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Reaction of 13-Vertex Carboranes with Nucleophiles: Unprecedented Cage-Carbon Extrusion and Formation of Monocarba-*closo*-dodecaborate Anions**

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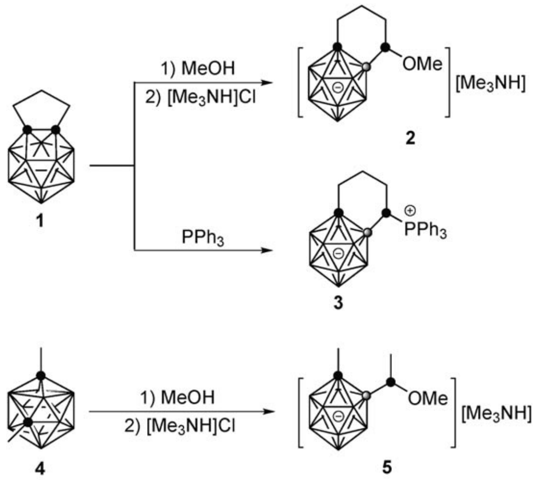
Only in recent years has significant progress been made in the chemistry of supercarboranes (carboranes with more than 12 vertices).[1] A number of 13- and 14-vertex carboranes have been prepared and structurally characterized since 2003.[2–7] They are readily reduced by Group 1 metals to give the corresponding *nido*-supercarborane dianions.[3–7] The carbon-atoms-adjacent (CAd) carborane 1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$ can even undergo single-electron reduction to generate a stable carborane radical anion with $2n+3$ framework electrons.[8] It can also react with various electrophiles to afford hexasubstituted CAd 13-vertex carboranes 8,9,10,11,12,13-X_6-1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_5$ (X = Me, Br, I).[4] We are interested in the reaction of supercarboranes with nucleophiles. We now report that unprecedented products of cage-carbon extrusion are isolated instead of the expected deborated species after treatment of 13-vertex carboranes with nucleophiles.



Scheme 1. Reaction of CAd and CAp 13-vertex carboranes with nucleophiles.

A solution of 1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$ (**1**)[3] in methanol was stirred at room temperature for one day to give, after addition of $[Me_3NH]Cl$, $Me_3NH[1,2\text{-}(CH_2)_3CH(OMe)\text{-}1\text{-}CB_{11}H_{10}]$ (**2**), which was isolated in 75% yield (Scheme 1). This reaction can be monitored by ^{11}B NMR spectroscopy. Whereas **1** reacted with MeOH/NaOH to afford a mixture of inseparable products, its icosahedral cousin 1,2-$(CH_2)_3$-1,2-$C_2B_{10}H_{10}$ is stable in refluxing MeOH and is converted to the *nido* species $(CH_2)_3C_2B_9H_{10}^-$ in refluxing MeOH/NaOH solution.[9] When PPh_3 was used as nucleophile, the zwitterionic compound $[1,2\text{-}(CH_2)_3CH(PPh_3)\text{-}1\text{-}CB_{11}H_{10}]\cdot CH_2Cl_2$ (**3**) was isolated in 80% yield after recrystallization from CH_2Cl_2. Similarly, the carbon-atoms-apart (CAp) 13-vertex carborane 1,6-Me_2-1,6-$C_2B_{11}H_{11}$ (**4**)[7] reacted with MeOH to afford, on addition of $[Me_3NH]Cl$, $Me_3NH[1\text{-}Me\text{-}2\text{-}CH(OMe)Me\text{-}1\text{-}CB_{11}H_{10}]$ (**5**) in 55% yield.

The ^{11}B NMR spectra of **2** and **5** show similar 1:1:6:3 patterns, whereas that of **3** displays a 1:3:7 pattern. The signal of the substituted B2 atom in both **2** and **5** is clearly distinguished from others at $\delta = -7.7$ and -5.0 ppm as a singlet in the proton-coupled ^{11}B NMR spectra. However, the resonance of B2 in **3** overlaps with other cage B peaks, and is hardly resolved. The α-C atom bonded to B2 is unambiguously identifiable, as it appears as a broad signal in the ^{13}C NMR spectra due to coupling to a ^{11}B nucleus, at $\delta = 74.2$ ppm in **2**, $\delta = 72.2$ ppm in **5**, and $\delta = 17.2$ ppm in **3**. The ^{31}P NMR spectrum of **3** exhibits one sharp peak at $\delta = 32.7$ ppm, supportive of a tertiary phosphonium salt.[10]

Single-crystal X-ray analyses confirm the molecular structures of **2**, **3**, and **5**, as shown in Figures 1–3, respectively.[11] The icosahedral cages in the three compounds have the same structural features of a monocarba-*closo*-dodecaborate anion.[12]

Cage-carbon extrusion from carborane clusters is very rare but not unknown. Two examples have been reported. A recent *closo*-to-*closo* example is the transformation of $[1\text{-}H_2N\text{-}closo\text{-}CB_{11}F_{11}]^-$ into $[3\text{-}NC\text{-}closo\text{-}B_{11}F_{10}]^{2-}$, which is limited to highly fluorinated boron clusters.[13] The other is the conversion of $[7\text{-}R\text{-}\mu\text{-}(9,10\text{-}HR'C)\text{-}7\text{-}nido\text{-}CB_{10}H_{11}]^-$ to $[1\text{-}R\text{-}6\text{-}CH_2R'\text{-}1\text{-}closo\text{-}CB_9H_8]^-$, in which cage-carbon extrusion is suggested to proceed after removal of one BH vertex.[14] In this regard, a plausible pathway for formation of monocarba-*closo*-dodecaborate anions is proposed in Scheme 2. Attack of the nucleophile on one of the cage carbon atoms of the 13-vertex carborane[15] leads to cleavage of the C_{cage}–C_{cage} bond and formation of new C_{cage}–B bonds to preserve cluster integrity. Hydrogen migration then generates the final icosahedral product. This behavior is significantly different from that of *o*-carboranes, in which a cage boron atom is attacked by nucleophiles to give deboration products.[16,17] Although the reasons are not yet clear, comparison of the ^{13}C chemical shift of the cage carbon atoms of 136 ppm in **1** with

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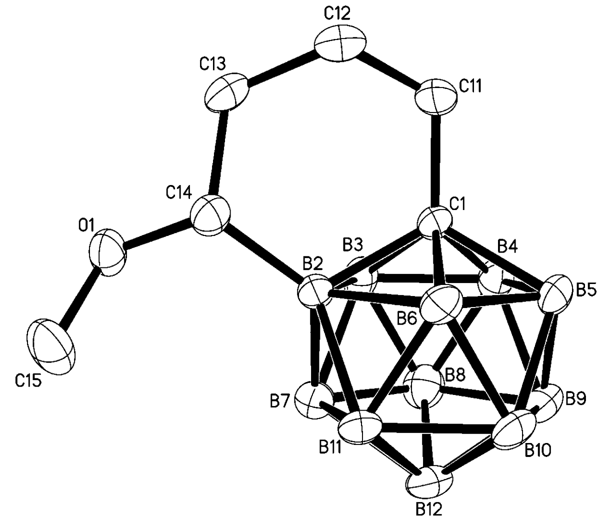


Figure 1. Molecular structure of $[1,2\text{-}(CH_2)_3CH(OCH_3)\text{-}1\text{-}CB_{11}H_{10}]^-$ in **2**. Selected bond lengths [Å]: C1–B2 1.721(4), C1–B3 1.714(4), C1–B4 1.719(5), C1–B5 1.709(4), C1–B6 1.705(4), C1–C11 1.527(4), C11–C12 1.519(5), C12–C13 1.520(5), C13–C14 1.527(4), C14–B2 1.603(4), C14–O1 1.459(4), av B–B 1.771(5).

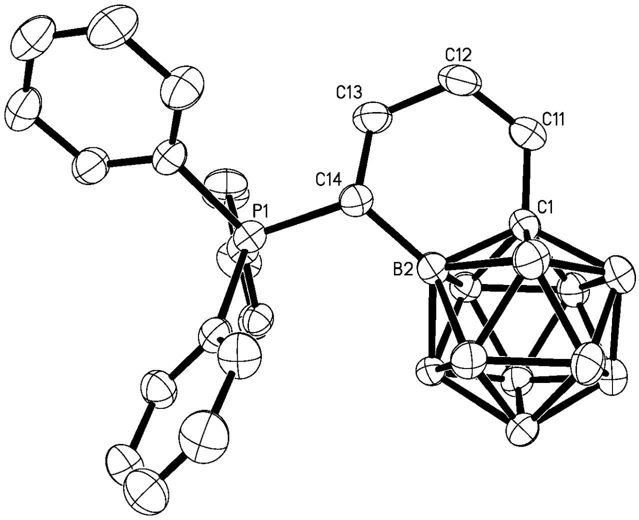


Figure 2. Molecular structure of $[1,2\text{-}(CH_2)_3CH(PPh_3)\text{-}1\text{-}CB_{11}H_{10}]$ (**3**). Selected bond lengths [Å]: C1–B2 1.724(4), C1–B3 1.719(4), C1–B4 1.713(4), C1–B5 1.727(5), C1–B6 1.700(5), C1–C11 1.517(4), C11–C12 1.532(5), C12–C13 1.523(5), C13–C14 1.560(4), C14–B2 1.625(4), C14–P1 1.815(3), av B–B 1.773(5).

that of 84 ppm in the corresponding 12-vertex carborane $1,2\text{-}(CH_2)_3\text{-}1,2\text{-}C_2B_{10}H_{10}$ offers some insight into the charge density of the cage carbon atoms. Clearly, the cage carbons in 13-vertex carboranes are much more electron-deficient than those in 12-vertex carboranes.

In conclusion, compared with 12-vertex carboranes, 13-vertex carboranes exhibit significantly different reactivity toward nucleophiles. A new cage-carbon extrusion reaction is observed that leads to formation of monocarba-*closo*-dodecaborate anions.

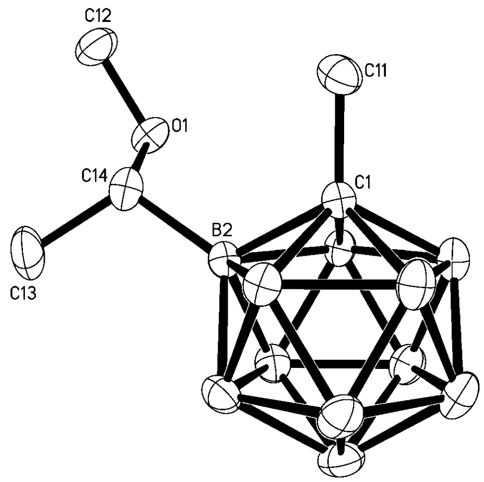
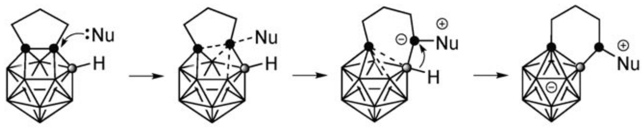


Figure 3. Molecular structure of $[1\text{-}CH_3\text{-}2\text{-}CH_3CH(OCH_3)\text{-}1\text{-}CB_{11}H_{10}]^-$ in **5**. Selected bond lengths [Å]: C1–B2 1.718(4), C1–B3 1.715(4), C1–B4 1.702(5), C1–B5 1.705(5), C1–B6 1.706(5), C1–C11 1.516(4), B2–C14 1.592(5), C14–C13 1.527(5), C14–O1 1.457(4), av B–B 1.767(6).



Scheme 2. Possible reaction pathway.

Experimental Section

2: Compund **1** (196 mg, 1.00 mmol) was dissolved in MeOH (10 mL), and the solution was stirred at room temperature for 1 d. After addition of $[Me_3NH]Cl$ (191 mg, 2.00 mmol), the mixture was further stirred for 1 h. MeOH was then pumped off, and the residue was thoroughly washed with water to give a white solid. Recrystallization from acetone gave **2** as colorless crystals (215 mg, 75 %). ^1H NMR (400 MHz, $[D_6]$acetone): $\delta = 3.87$ (br s, 1H; NH), 3.34 (s, 3H; OCH_3), 3.20 (s, 9H; NCH_3), 3.11 (t, J = 6.6 Hz, 1H; BCH), 1.81 (m, 2H; δ-CH_2), 1.68 (m, 1H; β-CH_2), 1.46 (m, 1H; γ-CH_2), 1.39 (m, 1H; β-CH_2), 1.21 ppm (m, 1H; γ-CH_2); $^{13}C\{^1H\}$ NMR (100 MHz, $[D_6]$acetone): $\delta = 74.2$ (br; BCH), 69.2 (cage C), 57.7 (OCH_3), 46.2 (NCH_3), 36.7 (δ-CH_2), 29.6 (β-CH_2), 23.2 ppm (γ-CH_2); ^{11}B NMR (96 MHz, $[D_6]$acetone): $\delta = -7.7$ (s, 1B), −9.3 (d, $J_{B,H} = 145$ Hz, 1B), −12.3 (d, $J_{B,H} = 113$ Hz, 6B), −13.5 (overlapping, 1B), −13.9 ppm (overlapping, 2B); IR (KBr): $\tilde{\nu} = 2539\ cm^{-1}$ (B–H); elemental analysis (%) calcd for $C_9H_{30}B_{11}NO$: C 37.63, H 10.53, N 4.88; found: C 37.98, H 11.05, N 4.79.

3: PPh_3 (276 mg, 1.05 mmol) was added to a solution of **1** (196 mg, 1.00 mmol) in toluene (20 mL), and the reaction vessel was closed. The mixture was heated at 110 °C for 12 h to give a white suspension. After removal of toluene, the white solid was recrystallized from CH_2Cl_2 to give **3** as colorless crystals (435 mg, 80 %). ^1H NMR (400 MHz, $[D_6]$acetone): $\delta = 8.08$ (m, 6H; C_6H_5), 7.80 (m, 3H; C_6H_5), 7.70 (m, 6H; C_6H_5), 5.62 (s, 2H; CH_2Cl_2), 3.73 (m, 1H; BCH), 2.14 (m, 1H; β-CH_2), 1.98 (m, 1H; δ-CH_2), 1.64 (m, 2H; δ-CH_2 and γ-CH_2), 1.56 (m, 1H; γ-CH_2), 1.47 ppm (m, 1H; β-CH_2); $^{13}C\{^1H\}$ NMR (100 MHz, $[D_6]$acetone): $\delta = 135.2$ (d, $^2J_{P,C} = 9.3$ Hz), 134.8 (d, $^4J_{P,C} = 2.9$ Hz), 130.4 (d, $^3J_{P,C} = 12.2$ Hz), 121.6 (d, $^1J_{P,C} = 82.9$ Hz) (C_6H_5), 67.7 (cage C), 55.0 (CH_2Cl_2), 36.2 (δ-CH_2), 25.3 (d, $^3J_{P,C} = 14.3$ Hz; γ-CH_2), 24.9 (d, $^2J_{P,C} = 3.6$ Hz; β-CH_2), 17.2 ppm (br; BCH); ^{11}B NMR (128 MHz, $[D_6]$acetone): $\delta = -8.4$ (d, $J_{B,H} = 151$ Hz, 1B), −11.1 (d, $J_{B,H} = 144$ Hz, 3B), −12.4 ppm (d, $J_{B,H} = 122$ Hz, 7B); ^{31}P NMR (121 MHz, $[D_6]$acetone): $\delta = 32.7$ ppm; IR (KBr): $\tilde{\nu} = 2539\ cm^{-1}$

(B−H); elemental analysis (%) calcd for $C_{23}H_{32}B_{11}P$ (**3**−CH_2Cl_2): C 60.26, H 7.04; found: C 60.38, H 6.81.

5: Compound **4** (184 mg, 1.00 mmol) was dissolved in MeOH (10 mL), and the solution was stirred at room temperature for 1 d. After addition of $[Me_3NH]Cl$ (191 mg, 2.00 mmol), the mixture was stirred for a further 1 h. MeOH was pumped off and the residue was thoroughly washed with water to give a white solid. Recrystallization from acetone gave **5** as colorless crystals (152 mg, 55%). ^1H NMR (400 MHz, [D_6]acetone): $\delta = 3.30$ (br s, 1 H; NH), 3.23 (s, 3 H; OCH_3), 3.13 (s, 9 H; NCH_3), 3.03 (m, 1 H; BCH), 1.51 (s, 3 H; CH_3), 1.28 ppm (d, $J = 6.7$ Hz, 3 H; β-CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, [D_6]acetone): $\delta = 72.2$ (br; BCH), 65.2 (cage C), 57.1 (OCH_3), 46.1 (NCH_3), 25.0 (CH_3), 19.6 ppm (β-CH_3); ^{11}B NMR (96 MHz, [D_6]acetone): $\delta = -5.0$ (s, 1 B), −9.1 (d, $J_{B,H} = 123$ Hz, 1 B), −11.4 (d, $J_{B,H} = 180$ Hz, 6 B), −13.6 ppm (d, $J_{B,H} = 181$ Hz, 3 B); IR (KBr): $\tilde{\nu} = 2530\ cm^{-1}$ (B−H); elemental analysis (%) calcd for $C_8H_{30}B_{11}NO$: C 34.91, H 10.99, N 5.09; found: C 34.63, H 10.52, N 4.65.

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[11] Crystal data for **2**: $C_9H_{30}B_{11}NO$, $M_r = 287.3$, monoclinic, space group $P2_1/c$, $a = 7.924(3)$, $b = 23.339(9)$, $c = 9.662(4)$ Å, $\beta = 97.49(1)°$, $V = 1772(1)$ Å^3, $T = 293$ K, $Z = 4$, $\rho_{calcd} = 1.077\ g\,cm^{-3}$, $2\theta_{max} = 50°$, $\mu(Mo_{K\alpha}) = 0.71073$ Å, absorption corrections applied by using SADABS,[18] relative transmission factors in the range 0.411–1.000. A total of 9415 reflections were collected and led to 3118 unique reflections, 3118 of which with $I > 2\sigma(I)$ were considered as observed, $R_1 = 0.079$, $wR_2(F^2) = 0.199$. Crystal data for **3**: $C_{24}H_{34}B_{11}Cl_2P$, $M_r = 543.3$, orthorhombic, space group $P2_12_12_1$, $a = 10.629(1)$, $b = 12.942(1)$, $c = 21.764(1)$ Å, $V = 2994(1)$ Å^3, $T = 296$ K, $Z = 4$, $\rho_{calcd} = 1.205\ g\,cm^{-3}$, $2\theta_{max} = 50°$, $\mu(Mo_{K\alpha}) = 0.71073$ Å, absorption corrections applied by using SADABS,[18] relative transmission factors in the range 0.800–1.000. A total of 27791 reflections were collected and led to 5234 unique reflections, 5234 of which with $I > 2\sigma(I)$ were considered as observed, $R_1 = 0.049$, $wR_2(F^2) = 0.134$. Crystal data for **5**: $C_8H_{30}B_{11}NO$, $M_r = 275.2$, monoclinic, space group $P2_1/n$, $a = 7.966(3)$, $b = 11.576(4)$, $c = 19.451(7)$ Å, $\beta = 94.58(1)°$, $V = 1788(1)$ Å^3, $T = 293$ K, $Z = 4$, $\rho_{calcd} = 1.022\ g\,cm^{-3}$, $2\theta_{max} = 50°$, $\mu(Mo_{K\alpha}) = 0.71073$ Å, absorption corrections applied by using SADABS,[18] relative transmission factors in the range 0.979–1.000. A total of 9443 reflections were collected and led to 3150 unique reflections, 3150 of which with $I > 2\sigma(I)$ were considered as observed, $R_1 = 0.072$, $wR_2(F^2) = 0.189$. The structures were solved by direct methods and refined by full-matrix least-squares techniques on F^2 by using the SHELXTL/PC package of crystallographic software.[19] For the noncentrosymmetric structure of **3**, the appropriate enantiomorph was chosen by refining Flack's parameter x toward zero.[20] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were geometrically fixed using the riding model. CCDC 699713, 699714, 699715 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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