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-(PPh₂Me)₂-1,12-C₂B₁₀H₁₈]I₂ occurs in refluxing methanol to give the zwitterionic nido-7,9-carbornane 7,9-[PPh₂Me]₂-7,9-C₂B₉H₉. Notably, deboronation and cage substitution of the isomeric closo-1,7-carborane salt [1,7-(PPh₂Me)₂-1,7-C₂B₁₀H₁₈]I₂ takes place in methanol to afford the salt [10-OMe-7,9-(PPh₂Me)₂-7,9-C₂B₉H₉]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 (C₆B₆H₁₄), similar in size to the three-dimensional sweep of a benzene ring. Carboranes exhibit chemical properties best characterized as neither borane- nor benzene-like, and the intriguing chemical bonding of carboranes continues to be studied five decades after these clusters were first reported.³

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),⁴ hydrophobic pharmacophores in medicinal chemistry,⁵ and rigid frameworks for new materials,⁶ including nanostructures⁷ and molecular machines.⁸ 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,⁹,¹⁰ fluorides¹¹ and amines¹²,¹³ to yield the corresponding, anionic nido-7,8- and 7,9-[C₂B₉H₁₈]⁻ 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.

† Electronic Supplementary Information (ESI) available: Synthesis and characterisation details,¹⁵ ¹³C labelling studies, crystallographic data and computational details. See DOI: 10.1039/b000000x/s}

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.

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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, the phosphonium salt [PPh₂Me₂]X 8X (X = I⁻ or OH) and boric acid residues. The 11B[¹H] NMR spectrum of the carborane 7 revealed a 2:2:2:2:1:1 peak intensity pattern and the 31P[¹H] NMR spectrum contained a single peak at 27.6 ppm. These spectroscopic features are not consistent with the expected nido-2,9-C₃B₉ 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 11B[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 11B[¹H] NMR spectra of alkali metal salts of [7,8-C₂B₉H₁₁]⁺ and [7,9-C₂B₉H₁₁]⁻ where peaks between -17.2 and -26.4 ppm and single peaks between -41.8 and -48.8 ppm are observed. The 11B[¹H] NMR spectrum of 7 suggests a neutral species (PPh₂Me₂)C₂B₉H₄ with the cationic phosphonium groups attached to a formally nido-C₂B₉ dianion cluster.

The addition of HCl to 7 gave a salt 9-Cl with observed 11B NMR peaks clearly characteristic of a [7,9-C₂B₉H₁₂]⁺ monoanion and not of a [7,8-C₂B₉H₁₁]⁻ monoanion. Carborane 9 is therefore the [7,9-(PPh₂Me₂)₂-7,9-C₂B₉H₁₀]⁺ cation and, by implication, 7 is 7,9-(PPh₂Me₂)₂-7,9-C₂B₉H₄ on deprotonation but cage rearrangement may well occur to form the 7,8-(PPh₂Me₂)₂-7,8-C₂B₉H₄ instead.

The molecular structure of 7 as the 7,9-isomer, 7,9-(PPh₂Me₂)₂-7,9-C₂B₉H₄, 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; thus both 4 and 7 are viewed as zwitterions. Compound 7 is therefore, to our knowledge, the first [7,9-C₂B₉H₁₁]⁻ derivative to be structurally characterized.

Figure 1. The molecular structure of neutral 7 in 7·Me₂CO. 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-C₃B₉ clusters are usually obtained from 1,7-C₃B₁₀H₁₂ and its derivatives, the route to 7 from the deboronation of [1,7-(PPh₂Me₂)₁-1,7-C₃B₁₀H₁₀]I 10-2I with methanol was explored. Instead of 7, a salt [10-OMe-7,9-(PPh₂Me₂)₂-7,9-C₂B₉H₆]I 11-1 was isolated. The identity of the cation 11 was determined by detailed ¹H, ¹¹B[¹H], ¹³C[¹H] and ³¹P[¹H] NMR spectroscopies on the basis of known NMR data of [10-R-7,9-C₃B₉H₁₁] monoanions. Addition of KOH to 11-I gave the neutral species, 10-OMe-7,9-(PPh₂Me₂)₂-7,9-C₂B₉H₆ 12, with the ¹¹B[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 ¹¹B NMR peak shifts confirming their molecular geometries.

Scheme 3

As 11-1 was isolated. The identity of the cation 11 was determined by detailed ¹H, ¹¹B[¹H], ¹³C[¹H] and ³¹P[¹H] NMR spectroscopies on the basis of known NMR data of [10-R-7,9-C₃B₉H₁₁] monoanions. Addition of KOH to 11-I gave the neutral species, 10-OMe-7,9-(PPh₂Me₂)₂-7,9-C₂B₉H₆ 12, with the ¹¹B[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 ¹¹B NMR peak shifts confirming their molecular geometries.
The preference for the 7,9-C$_2$B$_9$ isomer instead of the expected 2,9-C$_2$B$_9$ product from the deboronation of 6-21 suggests a facile rearrangement of the cage from the 2,9-isomer to the 7,9-isomer taking place. The isomer 7,9-(PPh$_2$Me)$_2$-7,9-C$_2$B$_9$H$_8$ is calculated to be 31.8 kcal mol$^{-1}$ more stable than the 2,9-(PPh$_2$Me)$_2$-9,2-C$_2$B$_9$H$_8$ isomer A. The cage rearrangement from A to 7 involves two intermediates, 1,7-(PPh$_2$Me)$_2$-1,7-C$_2$B$_9$H$_8$ B and 2,8-(PPh$_2$Me)$_2$-2,8-C$_2$B$_9$H$_8$ 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](https://example.com/figure2.png)

**Figure 2.** Cage rearrangement pathways from 2,9-(PPh$_2$Me)$_2$-2,9-C$_2$B$_9$H$_8$ isomer A to 7 with computed intrinsic reaction coordinate steps. See http://www.dur.ac.uk/m.a.fox/oppolpo.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$_2$B$_9$H$_8$ and related derivatives, unlike the much more stable nido-7,8-[C$_2$B$_9$H$_8$] 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 close-1,12-dicarbaborodecaborane to form a nido-7,9-dicarbaborodecaborane 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-dicarbaborodecaboranes instead of nido-2,9-dicarbaborodecaboranes. The deboronation-rearrangement pathway may be exploited from a starting para-carborane derivative if the target nido-7,9-C$_2$B$_9$ derivative cannot be obtained from a meta-carborane derivative due to the deboronation-substitution pathway as demonstrated here.

### Notes and references