New Monocarbaboranes from Stepwise Degradation of Icosahedral 1,2- and 1,7-$C_2B_{10}H_{12}$ Dicarbaboranes

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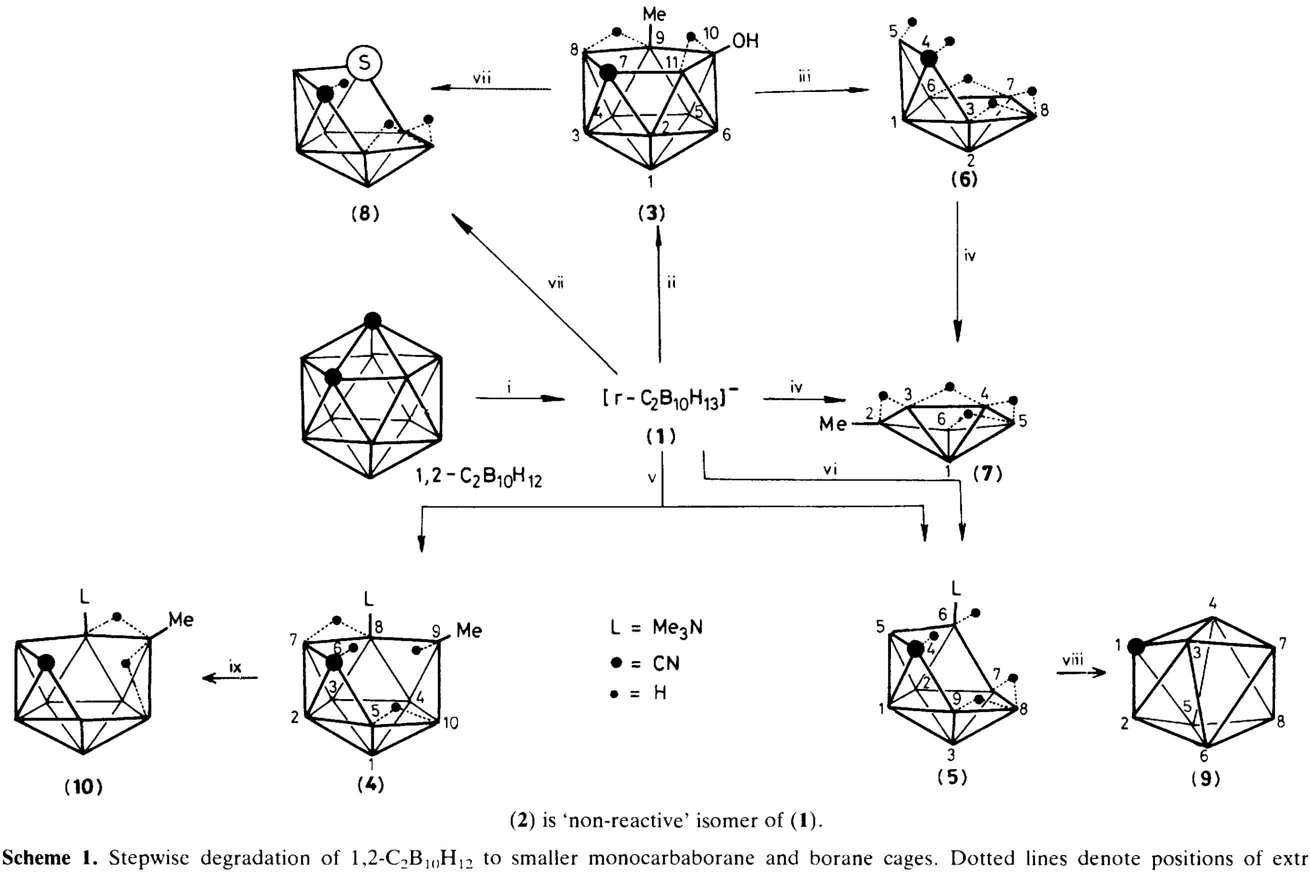
Specific degradation reactions of the 'reactive isomer' of the $[C_2B_{10}H_{13}]^-$ anion, $[r\text{-}C_2B_{10}H_{13}]^-$, result in the removal of one or two carbon atoms from the cage to produce a series of monocarbaboranes 9-Me-10-HO-*nido*-$[7\text{-}CB_{10}H_{11}]^-$, 8-$Me_3N$-*arachno*-4-$CB_8H_{12}$, and *arachno*-4-$CB_7H_{13}$, together with the binary borane 2-Me-*nido*-B_6H_9; further reactions give the compounds 8-Me_3N-9-Me-*nido*-6-CB_9H_{10}, *arachno*-4,6-CSB_7H_{11}, and *closo*-$[1\text{-}CB_7H_8]^-$.

Both 1,2- and 1,7-$C_2B_{10}H_{12}$ dicarbaboranes are known to afford quantitatively the $[C_2B_{10}H_{12}]^{2-}$ dianion *via* reduction with sodium metal in tetrahydrofuran (thf).[1—3] Dunks *et al.*[4,5] have reported that protonation of the latter anion produces the 'reactive isomer' of $[C_2B_{10}H_{13}]^-$, $[r\text{-}C_2B_{10}H_{13}]^-$ (**1**), and the 'non-reactive isomer,' $[nr\text{-}C_2B_{10}H_{13}]^-$ (**2**), under different conditions. The $[r\text{-}C_2B_{10}H_{13}]^-$ isomer rearranges by heating at 100 °C to the isomer (**2**). While the structure of (**1**) still remains unclear, the μ-9,10-CH_2-*nido*-$[7\text{-}CB_{10}H_{11}]^-$ structure of (**2**) has been determined unequivocally *via* *X*-ray diffraction studies on its *C*,*C*′-dimethyl and *C*,*C*′-diphenyl derivatives.[6,7] We now report another aspect of the formation of (**1**) and, particularly, our preliminary results on directed degradation reactions of (**1**) leading to an unexpected, stepwise degradation of the original *closo*-$C_2B_{10}H_{12}$ cage to smaller monocarbaborane and borane frameworks.

An aqueous–thf solution of crude (**1**) was obtained on the reduction of 1,2- and/or 1,7-$C_2B_{10}H_{12}$ with sodium metal in thf catalysed by naphthalene (5%),[1—3] followed by treatment with a mixture of 1 M HCl (1.2 mol. equiv.) and NaCl (10%). The solution obtained after the separation of the organic layer contained typically 75% of (**1**), and 25% of (**2**), which does not interfere in further syntheses. This solution is stable for several hours at 25 °C unless the thf is removed. If the thf is evaporated *in vacuo* (25 °C, pH 5), a turbid, very unstable, solution of (**1**) is obtained for further rapid reaction. If the solution is made slightly alkaline before the thf is removed, the resulting aqueous solution contains only an anion formulated as $[C_2B_{10}H_{14}OH]^-$ (**3**) contaminated by 25% of (**2**) already present from the synthesis. The anion (**3**) (characterized with $NBu^n_4{}^+$ or $PPh_4{}^+$ as counterion) is thought to be 9-Me-10-HO-*nido*-$[7\text{-}CB_{10}H_{11}]^-$, although unambiguous structural



(**2**) is 'non-reactive' isomer of (**1**).

Scheme 1. Stepwise degradation of 1,2-$C_2B_{10}H_{12}$ to smaller monocarbaborane and borane cages. Dotted lines denote positions of extra hydrogens and the vertices of individual deltahedra represent {BH} cluster units. *Reagents*: i, Na, thf, then dil. HCl; ii, K_2CO_3, 20 °C, 5 min (75%); iii, dil. HCl, pentane, 20 °C, 30 min (70%); iv, dil. HCl, pentane, 20 °C, 4 h (65%); v, Me_3N, H_2O–thf, 20 °C, 6 h [25% of (**4**) and 60% of (**5**)]; vi, Me_3N, H_2O–$CHCl_3$ (>90%); vii, $KHSO_3$, H_2O, 20 °C, 10 h (34%); viii, NaH, thf, 60 °C, 6 h (>60%); ix, Me_2CO, K_2CO_3, 20 °C, 1 h (>95%).

assignment by two-dimensional ^{11}B–^{11}B COSY n.m.r. techniques was not possible because of accidental near-coincidence of several ^{11}B n.m.r. resonances in the one-dimensional spectrum.† The formation of (**3**) is consistent with the removal of one of the skeletal carbons to an exo-polyhedral position. Further reactions leading to profound cage degradations of (**1**) and (**3**) are depicted in Scheme 1. Anion (**1**) and aqueous trimethylamine produce in the presence of thf a mixture of the *arachno* monocarbaboranes 8-Me_3N-9-Me-6-CB_9H_{12} (**4**) and 6-Me_3N-4-CB_8H_{12} (**5**) which can be separated *via* column chromatography on silica gel in chloroform. In the presence of chloroform, only compound (**5**) is obtained in high yield. Acid hydrolysis of both (**1**) and (**3**) with dilute hydrochloric acid (20 °C, 30 min) results in the formation of the *arachno*-4-CB_7H_{13} (**6**) carbaborane, which upon hydrolysis (25 °C, 4 h) generates the earlier reported[8] *nido*-hexaborane 2-MeB_6H_9 (**7**), as the final member of the degradation chain. The borane (**7**) is also formed on prolonged hydrolysis of both (**1**) and (**3**). Acid degradation of (**3**) with the sulphite ion affords the earlier reported[9] thiacarbaborane *arachno*-4,6=CSB_7H_{11} (**8**) which has been synthesised directly from (**1**).[9]

Treatment of (**5**) with NaH in thf results in the unexpected elimination of Me_3NBH_3 to give the new parent anion *closo*-$[1\text{-}CB_7H_8]^-$ (**9**). Of interest also is the oxidation of the *arachno*-compound (**4**) with acetone to give its *nido*-congener, 8-Me_3N-9-Me-6-CB_9H_{10} (**10**).

Gross geometries of compounds (**4**)—(**10**) are proposed on the basis of unambiguous n.m.r. data, ^{11}B–^{11}B COSY and mass spectral measurements.† The *arachno*-monocarbaborane (**6**) is the first known carba-analogue of an open cage octaborane and anion (**9**) is the first known 8-vertex *closo*-monocarbaborane. Compound (**5**) is isoelectronic and isostructural with the long known 4,6-$C_2B_7H_{13}$ dicarbaborane,[10,11] and compounds (**4**) and (**10**) represent hitherto unknown types of carbadecaboranes with a ligand attached asymmetrically at the B(8) site. The unique base-catalysed oxidation of (**4**) to (**10**) seems to be of general significance in the 10-vertex series of monocarbaboranes.

The most characteristic feature of the degradation reactions described above is the removal of one or two carbon atoms from the cage. In this respect these reactions, starting from the readily available 1,2- and 1,7-$C_2B_{10}H_{12}$ dicarbaboranes, now open new synthetic possibilities in the chemistry of monocarbaboranes.

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† Mass spectra: m/z (M^+): (**4**) 197; (**5**) 171; (**6**) 102; (**7**) 90; (**8**) 132; (**10**) 195 (parent ions).

N.m.r. data: [a] in $(CD_3)_2CO$, [b] in $CDCl_3$: ^{1}H (tentative assignments, δ with respect to Me_4Si, relative intensities in parentheses): (**1**)[a] (NMe_4^+ salt) CH(skeletal) +4.14 (2), NMe_4^+ +3.42 (12), μ-H −4.60 (1); (**3**)[a] (PPh_4^+ salt) Ph +7.88 (20), exo-Me +0.3 (3), μ-H −3.03 (2); (**4**)[b] 8-Me_3N +2.99 (9), 9-Me +0.34 (3), exo-H(6) +0.06 (1), μ-H −1.75 (1), endo-H(6) −1.93 (1), μ-H −3.40 (1); (**5**)[a] 6-Me_3N +2.88 (9), exo-H(6) −0.16(1), endo-H(6) −1.09 (1), μ-H −2.42 (2); (**6**)[b] exo and endo-H(4) +0.90 (2), μ-H −0.79 (3); (**7**)[b] 2-Me +0.64 (3), μ-H −1.96 (4); (**8**)[b] exo-H(4) +0.19 (1), endo-H(4) −0.32 (1), μ-H −0.92 (1), μ-H −2.45 (1); (**9**)[a] (NMe_4^+ salt) H(1) +4.14 (1), NMe_4^+ +3.46 (12); (**10**)[a] H(6) +5.62 (1), 8-Me_3N +3.21 (9), 9-Me +0.80 (3), μ-H −0.65 (1), μ-H −3.09 (1).

^{13}C n.m.r. spectra (tentative assignments, δ with respect to Me_4Si, relative intensities in parentheses): (**5**)[a] 6-Me_3N +54.22 (3), C(4) −12.42 (1); (**6**)[b] C(4) −12.01; (**7**)[b] 2-Me 0.00.

^{11}B n.m.r. spectra [tentative assignments by ^{11}B–^{11}B COSY experiments, δ (^{11}B)/p.p.m., with respect to $Et_2O.BF_3$, relative intensities in parentheses]: (**1**)[a] BH +12.01, BH 2.31 (2), BH −5.01 (1), BH −8.14 (2), BH −17.84 (1), BH −20.31 (1), BH −21.65 (2); (**3**)[a] B(10) +8.37 (1), BH 6.39 (1), B(8) −0.83 (1), BH −3.04 (2), BH −7.49 (1), BH −26.99 (1), BH −35.98 (3); (**4**)[a] BH(4) +4.74, BH(9) −5.15, BH(5,7) −9.32, BH(2) −12.68, B(8) −15.64, BH(10) −23.35, BH(3) −35.04, BH(1) −40.67; (**5**)[a] BH(5) +0.39, BH(9) +0.53, BH(7) −4.78, BH(2) −12.19, BH(6) −18.93, BH(1) −22.15, BH(8) −25.9, BH(3) −52.71; (**6**)[b] BH(7) +8.61, BH(6) +3.65, BH(3) −0.26, BH(1) −5.70, BH(8) −6.53, BH_2(5) −14.68, BH(2) −55.22; (**7**)[b] B(2) +29.36, BH(4,5) +17.26, BH(3,6) +5.77, BH(1) −50.53; (**8**)[b] BH(7,9) +1.41, BH(1) −0.55, BH(2) −14.75, BH(5) −27.16, BH(8) −33.09, BH(3) −50.07; (**9**)[a] BH(6,7,8) +3.14, BH(2,3,4,5) −4.35 (fluxional behaviour between −40 and +25 °C); (**10**)[a] B(9) +7.94, BH(5) +5.16, BH(7) +0.79, B(8) −4.48, BH(1,3) −5.93, BH(10) −15.02, BH(2,4) −32.82.