Polyhedral monocarbaborane chemistry. Routes to neutral, monoanionic and dianionic carbo-carbaborane rods

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Reaction of $[BrC_6H_4CB_9H_{11}]^-$ with $[BH_3(SMe_2)]$ followed by iodination and treatment with $[MeC_6H_4MgBr]$ gives the 23 Å $[MeC_6H_4C_6H_4CB_{11}H_{10}C_6H_4Me]^-$ monoanion, treatment of $[1-Ph-1-CB_9H_{11}]^-$ with $FeCl_3$ and NC_5H_4-4-$CH_2C_6H_5$ gives 21.5 Å neutral $[PhCB_9H_8NC_5H_4CH_2C_6H_5]$, and reaction of $[1-(4-H_2NC_6H_4)-1-CB_9H_9]^-$ with $ClCOC_6H_4COCl$ gives the 30 Å $[(B_9H_9C)C_6H_4NHCOC_6H_4CONHC_6H_4(CB_9H_9)]^{2-}$ dianion with a Kevlar-like central unit.

There is interest and activity in the construction of rod-like molecules that combine carbaborane clusters and organic units for purposes of nanoarchitectural construction[1,2] and for other types of effect chemistry such as liquid-crystal behaviour.[3] Interest has focused almost exclusively on the use of dicarbaborane residues. Here we report preliminary results on potentially generic routes to rod-like neutral, monoanionic and dianionic molecules based on monocarbaborane residues. The monocarbaboranes offer complementary charge and polarity effects to those based on dicarbaboranes. Entry to these new monocarbaborane systems derive from the versatile Brellochs reaction of *nido*-$B_{10}H_{14}$ with aldehydes.[4–6]

The monoanionic linear rod species $[1-(4-MeC_6H_4-4-C_6H_4)$-*closo*-$CB_{11}H_{10}-12-(C_6H_4-4-Me)]^-$ **1** can be made as follows.[7] Reaction of 4-BrC_6H_4CHO with *nido*-$B_{10}H_{14}$ in aqueous alcoholic KOH gives the $[6-(4-BrC_6H_4)$-*nido*-$6-CB_9H_{11}]^-$ anion, which upon treatment with $[BH_3(SMe_2)]$ gives the $[1-(4-BrC_6H_4)$-*closo*-$1-CB_{11}H_{11}]^-$ anion **2**.[5] Reaction of the latter with I_2 in CH_3COOH gives the $[1-(4-BrC_6H_4)$-*closo*-$1-CB_{11}H_{10}-12-I]^-$ anion **3**, which upon treatment with 4-MeC_6H_4MgBr gives the rod-like monoanion **1** (Fig. 1, left),[8] isolatable as its $[NEt_4]^+$ salt **1a** (16% in four steps from $B_{10}H_{14}$). The distance between the most distal hydrogen-atom centres of the two terminal methyl groups is 20.1 Å, implying an overall Van-der-Waals length of nearly 23 Å.

Related neutral species can be structurally envisaged *via* the effective replacement of the group-14 carbon atom in such architectures by an atom of a group-15 element, for example by the use of pyridine-based residues rather than benzene-based residues. In accord with this idea, neutral $[1-Ph$-*closo*-$1-CB_9H_8-6-(NC_5H_4-4-CH_2Ph)]$ **4** (Fig. 1, right) can be made by the reaction of C_6H_5CHO with *nido*-$B_{10}H_{14}$ to give the $[6-Ph$-*nido*-$6-CB_9H_{11}]^-$ anion **5**. Anion **5**, upon treatment with NC_5H_4-4-$CH_2C_6H_5$ and $FeCl_3$ as oxidant, followed by chromatographic separation, thence gives neutral **4** (35 % in two steps from $B_{10}H_{14}$).[7] The preference for '*meta*' 6-substitution of the {*closo*-$1-CB_9$} cluster, compared to '*para*' 12-substitution of the {*closo*-$1-CB_{11}$} cluster, is as also noted for halogenation.[5,9] In neutral **4** this *meta*-type configuration entails a 'bend' in the rod-like molecule, the angle between the C(1)–C(aryl) and B(6)–N(pyridyl) directions being 119.7°, and in this species the benzylic {CH_2} group also introduces additional angularity together with chain flexibility. The overall Van-der-Waals length *via* the {CB_9} and {CH_2} centres is *ca.* 21.5 Å.

Conversely to the more positive nature of the neutral rod species **4** when compared to monoanionic **1**, rods that are more negative in nature are available by the linkage of two monoanionic monocarbaborane residues by a neutral spacer. In

accord with this idea, the $[(H_9B_9C)C_6H_4-4-NHCOC_6H_4CONH-4-C_6H_4(CB_9H_9)]^{2-}$ dianion **6** (Fig. 2),[8] with a Kevlar-like spacer, results from the reaction of $[C_6H_4-1,4-(COCl)_2]$ with the $[1-(4-NH_2-C_6H_4)$-*closo*-$1-CB_9H_9]^-$ monoanion **7**, and is isolatable as its $[NEt_4]^+$ salt **6a**.[7] The starting monoanion **7** can be prepared from *nido*-$B_{10}H_{14}$ according to Sivaev *et al.*,[6] the yield of dianion **6** being 40% overall in two steps from $B_{10}H_{14}$. The distance between the hydrogen-atom centres at the terminal 10-positions of the two {CB_9H_9} units in dianion **6** is 27.5 Å, implying an overall Van-der-Waals length of *ca.* 30 Å.

These three approaches, *viz.* to neutral, to monoanionic and to dianionic monocarbaborane-based rods, all in reasonable yields from *nido*-$B_{10}H_{14}$, are in principle applicable to other organic spacers and to other substituents that have alternative dimensions, directional geometries, and flexibilities, for example by choice of aldehydes for the initial monocarbaborane entry from $B_{10}H_{14}$, and by subsequent choice of pyridines, Grignard reagents, acyl chlorides and related carbonyl reagents, as appropriate. These potentially generic approaches will therefore have utility in several areas of developing effect chemistry.[1–3,10] We are currently devising experimentation to examine some of the possibilities thus realised.
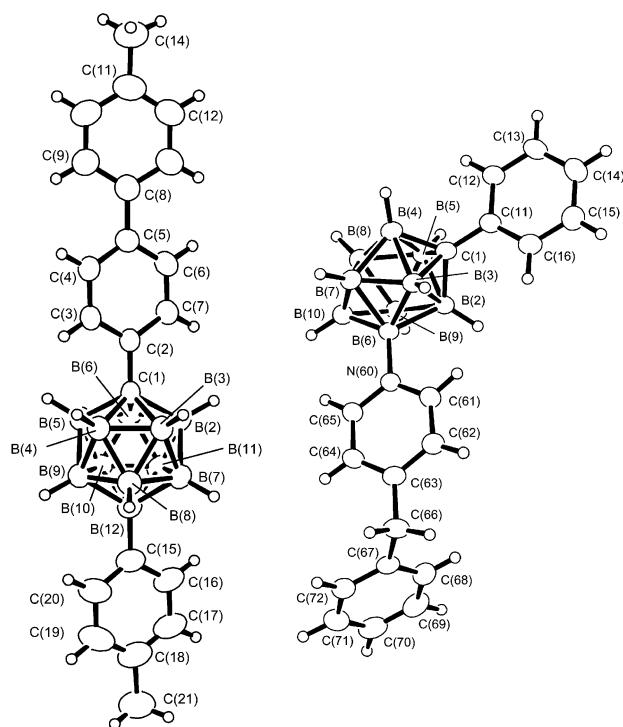
Fig. 1 Crystallographically determined molecular structures[8] of (left) the 23 Å $[1-(4-MeC_6H_4-4-C_6H_4)$-*closo*-$CB_{11}H_{10}-12-(C_6H_4-4-Me)]^-$ monoanion **1** in its $[NEt_4]^+$ salt **1a**, and (right) neutral $[1-Ph$-*closo*-$1-CB_9H_8-6-(NC_5H_4-4-CH_2Ph)]$ **4**.[8] Crystal packing results in a slight deviation from linearity for anion **1**, the angle between the two terminal C(aryl)–C(methyl) directions being 176.5°. In compound **4**, the overall Van-der-Waals length, *via* the bends associated with the {CB_9H_8} and {CH_2} centres, is *ca.* 21.5 Å.
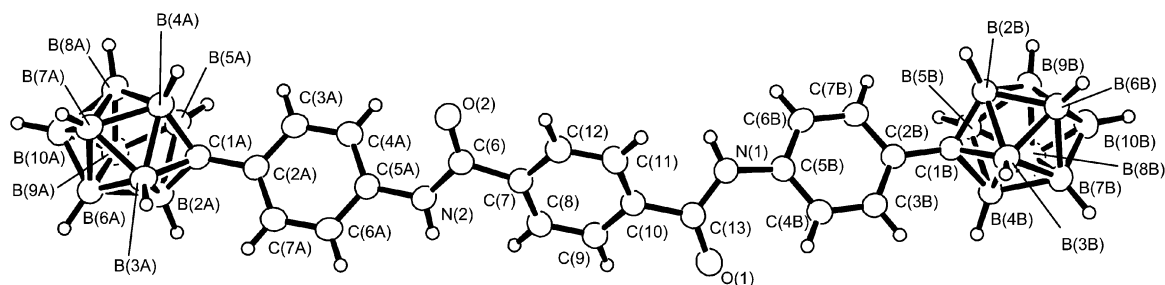
Fig. 2 Molecular structure of the [(B$_9$H$_9$C)C$_6$H$_4$-4-NHCOC$_6$H$_4$CONH-4-C$_6$H$_4$(CB$_9$H$_9$)]$^{2-}$ dianion **6** as determined crystallographically in its [NEt$_4$]$^+$ salt **6a**.[8] The deviation from linearity, as indicated by the angle of 165.3° between the two C(aryl)–C(monocarbaborane) directions, will presumably arise from solid-state packing.

Notes and references

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7 All reactions were carried out under dry N$_2$, followed by work-up in air. **Anion 1** : Elemental I$_2$ (4.0 g, 15.9 mmol), the Cs$^+$salt of the [1-(4-BrC$_6$H$_4$)-*closo*-1-CB$_{11}$H$_{11}$]$^-$ anion **2** (2.33 g, 5.4 mmol)[5] and CH$_3$COOH (40 ml) were heated at 100 °C for 48 hours. Then, at 20 °C, the CH$_3$COOH was removed *in vacuo*, H$_2$O (100 ml) and Na$_2$[SO$_3$] (1.0 g, 7.9 mmol) were added, and the solution filtered. Addition of [NEt$_4$]Cl (1.0 g, 6 mmol) to the filtrate gave a pale yellow precipitate. Aqueous HCl (10%, 200 ml) and CsCl (2.0 g, 13 mmol) were added to the filtered and dried precipitate. The resulting mixture was extracted with Et$_2$O. Evaporation of the extract *in vacuo* gave an oil, which was dissolved in H$_2$O (50 ml). Addition of CsCl (2.0 g, 12.8 mmol) gave a white precipitate, of which crystallisation from 1 : 1 hot H$_2$O–MeOH gave the Cs$^+$ salt **3a** of the [1-(4-BrC$_6$H$_4$)-*closo*-1-CB$_{11}$H$_{10}$-12-I]$^-$ anion **3** (white crystals, 2.35 g, 4.2 mmol, 78%). The salt **3a** (0.56 g, 1.0 mmol) was dissolved in THF (20 ml), 4-MeC$_6$H$_4$MgBr in THF (1.0 M, 10 ml) and [PdCl$_2$(PPh$_3$)$_2$] (100 mg, 0.14 mmol) were added, the mixture was heated at reflux for 18 hours, then cooled to 0 °C, and EtOH (2 ml) and H$_2$O (50 ml) added. The THF and EtOH were removed *in vacuo*, and the resulting aqueous solution acidified with aqueous HCl (5%, 40 ml). Extraction with Et$_2$O followed by evaporation of the extracts gave a reddish oil. Dissolution in 2 : 1 EtOH–MeCN (20 ml) and passing through an acidified cation-exchange column gave an acidic colourless fraction. Evaporation gave a colourless oil, which was dissolved in H$_2$O (50 ml). Precipitation with [NEt$_4$]Cl (0.5 g, 3.0 mmol) gave the [NEt$_4$]$^+$ salt **1a** of the [(MeC$_6$H$_4$)(C$_6$H$_4$)(CB$_{11}$H$_{10}$)(C$_6$H$_4$Me)]$^-$ anion **1** (white crystals, 0.23 g, 0.43 mmol, 43%). **Compound 4**: [FeCl$_3$(H$_2$O)$_6$] (3 g, 11 mmol) and 4-benzylpyridine (10 ml, 62 mmol) were added to a solution in CHCl$_3$ (30 ml) of the [NEt$_4$]$^+$ salt **5a** (1.0 g, 3.1 mmol) of the [6-Ph-6-CB$_9$H$_{11}$]$^-$ anion **5**,[5] and the mixture stirred at reflux temperature for 10 days. Cooling, removal of the CHCl$_3$ and acidification with aqueous HCl (5%, 50 ml), followed by Et$_2$O extraction and evaporation of the Et$_2$O solution, gave a pale yellow solid consisting mostly of [PhCB$_9$H$_8$NC$_5$H$_4$CH$_2$Ph] **4** (0.72 g, 2 mmol, 64%,), of which preparative TLC [silica gel G (Fluka GF$_{254}$), CH$_2$Cl$_2$–*n*-hexane 60 : 40] gave pure **4** (white crystals, 0.62 g, 1.7 mmol, 55%) as the one principal component (colourless, R_F 0.5). **Dianion 6** : A solution of [NEt$_4$]$^+$[1-(4-H$_2$NC$_6$H$_4$)-*closo*-1-CB$_9$H$_9$]$^-$ **7a** (0.34 g, 1.0 mmol)[6] and C$_6$H$_4$-1,4-(COCl)$_2$ (0.1 g, 0.5 mmol) in MeCN (10 ml) was stirred for 18 hours at *ca.* 20 °C. The MeCN was removed *in vacuo* and aqueous HCl (5%, 50 ml) was added. Extraction with Et$_2$O, addition of H$_2$O (50 ml) to the extracts, removal of the Et$_2$O *in vacuo*, filtration, and addition of [NEt$_4$]Cl (1.0 g, 6 mmol) to the resulting aqueous solution precipitated the [NEt$_4$]$^+$ salt **6a** of the [(B$_9$H$_9$C)C$_6$H$_4$-4-NHCOC$_6$H$_4$CONH-4-C$_6$H$_4$(CB$_9$H$_9$)]$^-$ dianion **6** (white crystals, 0.37 g, 0.45 mmol, 45%).

8 Crystallographic data. For compound **1a**: [(MeC$_6$H$_4$-C$_6$H$_4$)CB$_{11}$H$_{10}$(C$_6$H$_4$Me)][NEt$_4$], C$_{29}$H$_{48}$B$_{11}$N, M = 529.59, monoclinic (colourless plate from Et$_2$O–Me$_2$CO), space group $P2_1/c$, a = 24.8134(2), b = 14.0073(2), c = 19.4920(10) Å, β = 107.1260(5)°, U = 6474.44(11) Å^3, D_{calc} = 1.087 Mg m^{-3}, Z = 4, MoK$_\alpha$, λ = 0.71073 Å, μ = 0.056 mm^1, T = 150(2) K, R_1 = 0.0936 for 9593 reflections with $I > 2\sigma(I)$, and wR_2 = 0.2749 for all 12649 unique reflections; CCDC 184236. For compound **4**: [PhCB$_9$H$_8$(NC$_5$H$_4$CH$_2$Ph)], C$_{19}$H$_{24}$B$_9$N, M = 363.68, monoclinic (colourless prism from dichloromethane–benzene–hexane), space group $P2_1/c$, a = 9.9181(2), b = 10.8545(3), c = 19.3643(4) Å, β = 97.2720(10)°, U = 2067.91(8) Å^3, D_{calc} = 1.168 Mg m^{-3}, Z = 4, MoK$_\alpha$, λ = 0.71073 Å, μ = 0.06 mm^1, T = 150(2) K, R_1 = 0.0431 for 3363 reflections with $I > 2\sigma(I)$, and wR_2 = 0.1183 for all 4053 unique reflections; CCDC 204007. For compound **6a**: [(H$_9$B$_9$C)C$_6$H$_4$NHCOC$_6$H$_4$CONHC$_6$H$_4$(CB$_9$H$_9$)][NEt$_4$]$_2$, C$_{38}$H$_{72}$-B$_{18}$N$_4$O$_2$: M = 811.58, monoclinic (colourless plate from Et$_2$O–MeCN), space group $P2_1/c$, a = 14.25280(10), b = 24.5742(3), c = 14.40150(10) Å, β = 102.9230(10)°, U = 4916.38(8) Å^3, D_{calc} = 1.096 Mg m^{-3}, Z = 4, MoK$_\alpha$, λ = 0.71073 Å, μ = 0.061 mm^1, T = 150(2) K, R_1 = 0.0619 for 7882 reflections with $I > 2\sigma(I)$, and wR_2 = 0.1882 for all 9637 unique reflections; CCDC 204008. Methods and programs were standard (Z. Otwinowski and W. Minor, *Methods Enzymol.*, 1997, **276**, 307; COLLECT, Data Collection Strategy Program, Nonius, 1999). See http://www.rsc.org/suppdata/cc/b3/b303589a/ for crystallographic data in .cif or other electronic format.

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