A simple entry into *nido*- C_2B_{10} clusters: HCl promoted cleavage of the C–C bond in *ortho*-carboranyl diphosphines[†] \ddagger §

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Treatment of the diphosphines *ortho*- $B_{10}H_{10}C(P^{t}Bu_{2})C(PR_{2})$ (R = Et, Cy, Ph) with HCl gives the zwitterionic, *nido*-12vertex species $B_{10}H_{10}C(PH^{t}Bu_{2})C(PClR_{2})$; these reactions are reversed by the addition of NEt₃.

The high thermodynamic stability of *closo*-12-vertex clusters such as *closo*-1,2-dicarbadodecaborane(12) (commonly known as *ortho*-carborane) is an impediment to the synthesis of supraicosahedral clusters¹ although alkali metals do reduce *ortho*carborane to the *nido*-anion $[C_2B_{10}H_{12}]^{2-}$ which provides a gateway to 13-vertex clusters and beyond.² Here we report a very mild and reversible cage opening reaction of *ortho*-carboranyl diphosphines.

The bulky monophosphine **1** was prepared from *ortho*carborane by the route shown in Scheme 1; no *ortho*- $B_{10}H_{10}C_2(P^tBu_2)_2$ was observed presumably because of the steric inhibition to disubstitution by the bulky 'Bu₂P substituent in **1**. Deprotonation of **1** with "BuLi followed by addition of ClPEt₂ gave the unsymmetrical diphosphine **2**. The ³¹P NMR spectrum of **2** in CDCl₃ shows a characteristic AX pattern with a large ³*J*(PP) of 99 Hz.¶



It was noted that the ³¹P NMR spectrum of a sample of **2** that had been standing in CDCl₃ for 28 d was very different from that of a freshly prepared solution. The AX pattern for **2** was absent and had been replaced by two singlets, one of which had an unusual chemical shift of 122 ppm and the other at 28 ppm showed a large J(PH) of 435 Hz, consistent with the presence of a P–H bond. Crystals of the new product **3** grew from its CDCl₃ solution and its structure was determined by X-ray crystallography (Fig. 1).

The reaction between 2 and CDCl₃ is formally the addition of DCl to the two phosphine groups with concomitant cluster opening *via* C–C cleavage. A more rational synthesis of 3 is shown in eqn (1);the addition of one equivalent of ethereal HCl to 2



Fig. 1 The molecular structure of **3**. Important molecular dimensions (Å) include: P1–C1 1.767(4), C3–P1 1.859(5), C7–P1 1.854(4), P2–C2 1.701(5), C13–P2 1.767(6), C11–P2 1.802(5), C11–P2 2.041(2), C1 ··· C2 2.851(9).



gave 3 rapidly and quantitatively. This reaction is readily and quantitatively reversed by treatment of 3 with NEt₃ (eqn (1)). It is notable that a single regioisomer of 3 is formed in this reaction, *i.e.* the PHEt₂/PCl⁺Bu₂ isomer was not observed.

A reaction outline which accounts for the formation of 3 is shown in Scheme 2. The ylide structure 3y is a resonance form of the zwitterionic structure 3z which has the charges on the two phosphonium centres balanced by the dianionic charge on the carborane cage.



From the zwitterion formulation 3z, a 12-vertex, *nido* structure is predicted on the basis of the 14 cluster valence electron pairs.³ However the 13-vertex polyhedron on which **3** is based is not a C_{2v} -docosahedron,⁴ a henicosahedron⁵ nor an edge-bridged *nido*-icosahedral fragment.⁶ Intriguingly, the structure is formally derived from an unprecedented C_2 -symmetric docosahedron (Scheme 3). The additional vertex in the parent deltahedron is connected to 6 other vertices; two of these are 6-connected BH

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[†] This Communication is dedicated to Professor Ken Wade on the occasion of his 75th birthday.

[‡] The HTML version of this article has been enhanced with colour images. § CCDC reference numbers 671421–671423. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b719404h



vertices leading to a highly unusual situation in which there are 3 adjacent 6-connected vertices. There are also two 4-connected CR vertices and 8 conventional 5-connected BH vertices completing the cage. It may be noted that the C_2 symmetry of both the parent and *nido* structures renders them chiral even in a situation in which the CR groups are equivalent.

The conversion of **2** to **3** is the first example of a *closo*to *nido*-carborane transformation effected by manipulation of exopolyhedral substituents. In effect, the addition of HCl has simultaneously oxidised the P centres and reduced the carborane cage. To explore the generality of this reaction, the unsymmetrical diphosphines **4** and **5** (made from **1** by a modification of the route shown in Scheme 1) and symmetrical diphosphines **6** and **7** were treated with HCl in Et_2O and the products examined by ³¹P NMR spectroscopy.



No reaction was observed between HCl and 7 but with 4–6, it was clear that products analogous to 3 were regioselectively formed since a single product was observed in each case. Thus reaction between 4 and ethereal HCl (1 equiv.) gave a species with ³¹P parameters (singlet at 125 ppm and doublet at 39 ppm, J(PH) 447 Hz) similar to those for 3. The reaction of 5 required a 2-fold excess of HCl to give a cage-opened product (singlet at 121 ppm and doublet at 21 ppm, J(PH) 476 Hz). The symmetrical diphosphine 6 required a 10-fold excess of HCl to give the cageopened product (singlet at 102 ppm and doublet at 34 ppm, J(PH) 446 Hz) but only 75% conversion of 6 was observed. From these experiments, HCl promoted cage-opening occurs readily with electron-rich diphosphinocarboranes to give the regioisomer expected from a mechanism involving protonation of the more electron-rich phosphine group (Scheme 2).

The reactions between **2** or **4**–7 and HCl can be described by the equilibria shown in eqn (2). With **2** and **4**, the equilibria lie fully to



the side of the *nido*-cage, with **7**, fully to the side of the *closo*-cage and with **5** and **6**, between these extremes.

The propensity of diphosphines **2** and **4–6** to undergo cageopening by C–C rupture may be a consequence of two effects: (i) the relief of steric congestion caused by the bulky P-substituents and (ii) the C–C weakening which has been calculated to be promoted by electron-rich C-substituents in o-C₂R₂B₁₀H₁₀.⁷ Consistent with this conjecture, in the structure of **4** (Fig. 2), the C–C distance of 1.7642(16) is at the high end of the range of C–C bonds in *ortho*-carboranes. A search of the Cambridge Structural Database (Version 5.29, November 2007) reveals that the mean



Fig. 2 The molecular structure of **4**. Important molecular dimensions (Å) include: P1–C1 1.8891(11), P1–C3 1.8704(12), P1–C9 1.8580(11), P2–C2 1.9162(11), P2–C15 1.9075(12), P2–C19 1.9195(12), C1–C2 1.7642(16).

bond length of C–C bonds found in *closo*-12-vertex C_2B_{10} cages is 1.686 Å (with sample standard deviation 0.050 Å).

During the synthesis of 2 by the route shown in Scheme 1, a minor product crystallised from the reaction mixture and its crystal structure (Fig. 3) revealed it to be compound 8 with a *nido*carborane cage analogous to 3 and therefore can be represented by the zwitterionic formulation 8z. The elements of BuH have formally added to the two P groups of 2 in the formation of 8 (though the origin of 8 is possibly a halobutane impurity in the commercial BuLi solution). Regardless of the mechanism of formation of 8, its crystal structure establishes that the unusual *nido*-12-vertex polyhedron of 3 is not unique.



Fig. 3 The molecular structure of 8. Important molecular dimensions (Å) include: C1–P1 1.763(3), C3–P1 1.868(3), C7–P1 1.874(3), C11–P1 1.822(3), C2–P2A 1.740(3), C15–P2A 1.805(3), C17–P2A 1.783(3), C1… C2 2.892(5).



In conclusion, a surprisingly easy route to neutral, *nido*-12-vertex carboranes has been discovered which might prove to be useful *en route* to higher nuclearity carboranes.

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Notes and references

¶ Unless otherwise stated, all compounds reported here have been characterised by a combination of ¹H, ¹³C and ³¹P NMR spectroscopy.³¹P NMR data (CDCl₃): δ **1**, 94.8; **2**, 71.6 (d, *J*(PP) 99 Hz, P⁴Bu₂), 1.4 (d, *J*(PP) 99 Hz, PEt₂): **4**, 70.3 (d, *J*(PP) 87 Hz, P⁴Bu₂), 23.4 (d, *J*(PP) 87 Hz, PCy₂); **5**, 71.0 (d, *J*(PP) 97 Hz, P⁴Bu₂), 3.0 (d, *J*(PP) 97 Hz, PPh₂); **6**, 27.0 Crystal data: **3**: Cl₄H₃₉Bl₁₀ClP₂, *M* = 412.94, monoclinic, *a* = 17.625(4), *b* = 8.5424(17), *c* = 17.324(4) Å, β = 113.60(3)°, *V* = 2390.0(11) Å³, *T* = 100 K, space group *P*2₁/*c*, *Z* = 4, μ = 0.293 mm⁻¹, *R*_{int} = 0.1403 (for 19691 measured reflections), *R*₁ = 0.0717 [for 2388 unique reflections with >2 σ (*I*)], *wR*₂ = 0.1794 (for all 3746 unique reflections); **4**: C₂₂H₅₀Bl₁₀P₂, *M* = 484.66, monoclinic, *a* = 9.936(2), *b* = 17.900(4), *c* = 16.742(3) Å, β = 106.23(3)°, *V* = 2859.0(10) Å³, *T* = 100 K, space group *P*2₁/*c*, *Z* = 4, μ = 0.184 (mam⁻¹, *R*_{int} = 0.0384 (for 31046 measured reflections), *R*₁ = 0.0349 [for 5875 unique reflections with *I* >2 σ (*I*)], *wR*₂ = 0.1085 (for all 6552 unique reflections); **8**: Cl₁₈H₄₈Bl₁₀O₀-12P₂, *M* = 436.52, triclinic, *a* = 8.964(3), *b* = 10.496(3), *c* = 15.234(4) Å, *a* = 70.82(2), β = 80.68(2), γ = 89.78(3)°, *V* = 1334.1(7) Å³, *T* = 100 K, space group *P*1, *Z* = 2, μ =

1.478 mm⁻¹, $R_{\text{int}} = 0.0584$ (for 10218 measured reflections), $R_1 = 0.0678$ [for 3645 unique reflections with $I > 2\sigma(I)$], $wR_2 = 0.1892$ (for all 4529 unique reflections).

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