Polyhedral monocarbaborane chemistry. Carboxylic acid derivatives of the [*closo*-2-CB_9H_{10}]$^-$ anion.

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Reaction of $B_{10}H_{14}$ with *para*-(OHC)C_6H_4(COOH) in aqueous KOH gives the [*nido*-6-CB_9H_{11}-6-(C_6H_4-*para*-COOH)]$^-$ anion **1** which upon cluster closure with iodine in alkali solution gives the [*closo*-2-CB_9H_9-2-(C_6H_4-*para*-COOH)]$^-$ anion **2**; an analogous procedure with $B_{10}H_{14}$ and glyoxalic acid OHCCOOH gives the [*closo*-2-CB_9H_9-2-(COOH)]$^-$ anion **4** *via* the [*arachno*-6-CB_9H_{13}-6-(COOH)]$^-$ anion **3**.

There is interest in the functionalization of stable *closo* boranes and *closo* dicarbaboranes for use as synthons or building-blocks for potential life-science [1,2] and nanoarchitectural applications.[3,4,5] Our laboratory has become interested in extending this functionalisation chemistry to the intermediate monocarbaboranes. Monocarbaboranes offer complementary charge and polarity possibilities compared to the boranes on one hand and to the dicarbaboranes on the other hand. In this regard, monocarbaborane units with synthetically useful amine residues {NH_2} are readily available. These {NH_2} units may be directly bound to the monocarbaborane cluster, as in the [1-(H_2N)-*closo*-1-$CB_{11}H_{11}$]$^-$ anion that is isolatable from the classical route to the *closo* twelve-vertex monocarbaborane clusters,[6,7] or less directly bound, as in the isomers of [*para*-(H_2N)-C_6H_4-*closo*-CB_9H_9]$^-$ pioneered by Sivaev and co-workers.[8,9] Carboxylate units are complementary to {NH_2} groupings in synthetic reactions,[9,10] and in this context we here report preliminary results on the hitherto elusive carboxylic acid {COOH} derivatives of the *closo* {CB_9} residue. We have established examples that show that the acid unit can be bound either directly to the carbon atom of the constituents of the cluster, or indirectly, here by utilization of a {*para*-C_6H_4(COOH)} unit bound to the cluster. Both procedures make initial use of the Brellochs Reaction[11] for the direct generation of functional ten-vertex {CB_9} monocarbaboranes from the reaction of functional aldehydes with *nido*-$B_{10}H_{14}$, and further demonstrate the useful versatility of this reaction.

Thus, 4-carboxybenzaldehyde, *para*-(OHC)C_6H_4(COOH), reacts in strong alkaline solution with *nido*-$B_{10}H_{14}$ to form the ten-vertex [*nido*-6-CB_9H_{11}-6-(C_6H_4-*para*-COOH)]$^-$ anion **1**, isolatable in 62 % yield as its [NEt_4]$^+$ salt **1a**.[12(a)] In strong alkaline solution anion **1** thence reacts with elemental iodine with cage closure to form the [*closo*-2-CB_9H_9-2-(C_6H_4-*para*-(COOH)]$^-$ anion **2,** isolatable as its [NEt_4]$_3$[CB_9H_9(C_6H_4COOH)]$_2$Br double salt **2a** in 73 % yield.[12(b)] In a similar manner, by the successive dissolution in strong alkaline solution of glyoxylic acid monohydrate, [$OHCCO_2H(OH_2)$], and *nido*-$B_{10}H_{14}$, the [*arachno*-6-CB_9H_{13}-6-(COOH)]$^-$ anion **3** can be obtained in 53 % yield as its [NEt_4]$^+$ salt **3a**.[12(c)] In strong alkaline solution anion **3** undergoes cage closure with elemental iodine to

give the [*closo*-2-CB_9H_9-2-(COOH)]$^-$ anion **4,** isolatable as its $[NEt_4]^+$ salt **4a** in 92 % yield.[12(d)] Both new *closo* anions **2** and **4** are characterised by single-crystal X-ray diffraction analysis,[13] anion **4** in its $[NEt_4]^+$ salt **4a**, and anion **2** in the $[NEt_4]_3$[*closo*-2-CB_9H_9-2-(*para*-C_6H_4COOH)]$_2$Br double salt **2a** (Figure 1). Salient interatomic dimensions are given in the caption to Figure 1.

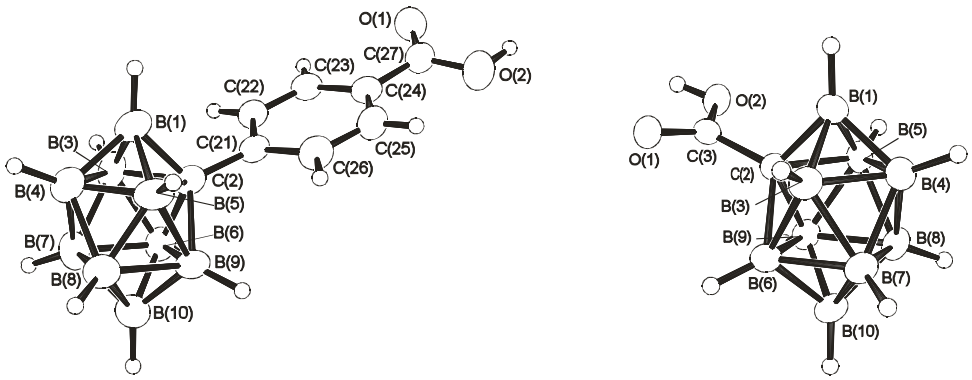

Figure 1. Crystallographically determined molecular structures[13] of (left) the [*closo*-2-CB_9H_9-2-(C_6H_4-*para*-COOH)]$^-$ anion **2** in its $[NEt_4]_3[CB_9H_9(C_6H_4COOH)]_2Br$ double salt **2a** and (right) the [*closo*-2-CB_9H_9-2-(COOH)]$^-$ anion **4** in its $[NEt_4]^+$ salt **4a**. In **2a** the C(2)-C(21) distance is 1.497(4), the C(24)C(27) distance is 1.492(4) Å, the O(1)C(27) distance is 1.207(4) Å, the O(2)C(27) distance is 1.320(4) Å and the O(1)C(27)O(2) angle is 123.5(3)°; within the cluster, C(2)B(1) is 1.637(4), C(2)B(3) is 1.753(5), C(2)B(5) is 1.769(4), C(2)B(6) is 1.752(4) and C(2)B(9) is 1.756(4) Å. There are two independent molecules, A and B, of **4** in the unit cell of **4a**; the molecular structure of only one of these (anion A) is shown. Dimensions for the anions A and B are closely related (see text). In anion A, the C(2)C(3) distance is 1.465(3) Å, the O(1)C(3) distance is 1.221(2) Å, the O(2)C(3) distance is 1.293(2) Å and the O(1)C(3)O(2) angle is 123.14(18)°; within the cluster, C(2)B(1) is 1.603(3), C(2)B(3) is 1.703(3), C(2)B(5) is 1.761(3), C(2)B(6) is 1.754(3) and C(2)B(9) is 1.730(3) Å. In anion B, the C(2)C(3) distance is 1.473(3) Å, the O(1)C(3) distance is 1.188(2) Å, the O(2)C(3) distance is 1.291(2) Å and the O(1)C(3)O(2) angle is 121.57(19)°; within the cluster, C(2)B(1) is 1.606(3), C(2)B(3) is 1.765(3), C(2)B(5) is 1.698(3), C(2)B(6) is 1.732(3) and C(2)B(9) is 1.732(3) Å.

The crystallographically determined cluster structure of anion **2** is relatively symmetrical across the B(1)C(2)B(10) plane. By contrast, the crystallographic analysis of intramolecular C-B distances in anion **4** gives an apparent significant asymmetry about C(2). There are two independent molecules of **4** in the crystal of **4a**. In molecule A, C(2)-B(3) is much shorter than C(2)-B(5), and, conversely, C(2)-B(6) is much longer than C(2)-B(9). At first sight, it is tempting to ascribe this to differential *trans* effects arising from C=O *versus* COH in the {COOH} group, but molecule B shows the converse asymmetry, with C(2)-B(3) being much longer than C(2)-B(5), and C(2)-B(6) is much shorter than C(2)-B(9), suggesting a crystallographic artefact. A more definitive difference between anions **2** and **4** is that the C(2)-B(1) distance in the directly carboxylated cluster species **4** is shorter than C(2)-B(1) in **2**, and C(2)-C(3) in **4** is shorter than both C(2)C(21) and C(24)-C(27) in **2**, which suggest some multiple-bonding character in the cluster to carboxylate linkage C(2)-C(3) in **4**. There is also an interesting difference in intermolecular interaction behaviour when the anions in **2a** and **4a** are compared. Whereas hydrogen bonding between the carboxylic acid residues in **2a** results in an association of pairs of anions **2** to give conventional carboxylic acid dimeric units, for anion **4** the hydrogen bonding in **4a** gives the less common planar assembly of four {COOH} units, rather than the

dimeric configuration. We hope to address these and related phenomena in more detail when this and related work is complete and presented in full description.

It is anticipated that these carboxylic acid species, and analogous derivatives of related cluster species, will constitute very useful intermediates for molecular architectural constructions and for the synthesis of molecules to be investigated for potential life-science applications. They offer opportunity for derivatisation for further useful functionalization, *e.g.* for acid chloride formation which could be useful for the generation of amide linkages, and for reduction to alcohols and subsequent reoxidation to aldehydes, both of which offer further synthetic potential. Also, in principle, they can be isomerised to their *closo*-1-monocarbadecaborane isomers,[8] permitting more subtle permutations in molecular configuration that could be useful in the fine tuning of any emerging effect chemistry. We are currently devising experimentation to examine some of these possibilities.

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12. All reactions were carried out under dry N_2, followed by work-up in air. *(a)* **Anion 1.** *para*-$(OHC)C_6H_4(COOH)$ (15 g, 100 mmol) was added to a stirred solution of KOH (11.2 g, 200 mmol) in H_2O (100 ml) at 0 °C, and after 5 min, $B_{10}H_{14}$ (2.0 g, 16.4 mmol) was added. The orange solution was stirred for 3 h at ca. 20 °C, cooled to 0 °C, aqueous HCl (5 %, 100 ml) added dropwise, the solution filtered, and $[NEt_4]^+Br^-$ (4.20 g, 20 mmol) added to the filtrate. The $[NEt_4]^+$ salt **1a** of the [*nido*-6-CB_9H_{11}-6-(C_6H_4-*para*-COOH)]$^-$anion **1** precipitated as a white solid, which was filtered off and dried in *vacuo* (2.46 g, 10.2 mmol, 62 %). NMR, $(CD_3)_2CO$, 294–299 K, ordered as assignment $\delta(^{11}B)$/ppm

[δ(^{1}H)/ppm]: BH(5,7) +2.2 [+3.36], BH(9) –1.5 [+2.98], BH(1,3) –4.4 [+2.49], BH(8,10) –12.2 [+2.02], BH(2) –26.2 [+0.63], BH(4) –37.5 [+0.47] with δ(^{1}H) for μH(8,9)/(9,10) at –3.30 ppm; additionally δ(^{1}H)(COOH) +9.92 (broad), δ(^{1}H)(Ph) +7.85 (2H) and +7.23 (2H) (both apparent doublets), and δ(^{1}H)(Et) at +3.49 (8H, quartet) and +1.40 ppm (12H, triplet), also δ(^{13}C)(COOH) +173.0, δ(^{13}C)(Ph) +153.2 (1C), +135.7 (1C), +128.9 (2C) and +127.0 (2C), with δ(^{13}C)(cluster) +62.7 and δ(^{13}C)(Et) +7.2 and +52.4 ppm. *(b)* **Anion 2.** A solution of **1a** (2.46 g, 10.2 mmol) in aqueous HCl (10 %, 100 ml) was extracted with Et_2O (3 × 50 ml), the organic layers separated, combined, aqueous KOH (*ca.*1 M; 200 ml) added, and the Et_2O evaporated *in vacuo*. Elemental I_2 (2.0 g, 8.0 mmol) was added to the resulting alkaline aqueous solution, which was then stirred for 3 h at *ca.* 20 °C, then cooled to 0 °C, whereupon Na_2SO_3 (1.26 g, 10 mmol) and aqueous HCl (5 %, 100 ml) were added, the solution filtered, and $[NEt_4]^+Br^-$ (2.1 g, 10.0 mmol) added to the filtrate. After brief stirring, the $[NEt_4]^+$ / $[NEt_4]$Br double salt **2a** of the [*closo*-2-CB_9H_9-2-(C_6H_4-*para*-COOH)]$^-$ anion **2** precipitated as a white microcrystalline solid, which was filtered off and dried *in vacuo* (4.32 g, 7.45 mmol, 73 %). NMR, $(CD_3)_2CO$, 294-299 K, ordered as assignment δ(^{11}B)/ppm [δ(^{1}H)/ppm]: BH(10) +2.2 [+3.89], BH(1) –2.7 [+3.38], BH(4) –20.8 [+1.29], BH(6,7) -25.5 [+0.92], BH(3,5) -28.4 [+1.73], BH(7,8) –28.4 [+0.64]; additionally δ(^{1}H)(COOH) +10.79 (broad), δ(^{1}H)(Ph) at +7.72 (2H) and +6,99 (2H) (both apparent doublets) and δ(^{1}H)(Et) at +3.48 (16H, quartet) and +1.39 ppm (24H, triplet); also δ(^{13}C)(COOH) at +167.1, δ(^{13}C)(Ph) at +150.9 (1C), +141.9 (1C), +128.5 (2C) and +126.7 (2C), δ(^{13}C)(cluster) at +47.12 and δ(^{13}C)(Et) at +7.1 and +52.5 ppm. *(c)* **Anion 3.** $[OHCCO_2H(OH_2)]$ (9.2 g, 100 mmol) was added to a stirred solution of KOH (11.2 g, 200 mmol) in H_2O (100 ml) at 0 °C, and, after 5 minutes, $B_{10}H_{14}$ (2.0 g, 16.4 mmol) was added. The yellow solution was stirred for 2 h at *ca.* 20 °C. $[NEt_4]^+Br^-$ (4.2 g, 20 mmol) added, the solution cooled to 0 °C and aqueous HCl (5 %, 150 ml) added dropwise. The $[NEt_4]^+$ salt **3a** of the [*arachno*-6-CB_9H_{13}-6-(COOH)]$^-$ anion **3** precipitated as a white solid that was filtered off and dried in *vacuo* (2.68 g, 8.73 mmol, 53 %). NMR, $(CD_3)_2CO$, 294–299 K, ordered as assignment δ(^{11}B)/ppm [δ(^{1}H)/ppm]: BH(4) –0.6 [+2.35], BH(2) –9.4 [+2.02], BH(5,7) –9.4 [+2.43], BH(9) -20.0 [+1.14], BH(8,10) –27.9 [+0.89] and BH(1,3) –39.1 [+0.46], with δ(^{1}H) for μH(7,8)/(5,10) at –3.61 and for CH(6) at –0.75 ppm; additionally δ(^{1}H)(COOH) +10.14 (broad), δ(^{1}H)(Et) at +3.45 (8H, quartet) and +1.38 (12H, triplet) ppm, with δ(^{13}C)(COOH) at +172.4, δ(^{13}C)(cluster) at + 17.0 and δ(^{13}C)(Et) at +7.0 and +51.9 ppm. *(d)* **Anion 4.** A solution of **3a** (2.68 g, 8.73 mmol) in aqueous HCl (10 %, 100 ml) was extracted with Et_2O (3 × 50 ml), the organic layers separated and combined, then aqueous KOH (*ca.* 1.5 M; 300 ml) was added to these, and the Et_2O evaporated *in vacuo*. Elemental I_2 (6.0 g, 24 mmol) was added to the resulting alkaline aqueous solution, which was then stirred for 3 h at *ca.* 20 °C, cooled to 0 °C, and then Na_2SO_3 (2.92 g, 23 mmol), and $[NEt_4]^+Br^-$ (2.10 g, 10 mmol) were added, followed by aqueous HCl (5 %, 200 ml) dropwise. After brief stirring, the white microcrystalline precipitate of the $[NEt_4]^+$ salt **4a** of the [*closo*-2-CB_9H_9-2-(COOH)]$^-$ anion **4** was filtered off, washed with H_2O (50 ml) and dried *in vacuo* (1.31 g, 8.03 mmol, 92 %). NMR, $(CD_3)_2CO$, 294-299 K, ordered as assignment δ(^{11}B)/ppm [δ(^{1}H)/ppm]: BH(10) +0.81 [+3.76], BH(1) –5.2 [+3.53], BH(4) –21.7 [+1.20], BH(6,7) –26.7 [+0.92], BH(3,5) –29.2 [+1.49], BH(7,8) –29.7 [+0.51]; additionally δ(^{1}H)(COOH) +10.52 (broad), δ(^{1}H)(Et) at +3.52 (8H, quartet) and +1.40 ppm (12H, triplet), with δ(^{13}C)(COOH) at +173.6, (^{13}C)(cluster) at +45.8 and (^{13}C)(Et) at +7.1 and +52.4 ppm.

13. Crystallographic data. The $[NEt_4]_3[CB_9H_9(C_6H_4COOH)]_2Br$ double salt **2a** of anion **2**: $C_{40}H_{88}B_{18}BrN_3O_4$: M = 949.62, monoclinic (colourless prism from Et_2O-acetone), Space Group C2/*c*, a = 23.2400(4), b = 20.6240(4), c = 11.8850(2) Å, β = 103.3860(10)°, U = 5541.74(17) Å^3, D_{calc} = 1.138 Mg m^{-3}, Z = 4, Mo-Kα, λ = 0.71073 Å, μ = 0.781 mm^{-1}, T = 150(2) K, R_1 = 0.065 for 4834 reflections with $I > 2\sigma(I)$, and wR_2 = 0.1722 for all 6354 unique reflections; CCDC 211907. The $[NEt_4]^+$ salt **4a** of anion **4**: $C_{20}H_{60}B_{18}N_2O_4$: M = 587.28, monoclinic (colourless prism from Et_2O-acetone), Space Group C2/*c*, a = 30.0062(3), b = 15.1936(2), c = 16.7407(2) Å, β = 112.0290(10)°, U = 7074.93(14) Å^3, D_{calc} = 1.106 Mg m^{-3}, Z = 8, Mo-Kα, λ = 0.71073 Å, μ = 0.063 mm^{-1}, T = 150(2) K, R_1 = 0.0726 for 5668 reflections with $I > 2\sigma(I)$, and wR_2 = 0.2306 for all 6957 unique reflections; CCDC 211908. Methods and programs were standard (*Z*. Otwinowski, W. Minor, Methods Enzymol. 1997, **276**, 307; COLLECT, Data Collection Strategy Program, Nonius,1999.

Graphical Abstract

$B_{10}H_{14}$ with *para*-(OHC)C_6H_4(COOH) or OHCCOOH in aqueous KOH gives the [*nido*-6-CB_9H_{11}-6-(C_6H_4-*para*-COOH)]$^-$ anion or the [*arachno*-6-CB_9H_{13}-6-(COOH)]$^-$ anion, respectively; oxidation with I_2 thence gives the [*closo*-2-CB_9H_9-2-(C_6H_4-*para*-COOH)]$^-$ anion or the [*closo*-2-CB_9H_9-2-(COOH)]$^-$ anion, respectively.