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Deboronation of *ortho*-carborane by an iminophosphorane: crystal structures of the novel carborane adduct *nido*-$C_2B_{10}H_{12}\cdot HNP(NMe_2)_3$ and the borenium salt $[(Me_2N)_3PNHBNP(NMe_2)_3]_2O^{2+}(C_2B_9H_{12}^-)_2$

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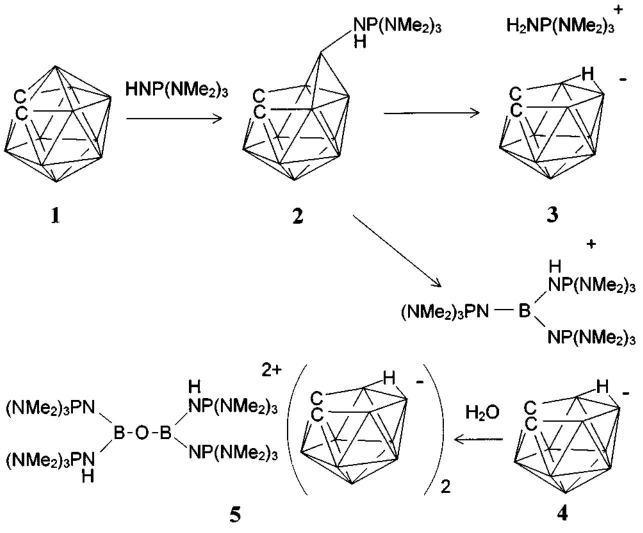
The structures of the adduct *nido*-$C_2B_{10}H_{12}\cdot HNP(NMe_2)_3$ and the borenium salt $[(Me_2N)_3PNHBNP(NMe_2)_3]_2O^{2+}(C_2B_9H_{12}^-)_2$, both obtained from 1,2-$C_2B_{10}H_{12}$ and $HNP(NMe_2)_3$, were determined by X-ray crystallography; the adduct represents the first structurally determined carborane of its type, a possible intermediate in the well known conversion of *closo*-1,2-$C_2B_{10}H_{12}$ into the *nido*-7,8-$C_2B_9H_{12}^-$ anion by bases.

The *closo*-icosahedral carboranes $C_2B_{10}H_{12}$ have an extensive (3-dimensional aromatic) chemistry with implications for neutron scavenging, for materials (thermally stable or conducting or otherwise electroactive oligomers and polymers), for metal extraction, supramolecular chemistry and catalysis.[1] Remarkably resilient to heat and oxidising agents, they are known to have one very important degradation reaction, being susceptible to nucleophilic attack by a select few powerful Lewis bases (*e.g.* alkoxides, fluoride, amines)[2–5] which can remove one of their BH units, formally as BH^{2+}, leaving *nido*-shaped $C_2B_9H_{11}^{2-}$ (or $C_2B_9H_{12}^-$) anionic residues that can strongly bind metal ions to their open C_2B_3 faces,[6] useful for metal-extraction and catalytic applications. However, although such base deboronations have been known for 35 years, details of their mechanisms have remained elusive. Here, we describe work that sheds light on the mechanism, reporting the X-ray structural characterization of an adduct $C_2B_{10}H_{12}\cdot HNP(NMe_2)_3$ **2**, formed in the nucleophilic attack by the new deboronating base $HNP(NMe_2)_3$ on *ortho* carborane, 1,2-$C_2B_{10}H_{12}$ **1**. We also show that the hitherto unknown monoboron cation $(Me_2N)_3PNHB[NP(NMe_2)_3]_2^+$ is a later product of the same reaction, and that the dication $[(Me_2N)_3PNHBNP(NMe_2)_3]_2O^{2+}$ is an unexpected product if traces of water are present.

Iminotris(dimethylamino)phosphorane $HNP(NMe_2)_3$ is very effective in the conversion of *closo*-$C_2B_{10}H_{12}$ **1** into *nido*-7,8-$C_2B_9H_{12}^-$. Several NMR-scale reactions of carborane **1** with dry $HNP(NMe_2)_3$ in anhydrous deuterated toluene at varying temperatures (−20 to 20 °C), ratios (carborane : base 1 : 10 to 10 : 1) and concentrations (0.1 to 0.01 M) were monitored by ^{11}B NMR spectroscopy. We found that boron peaks corresponding to a carborane intermediate were best observed using a 1 : 1 ratio mixture of low concentration (0.01 M) at room temperature after only two minutes reaction time. The peaks observed arising from the intermediate at 34.8 (br), −18.2 (d) and −27.8 (d) ppm accounted for only 2% of the total boron peak intensities (the major carborane is **1** with peaks at −2.0, −8.7, −13.2 and −14.4 ppm at this stage) and disappeared rapidly to peaks corresponding to the carborane anion, $C_2B_9H_{12}^-$.[4] This anion was observed by multinuclear NMR spectroscopy accompanied by a 1 : 1 mixture of the cation $H_2NP(NMe_2)_3^+$ **3** and the novel protonated tris(imino)borane $(Me_2N)_3PNHB[NP(NMe_2)_3]_2^+$ **4** respectively (Scheme 1).†



Scheme 1

A preparative scale reaction was carried out to allow structural characterization of the products. Under nitrogen, slow addition of dry $HNP(NMe_2)_3$ (1.78 g, 10 mmol) in anhydrous toluene (15 ml) to a solution of **1** (1.44 g; 10 mmol) in toluene (15 ml) resulted in the formation of a crystalline product (*ca.* 0.03 g) overnight. Although this product was identified by boron NMR spectroscopy as a mixture of **1** and 7,8-$C_2B_9H_{12}^-$ in solution, an X-ray structural determination on a crystal selected from the material revealed a carborane adduct $C_2B_{10}H_{12}\cdot HNP(NMe_2)_3$ **2** (Fig. 1).‡ The volume of the decanted solution was halved by solvent removal *in vacuo* and, after standing for a week at room temperature, the crystals formed were identified by NMR as the salt $H_2NP(NMe_2)_3^+$ (7,8-$C_2B_9H_{12})^-$ **3** (0.32 g) and confirmed by an X-ray structural determination.‡ The mother liquor was cooled to −20 °C to yield a white solid identified by NMR spectroscopy as the protonated tris(imino)borane salt **4** (0.43 g).

Calculated (GIAO HF/6-31G*) boron NMR shifts§ generated from the X-ray geometry of the carborane adduct **2** show good agreement with the intermediate observed in the NMR-scale reactions once masking of certain peaks by the starting carborane **1** is taken into account. This suggests that adduct **2** is the first structurally characterized intermediate in the well known conversion of *closo*-1,2-$C_2B_{10}H_{12}$ **1** into *nido*-7,8-$C_2B_9H_{12}^-$. As revealed by the X-ray structure of **2**, the first step of the *closo*–*nido* conversion is the attachment of the base to the most positively charged boron atom near the two neighbouring carbon atoms which pivots about B(10), cleaving the two B–C bonds and stretching the two B–B bonds to B(9) and B(11). The structure of adduct **2** may be contrasted with the hydrogen-bonded structures of $C_2B_{10}H_{12}\cdot OP(NMe_2)_3$ and $C_2B_{10}Cl_{10}H_2\cdot OSMe_2$ adducts.[7]

As expected from simple skeletal-electron counting rules for a 12-vertex 28 skeletal electron *nido* geometry, the cluster framework of carborane **2** is viewed as a 13-vertex *closo*-deltahedron with a 5-coordinate vertex removed.[8] Positions of

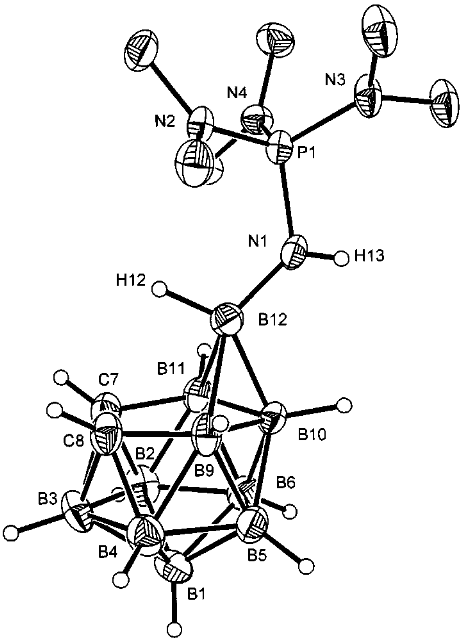


Fig. 1 Molecular structure of adduct **2** (50% ellipsoids; methyl hydrogens omitted for clarity). Important interatomic distances (Å) are: P(1)–N(1) 1.651(3), N(1)–H(13) 0.75(4), N(1)–B(12) 1.506(6), B(12)–H(12) 1.18(4), C(7)–C(8) 1.530(6), C(7)–B(11) 1.654(6), C(8)–B(9) 1.651(6), B(12)–B(10) 1.761(6), B(12)–B(9) 2.099(6), B(12)–B(11) 2.091(6), B(10)–B(9) 1.779(6), B(10)–B(11) 1.802(6). Selected angle (°): P–N(1)–B(12) 127.3(3).

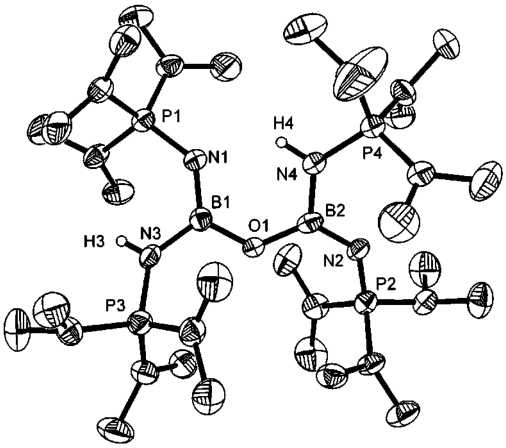


Fig. 2 Molecular structure of cation in **5** (50% ellipsoids; methyl hydrogens omitted for clarity). Important interatomic distances (Å) are: B(1)–N(1) 1.402(6), B(1)–N(3) 1.463(5), B(1)–O(1) 1.373(5), B(2)–N(2) 1.389(5), B(2)–N(4) 1.464(6), B(2)–O(1) 1.416(5), N(1)–P(1) 1.555(3), N(2)–P(2) 1.554(3), N(3)–P(3) 1.630(4), N(4)–P(4) 1.614(3).

the cage carbons in the carborane adduct **2** were conclusively determined by an *ab initio* optimization of a model of $C_2B_{10}H_{12}\cdot HNP(NH_2)_3$ at the HF/6-31G* level of theory where both theoretical and experimental geometries are nearly identical. These carbon placements are supported by a similar cage geometry observed in the *nido*-C_2B_{10} moiety of the two-cage anion $[PhCB_{10}H_{10}CB_{10}H_{10}C_2HPh]^-$ structurally characterized by X-ray crystallography.[9]

During attempts to obtain suitable crystals of the salt **4** containing the cation $(Me_2N)_3PNHB[NP(NMe_2)_3]_2{}^+$ from toluene, a single crystal was characterized by an X-ray study‡ as a salt **5** containing the dication $[(Me_2N)_3PNHBNP(NMe_2)_3]_2O^{2+}$ (Fig. 2). The oxygen atom apparently arose from inadequately dried toluene. According to bond order calculations¶ (AM1) carried out on the structure of the dication [RN(RNH)BOB(NHR)(NR)]$^{2+}$ there is strong BN π bonding within each RN(RNH)B unit to the imino (NR) residue, much less to the imine (RNH) residue, though evidently sufficient to ensure planarity of the $(PN)_2BO$ unit.

Our work suggests that the formation of an adduct $C_2B_{10}H_{12}\cdot L$, with an expected *nido*-structure, is the first step in the deboronation of *ortho*-carborane by $HNP(NMe_2)_3$ and presumably other Lewis bases L. Further studies, both experimental and theoretical, will be needed to clarify the later steps.

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Notes and references

† NMR data for cation of **3**: δ_P (d_8-toluene; standard 85% H_3PO_4) 43.2, δ_H 2.33 [J(PH) 10 Hz, CH_3] δ_C 36.7 [J(PC) 18 Hz, CH_3]; for cation of **4**: δ_P 40.2 (br, 1P), 23.6 (br, 2P), δ_B (standard $BF_3\cdot Et_2O$), 22.3 (s), δ_H 2.46 [^3J(PH) 10 Hz, 18H, CH_3], 2.43 [J(PH) 10 Hz, 36H, CH_3], δ_C 37.1 [J(PC) 18 Hz], 36.8 [J(PC) 18 Hz].

‡ *Crystal data* for **2**: $C_8H_{31}B_{10}N_4P$, M = 322.44, orthorhombic, space group *Pbca* (no. 61), a = 10.799(2), b = 17.252(4), c = 20.326(4) Å, U = 3786.9(13) Å^3, Z = 8, D_c = 1.131 g cm^{-3}, μ = 0.141 mm^{-1}, F(000) = 1376, T = 153(2) K, 25525 reflections (4337 unique), $2\theta \leqslant 55°$, R_1 = 0.077 (2221 data $I > 2\sigma(I)$), $wR(F^2)$ = 0.187, GOF (obs) = 1.053. For **3**: $C_8H_{32}B_9N_4P$, M = 312.64, monoclinic, space group $P2_1/n$ (no. 14), a = 11.580(2), b = 13.182(3), c = 12.385(2) Å, β = 91.88(5)°, U = 1889.5(6) Å^3, Z = 4, D_c = 1.099 g cm^{-3}, μ = 0.140 mm^{-1}, F(000) = 672, T = 150(2) K, 14804 reflections (4992 unique), $2\theta \leqslant 58°$, R_1 = 0.0435 (4283 data $I > 2\sigma(I)$), $wR(F^2)$ = 0.118, GOF(obs) = 1.085. All NMe_2 groups of the cation are disordered. For **5**: $C_{28}H_{98}B_{20}N_{16}P_4O$, M = 1015.30, orthorhombic, space group $P2_12_12_1$ (no. 19), a = 14.105(3), b = 16.529(3), c = 25.563(5) Å, U = 5960(2) Å^3, Z = 4, D_c = 1.132 g cm^{-3}, μ = 0.168 mm^{-1}, F(000) = 2184, T = 150(2) K, 44070 reflections (16579 unique), $2\theta \leqslant 61°$, R_1 = 0.062 (5792 data $I > 2\sigma(I)$), $wR(F^2)$ = 0.138, GOF (obs) = 0.893. The absolute configuration was determined; Flack parameter −0.04(9). CCDC 182/1339. See http://www.rsc.org/suppdata/cc/1999/1649/ for crystallographic files in .cif format.

§ Calculated (GIAO HF/6-31G*) ^{11}B NMR data for **2**: δ 35.7 (B12), −6.3 (B5,6), −6.6 (B2,4), −13.9 (B3), −15.4 (B9,11), −18.3 (B10), −24.0 (B1).

¶ Calculated (AM1) bond orders for **5** (π bond order in parentheses): B(1)–O(1) 1.029 (0.207), B(1)–N(1) 1.311 (0.441), B(1)–N(3) 0.829 (0.086), B(2)–O(1) 0.932 (0.152), B(2)–N(4) 0.920 (0.129), B(2)–N(2) 1.317 (0.444).

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