_2 10:90), gave the $[NEt_4]^+$ salts of $[PhCB_8H_8]^-$ (anion **3**, 68%) and [7-Ph-*nido*-7-$CB_{10}H_{12}]^-$ (anion **5**, 22%), together with trace quantities of the $[NEt_4]^+$ salt of $[PhCB_9H_9]^-$ (anion **2**). A crystallographic sample of the $[NEt_4]^+$ salt of the $[PhCB_8H_8]^-$ anion **3** was obtained from dichloromethane–diethyl ether. The *nido* eleven-vertex anion $[PhCB_{10}H_{12}]^-$ **5** may be synthesised more specifically in 78% yield by treatment of $[PhCB_9H_{11}]^-$ **4** with $[BH_3(SMe_2)]$ in 1,2-$Cl_2C_2H_4$, and thence converted to the $[PhCB_{11}H_{11}]^-$ anion **1** by treatment with $[BH_3(SMe_2)]$. More conveniently, this last reagent also converts $[PhCB_9H_{11}]^-$ **4** more directly to $[PhCB_{11}H_{11}]^-$ **1**. Thus, $[NEt_4]^+[PhCB_9H_{11}]^-$ (1.65 g, 5 mmol) was suspended in $[BH_3(NEt_3)]$ (2.3 g, 20 mmol), and the mixture heated on an oil bath (210 °C) under nitrogen for 6 h. After cooling to room temperature, the mixture was extracted with benzene (2 × 30 ml), and the solid residue was then decomposed by heating at reflux for 3 h in ethanol–concentrated hydrochloric acid (1:1, 50 ml). The ethanol was evaporated, the mixture mixed with

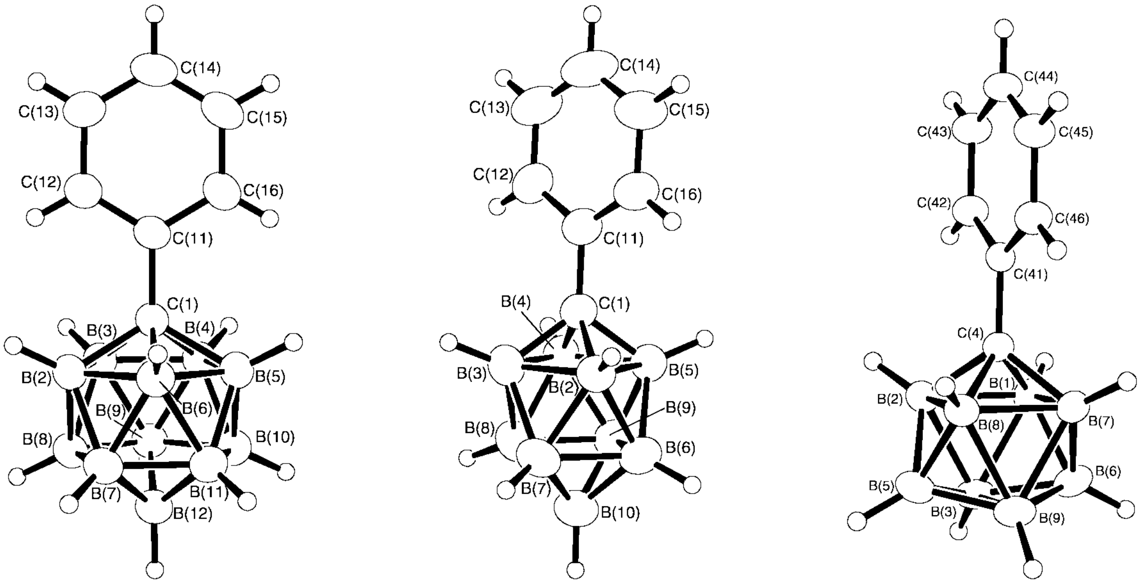

Fig. 1 From left to right, molecular structures of the $[PhCB_{11}H_{11}]^-$ twelve-vertex cluster anion **1**, and its corresponding ten- and nine-vertex $[PhCB_9H_9]^-$ and $[PhCB_8H_8]^-$ analogues, **2** and **3** respectively, as determined crystallographically for their $[NEt_4]^+$ salts.‡ Selected dimensions in Å are as follows: for anion **1**, C(1)–C(11) 1.512(3), C(1)–B(2) 1.729(4), C(1)–B(3) 1.715(3), C(1)–B(4) 1.725(4), C(1)–B(5) 1.722(4) and interboron distances 1.772(4)–1.791(4); for anion **2**, C(1)–C(11) 1.503(4), C(1)–B(2) 1.613(4), C(1)–B(3) 1.606(4), C(1)–B(4) 1.598(5) and interboron distances 1.694(6)–1.843(5); and for anion **3** C(4)–C(41) 1.490(2), C(4)–B(1) 1.623(2), C(4)–B(2) 1.622(2), C(4)–B(7) 1.620(2), C(4)–B(8) 1.623(2) and interboron distances 1.694(3)–1.975(3).

DOI: 10.1039/b105645j

water (50 ml), and the precipitate filtered off. The latter was a mixture of the $[NEt_4]^+$ salts of $[PhCB_{11}H_{11}]^-$ and $[PhCB_9H_9]^-$ (anions **1** and **2** respectively; molar ratio 2 : 1; combined yield 1.45 g; 76%). Crystallographic samples of these $[NEt_4]^+$ salts of **1** and **2** for diffraction analysis were obtained by fractional crystallisation from dichloromethane–diethyl ether. However, bulk separation of **1** and **2** is better achieved by ion-exchange of $[NEt_4]^+$ for Cs^+, followed by fractional crystallisation of the Cs^+ salts. Thus, a solution of the mixture of the two $[NEt_4]^+$ salts (1.20 g) was dissolved in ethanol–water (4 : 1, 60 ml) and passed through of column of ionex resin (Zerolit 325 in H^+ form, 2.5 cm × 30 cm) using ethanol–water (4 : 1) as eluting liquid. Evaporation of ethanol *in vacuo* from the resulting acidic solution, followed by neutralisation by Cs[OH] to pH 7, gave a white precipitate of the Cs^+ salts of **1** and **2**. This mixture was separated by fractional crystallisation from water, starting with *ca.* 15 ml of hot solution: $Cs^+[PhCB_9H_9]^-$ is much less soluble in cold water (*ca.* 12×) than $Cs^+[PhCB_{11}H_{11}]^-$.

The synthesis of these first of a new generation of C-arylated monocarbaborane anions by simple routes in relatively good yield in two steps from the common polyhedral borane starting material $B_{10}H_{14}$ significantly augments the range of materials available for 'least-coordinating anion' chemistry; the aromatic ring/delocalised cluster conjunction may also have implications for investigation of electronic 'push–pull ' phenomena,[6] and other related interactions between the delocalised cluster and ring systems.[7] The advantage of the method is that it starts with the carbon atom pre-substituted, and thereby avoids complex synthetic carborane carbon-substitution protocols. We currently explore possibilities for other C-substituted monocarbaboranes, and for the generality of this aromatic aldehyde route.

We thank the EPSRC and the DTI for support.

Notes and references

† *Crystal data*: for **1** (CH_2Cl_2 monosolvate), $C_{16}H_{38}B_{11}Cl_2N$: M = 434.28, monoclinic (from dichloromethane–hexane), space group $P2_1/c$, a = 15.7334(5), b = 10.8812(4), c = 15.7928(6) Å, β = 110.9350(14)°, U = 2525.22(16) Å^3, D_c = 1.14 Mg m^{-3}, Z = 4, Mo-Kα, λ = 0.71073 Å, μ = 0.262 mm^{-1}, T = 150(2) K, R_1 = 0.0654 for 3750 reflections with $I > 2\sigma(I)$, and wR_2 = 0.1731 for all 4857 unique reflections; CCDC reference number 164850.

For **2**: $C_{15}H_{34}B_9N$, M = 325.72, monoclinic (from dichloromethane–hexane), space group $C2/c$, a = 24.4404(16), b = 10.5641(6), c = 16.7478(14) Å, β = 99.099(3)°, U = 4269.7(5) Å^3, D_c = 1.01 Mg m^{-3}, Z = 8, Mo-Kα, λ = 0.71073 Å, μ = 0.051 mm^{-1}, T = 150(2) K, R_1 = 0.0826 for 2212 reflections with $I > 2\sigma(I)$, and wR_2 = 0.2285 for all 4147 unique reflections; CCDC reference number 164851.

For **3**, $C_{15}H_{33}B_8N$: M = 313.90, monoclinic (from dichloromethane–hexane), space group $P2_1/n$, a = 11.6480(3), b = 10.5204(3), c = 17.5709(6) Å, β = 107.9740(10)°, U = 2048.08(11) Å^3, D_c = 1.02 Mg m^{-3}, Z = 4, Mo-Kα, λ = 0.71073 Å, μ = 0.052 mm^{-1}, T = 150(2) K, R_1 = 0.0548 for 2417 reflections with $I > 2\sigma(I)$, and wR_2 = 0.1703 for all 4011 unique reflections; CCDC reference number 164852. For all three compounds, methods and programs were standard.[8]

See http://www.rsc.org/suppdata/cc/b1/b105645j/ for crystallographic data in CIF or other electronic format.

‡ *Measured NMR data* for anions [1-Ph-*closo*-1-$CB_{11}H_{11}]^-$ **1**, [1-Ph-*closo*-1-$CB_9H_9]^-$ **2**, [4-Ph-*closo*-4-$CB_8H_8]^-$ **3** and [7-Ph-*nido*-7-$CB_{10}H_{12}]^-$ **5**, $[NEt_4]^+$ salts in CD_3CN at 294–300 K, ordered as assignment $\delta(^{11}B)$/ppm [$\delta(^1H)$/ppm]: anion **1**: BH(12) −8.0 [+2.13], BH(2,3,4,5,6) and BH (7,8,9,10,11) coincident at *ca.* −12.9 [*ca.* +1.75]; $\delta(^1H)(C_6H_5)$ +7.29 to +7.63 (multiplet). Anion **2**, BH(10) +27.1 [+5.49], BH(2,3,4,5) −16.1 [+1.79], BH(6,7,8,9) −24.4 [+0.84], $\delta(^1H)(C_6H_5)$ +7.40 to +7.98 (multiplet). Anion **3**, BH(5,6) +13.4 [+4.44], BH(1,2,7,8) −10.8 [+1.71], BH(3,9) −17.2 [+0.88], $\delta(^1H)(C_6H_5)$ +7.32 to +7.93, multiplet. Anion **5**, BH(5) −0.8 [+2.32], BH(2,3) −9.1 [+2.09], BH(8,11) −10.0 [+1.98], B(9,10) −22.6 [*ca.* +1.24], BH(1) −25.2 [*ca.* +1.24] and BH(4,6) –31.5 [+0.45]; $\delta(^1H)(C_6H_5)$ +7.25 to +7.70 (multiplet), μ-H(8,9; 10,11) −3.33.

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