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Remarkable cage deboronation and rearrangement of a *closo*-1,12-dicarbadodecaborane to form a neutral *nido*-7,9-dicarbaundecaborane†

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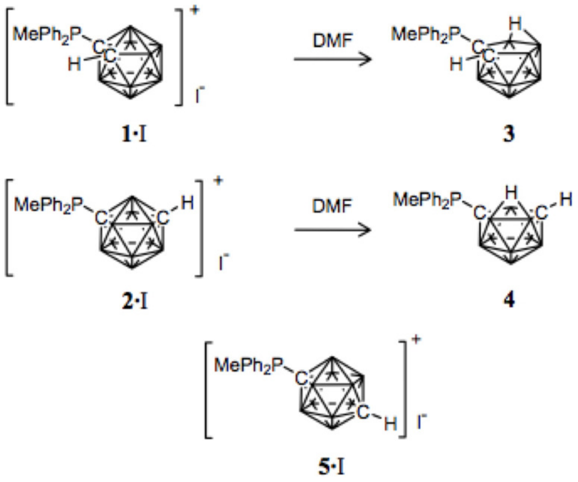
Deboronation and cage rearrangement of the *closo*-1,12-carborane salt [1,12-(PPh_2Me)$_2$-1,12-$C_2B_{10}H_{10}$]I_2 occurs in refluxing methanol to give the zwitterionic *nido*-7,9-carborane 7,9-(PPh_2Me)$_2$-7,9-$C_2B_9H_9$. Notably, deboronation and cage substitution of the isomeric *closo*-1,7-carborane salt [1,7-(PPh_2Me)$_2$-1,7-$C_2B_{10}H_{10}$]I_2 takes place in methanol to afford the salt [10-OMe-7,9-(PPh_2Me)$_2$-7,9-$C_2B_9H_9$]I.

The chemistry of the icosahedral carboranes is unique.[1,2] The carboranes are pseudo-aromatic polyhedral clusters consisting of boron, carbon and hydrogen atoms ($C_2B_{10}H_{12}$), similar in size to the three-dimensional sweep of a benzene ring. Carboranes exhibit chemical properties best characterized as neither borane- or benzene-like, and the intriguing chemical bonding of carboranes continues to be studied[3] five decades after these clusters were first reported.[4]

The three isomers of *closo*-carborane (1,2-, 1,7-, and 1,12-) have been used extensively in numerous compounds for potential application as boron delivery agents for boron neutron capture therapy (BNCT),[5] hydrophobic pharmacophores in medicinal chemistry,[6] and rigid frameworks for new materials,[7] including nanostructures[8] and molecular machines.[9] Such applications depend strongly upon the chemical stability and structural fidelity of the carborane cluster, which in turn depend upon conditions such as temperature and pH. It is well known that *closo*-1,2- and 1,7-carboranes undergo a selective deboronation reaction under basic conditions with bases like alkoxides,[10,11] fluorides[12] and amines[10,13] to yield the corresponding, anionic *nido*-7,8- and 7,9-[$C_2B_9H_{12}$]$^-$ isomers. In contrast, *closo*-1,12-carborane is robust to deboronation processes with many bases except hydroxides under extremely harsh conditions.[10,14] Herein we report a derivative of *closo*-1,12-carborane which in the *absence* of a base undergoes a rapid deboronation reaction and an unusual cluster rearrangement to afford a new and remarkably stable *nido*-carborane zwitterion.

When C-substituted carboranes contain electron-withdrawing groups at the cage carbon, the cage is more prone to deboronation. Thus, the carboranylphosphonium salts **1**·I and **2**·I were found to rapidly deboronate in DMF solution at room temperature forming the *nido*-7,8- and *nido*-7,9-carborane zwitterions **3** and **4**, respectively (Scheme 1).[15] By contrast, deboronation of the 1,12-isomer **5**·I under the same conditions was not observed.



Scheme 1

Deboronation reactions of *closo*-1,12-carboranes have not been reported for any of its substituted derivatives prior to our work. Indeed, two highly electron-withdrawing phosphonium groups instead of one at the cage carbon atoms of the icosahedral carboranes would more likely lead to deboronation. Deboronation processes were evident from changes in the NMR spectra of the diphosphonium salt [1,12-(PPh_2Me)$_2$-1,12-$C_2B_{10}H_{10}$]I_2, **6**·2I (Scheme 2) in polar protic and aprotic solvents such as CD_3OD, D_2O, d_7-DMF and d_6-DMSO when observed over a period of several hours at room temperature.[16] This degradation reaction involving the *closo*-1,12-carborane species **6**·2I is shown here as the first example of deboronation involving a *para*-carborane derivative.

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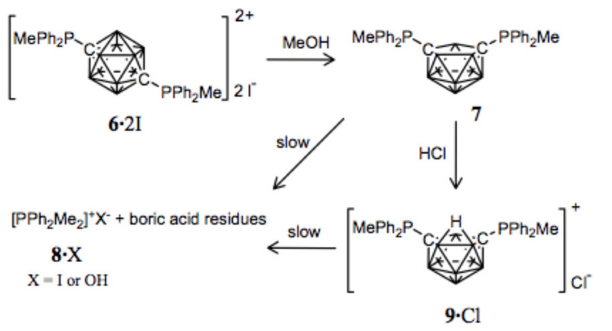


Scheme 2

A solution of **6**·2I in methanol was heated under reflux for three days and the insoluble yellow material that formed was collected by filtration. Analysis of this crude material by NMR spectroscopy and ESI-MS indicated a mixture of a carborane **7**, the phosphonium salt $[PPh_2Me_2]X$ **8**·X (X = I[17] or OH) and boric acid residues. The $^{11}B\{^1H\}$ NMR spectrum of the carborane **7** revealed a 2:3:2:1:1 peak intensity pattern and the $^{31}P\{^1H\}$ NMR spectrum contained a single peak at 27.6 ppm. These spectroscopic features are not consistent with the expected *nido*-2,9-C_2B_9 cluster which corresponds to a 2:2:2:2:1 boron peak pattern and two distinct phosphorus peaks on straightforward removal of one boron atom from the *para*-carborane **6**·2I.

The $^{11}B\{^1H\}$ NMR spectrum of the solid **7** showed peaks in the -12.9 to -20.8 ppm region in addition to one upfield peak at -46 ppm. The spectrum resembles the $^{11}B\{^1H\}$ NMR spectra of alkali metal salts of $[7,8\text{-}C_2B_9H_{11}]^{2-}$ and $[7,9\text{-}C_2B_9H_{11}]^{2-}$ where peaks between -17.2 and -26.4 ppm and single peaks between -41.8 and -48.8 ppm are observed.[18] The $^{11}B\{^1H\}$ NMR spectrum of **7** suggests a neutral species $(PPh_2Me)_2C_2B_9H_9$ with the cationic phosphonium groups attached to a formally *nido*-C_2B_9 dianion cluster.

The addition of HCl to **7** gave a salt **9**·Cl with observed ^{11}B NMR peaks clearly characteristic of a $[7,9\text{-}C_2B_9H_{12}]^-$ monoanion and not of a $[7,8\text{-}C_2B_9H_{12}]^-$ monoanion. Carborane **9** is therefore the $[7,9\text{-}(PPh_2Me)_2\text{-}7,9\text{-}C_2B_9H_{10}]^+$ cation and, by implication, **7** is $7,9\text{-}(PPh_2Me)_2\text{-}7,9\text{-}C_2B_9H_9$ on deprotonation but cage rearrangement may well occur to form the $7,8\text{-}(PPh_2Me)_2\text{-}7,8\text{-}C_2B_9H_9$ instead.

The molecular structure of **7** as the 7,9-isomer, $7,9\text{-}(PPh_2Me)_2\text{-}7,9\text{-}C_2B_9H_9$, was confirmed by an X-ray crystallography study on crystals grown from acetone solution (Figure 1). No counter-ion or a bridging hydrogen atom was located in the X-ray crystal structure of **7**. Comparison of the X-ray structure data for **4** and **7** reveals similar structural parameters in both cluster geometries except for a longer B10-B11 bond by 0.12 Å in **4** which is attributed to the bridging hydrogen present in **4**. The P–C bonds between 1.750(2) and 1.806(2) Å are considered as single bonds,[15,19] thus both **4** and **7** are viewed as zwitterions. Compound **7** is therefore, to our knowledge, the first $[7,9\text{-}C_2B_9H_{11}]^{2-}$ derivative to be structurally characterized.

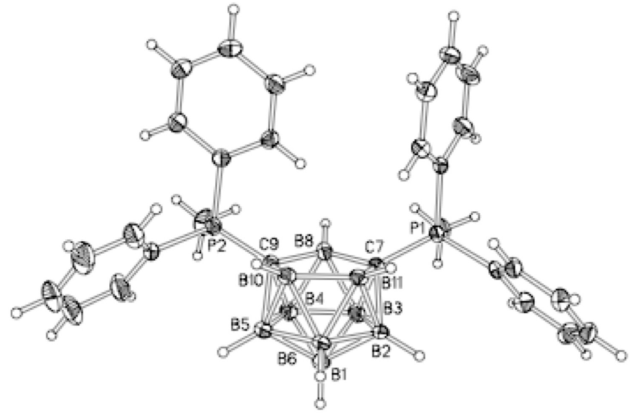
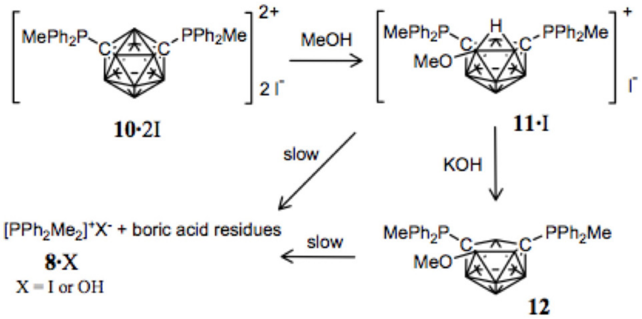


Figure 1. The molecular structure of neutral **7** in **7**·Me_2CO. The disordered acetone solvate molecule is omitted for clarity. Selected bond lengths in Å: C7-P1 1.765(2), C9-P2 1.750(2), C7-B8 1.620(3), C7-B11 1.673(3), C9-B8 1.628(3), C9-B10 1.667(3), B10-B11 1.713(4).

As *nido*-7,9-C_2B_9 clusters are usually obtained from 1,7-$C_2B_{10}H_{12}$ and its derivatives, the route to **7** from the deboronation of $[1,7\text{-}(PPh_2Me)_2\text{-}1,7\text{-}C_2B_{10}H_{10}]I_2$ **10**·2I with methanol was explored. Instead of **7**, a salt $[10\text{-}OMe\text{-}7,9\text{-}(PPh_2Me)_2\text{-}7,9\text{-}C_2B_9H_9]I$ **11**·I was isolated. The identity of the cation **11** was determined by detailed ^1H, $^{11}B\{^1H\}$, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopies on the basis of known NMR data of $[10\text{-}R\text{-}7,9\text{-}C_2B_9H_{11}]^-$ monoanions. Addition of KOH to **11**·I gave the neutral species, $10\text{-}OMe\text{-}7,9\text{-}(PPh_2Me)_2\text{-}7,9\text{-}C_2B_9H_8$ **12**, with the $^{11}B\{^1H\}$ NMR spectrum containing a peak at 7.6 ppm corresponding to the boron atom B10 with the methoxy group and the remaining peaks at similar shifts as carborane **7**. GIAO-NMR calculations on the optimised geometries for the *nido*-carboranes, **7**, **9**$^+$, **11**$^+$ and **12**, showed excellent agreement between observed and computed ^{11}B NMR peak shifts confirming their molecular geometries.



Scheme 3

The preference for the 7,9-C_2B_9 isomer instead of the expected 2,9-C_2B_9 product from the deboronation of **6**·2I suggests a facile rearrangement of the cage from the 2,9- isomer to the 7,9- isomer taking place. The isomer 7,9-$(PPh_2Me)_2$-7,9-$C_2B_9H_9$ **7** is calculated to be 31.8 kcal mol^{-1} more stable than the 2,9-$(PPh_2Me)_2$-2,9-$C_2B_9H_9$ isomer **A**. The cage rearrangement from **A** to **7** involves two intermediates, 1,7-$(PPh_2Me)_2$-1,7-$C_2B_9H_9$ **B** and 2,8-$(PPh_2Me)_2$-2,8-$C_2B_9H_9$ **C**, with the highest computed energy TS barrier at 47.0 kcal mol^{-1} corresponding to the transition state geometry from **A** *via* a cage carbon vertex flip (Figure 2). The route by cage rearrangement from the *para*-carborane **6** to *meta*-carborane **10** followed by deboronation with methanol is ruled out here as this would give the methoxy derivative **12** instead of **7**.

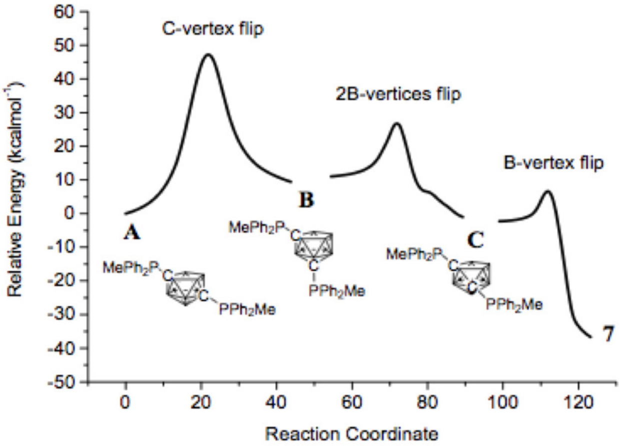


Figure 2. Cage rearrangement pathways from 2,9-$(PPh_2Me)_2$-2,9-$C_2B_9H_9$ isomer **A** to **7** with computed intrinsic reaction coordinate steps. See http://www.dur.ac.uk/m.a.fox/ioppolo.ppt for animations of the cage rearrangements.

All the *nido*-carboranes **7**, **9**$^+$, **11**$^+$ and **12** obtained here degrade further to boric acid derivatives and the phosphonium salt **8**·X. Thus, purification of these *nido*-carboranes is not possible for accurate elemental analyses. The degradation process of the entire cluster is typically found for *nido*-7,9-$[C_2B_9H_{12}]^-$ and related derivatives[15,16] unlike the much more stable *nido*-7,8-$[C_2B_9H_{12}]^-$ and related derivatives. One of the two methyl groups in **8**·X must be derived from the carborane C-atom following cleavage of all C_{cage}–B bonds which was confirmed by ^{13}C-labelling studies using [^{13}C]-MeI instead of standard MeI and [^{13}C]-MeOH instead of MeOH.

In conclusion, the first case of a deboronation and cluster rearrangement reaction involving a *closo*-1,12-dicarbadodecaborane to form a *nido*-7,9-dicarbaundecaborane is unequivocally demonstrated. This is the first example of a deboronation reaction involving a substituted *para*-carborane and suggests that deboronations of other *para*-carborane derivatives may, in general, form *nido*-7,9-dicarbaundecaboranes instead of *nido*-2,9-dicarbaundecaboranes. The deboronation-rearrangement pathway may be exploited from a starting *para*-carborane derivative if the target *nido*-7,9-C_2B_9 derivative cannot be obtained from a *meta*-carborane derivative due to the deboronation-substitution pathway as demonstrated here.

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