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Proton Mediated Partial Degradation of *Closo*-dicarbaboranes

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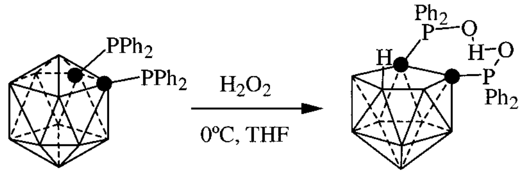
The *o*-carborane, the most intensively studied heteroborane, has an icosahedral structure and possesses tridimensional aromatic character.[1] While typical organic aromatic compounds are characterized by undergoing substitution rather than addition, thus preserving the original backbone structure, this does not take place with *o*-carborane, which upon nucleophilic attack loses B(3) or B(6) to yield the anion $[7,8\text{-}C_2B_9H_{12}]^-$.[2] As a consequence, the original *o*-carborane structure is not retained, which is in marked contrast with conventional aromatic compounds. The $[7,8\text{-}C_2B_9H_{12}]^-$ anion has a C_2B_3 pentagonal face made, which resembles the cyclopentadienyl anion in its coordinating capacity. We have proven earlier that anionic ligands incorporating the fragment $[7,8\text{-}C_2B_9H_{10}]^-$ can be easily produced from the closo precursors upon reaction with a transition metal ion. The necessary requirement for the reaction to take place is that the closo species incorporate coordinating elements, S or P, on the cluster carbon atoms.[3] In addition, this partial degradation was observed only with chelating closo derivatives.

In this paper we demonstrate for the first time that, given the necessary chemical and geometrical arrangements to produce proton chelation, the proton can also induce conversion of the *closo*-C_2B_{10} to the *nido*-C_2B_9 species. For this purpose, we have used an *o*-carborane C-substituted with H^+ scavenger elements, e.g., oxygen. The $1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ closo species[4] (**1**) was adequate as it is a chelating agent that can be oxidized to the corresponding phosphine oxide. Hydrogen peroxide, H_2O_2, recently[5] used to produce *closo*-$[B_{12}(OH)_{12}]^{2-}$, was a suitable oxidizing agent and a source of H^+. Thus it was expected that upon oxidation of the phosphorus atoms, and the possibility to chelate the proton, the closo cluster would progress to the anionic aromatic C_2B_9 cluster liberating one boron atom and overall producing a neutral species. Indeed this is what happened. In a typical experiment 5.56 mL (0.51 mmol) of a 0.1 M solution of H_2O_2 was added to a flask containing $1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ (**1**) (0.1 g, 0.20 mmol) in THF at 0 °C. After stirring for 24 h, $H[7,8\text{-}(OPPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]$, H[**2**], was formed.[6] The reaction is schematically represented in Scheme 1.

Scheme 1. Preparation of H[**2**] by Treatment of $1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ with H_2O_2



The nido nature of the cluster was clearly demonstrated by the ^1H NMR apical proton resonance at δ −2.01, and by the 2:2:1:2:1:1 ^{11}B NMR pattern observed in the range δ −5.6/−33.9 typical for *nido*-C_2B_9 derivatives. The only ^{31}P NMR resonance at δ 47.08 was in agreement with the proposed structure. Furthermore its chemical shift was in agreement with the expected chemical shift for oxidized phosphines.[7]

To ensure that H_2O_2 was the sole agent causing the closo to nido conversion, an alternative sequential process was developed, as schematically indicated in Scheme 2. Oxidation of $[NMe_4][7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]$, $[NMe_4]$[**3**],[8] with H_2O_2 was performed in acetone at 0 °C to yield after stirring for 4 h a white solid that corresponds to $[NMe_4][7,8\text{-}(OPPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]$, $[NMe_4]$[**2**].[9] Extra addition of $[NMe_4]Cl$ increased the yield. Thorough acidification of $[NMe_4]$[**2**] in CH_2Cl_2 with HCl gas yielded H[**2**] after previous separation of $[NMe_4]Cl$.[6] Compound $[NMe_4]$[**2**] was characterized by ^1H and ^{11}B NMR along with chemical analyses.[10] Compounds H[**2**] obtained by both procedures, directly from **1** and from $[NMe_4]$[**3**], were identical according to the spectroscopic data.[7]

Notwithstanding these results, the additional H^+ resonance could not be identified in the ^1H NMR spectra of H[**2**]. To get a

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(6) H[**2**], method A: To a solution of $1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ (0.1 g, 0.20 mmol) (**1**) in THF at 0 °C was added 5.56 mL (0.51 mmol) of a solution of 0.1 M H_2O_2. The mixture was stirred for 24 h, and a precipitate was formed. The solid was filtered off, washed with water, and dried in vacuo. Compound H[**2**] was obtained (yield: 94%). H[**2**], method B: A solution of $[NMe_4][7,8\text{-}(OPPh_2)_2\text{-}7,8\text{-}C_2B_{10}H_{10}]$, $[NMe_4]$[**2**], (1 g, 1.64 mmol) in CH_2Cl_2 (50 mL) was bubbled with a HCl stream for 15 min. A precipitate of $[NMe_4]Cl$ was separated, and the solution was evaporated in vacuo. A white solid was obtained (yield: 97.7%).

(7) Selected spectroscopic and analytical data for H[**2**]: FTIR (KBr, cm^{-1}) ν = 3058, 3012 (C_{ar}−H), 2525 (B−H); $^1H\{^{11}B\}$ NMR (300.13 MHz, $CDCl_3$, 25 °C, TMS) δ = −2.01 (br s, 1 H, B−H−B), 7.22−7.97 (m, 20 H, C_6H_5); ^{11}B NMR (96.29 MHz, $CDCl_3$, 25 °C, $Et_2O{\cdot}BF_3$) δ = −5.6 (d, 2 B, ^1J(B,H) = 128 Hz), −8.7 (d, 2 B, ^1J(B,H) = 133 Hz), −11.9 (1 B), 16.8 (2 B), −30.2 (d, 1 B, ^1J(B,H) = 123 Hz), −33.9 (d, 1 B, ^1J(B,H) = −147 Hz); $^{31}P\{^1H\}$ NMR (121.48 MHz, $CDCl_3$, 25 °C, 85% H_3PO_4) δ = 47.08 (s); $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 25 °C, TMS) δ = 128.49 (d, ^1J(P,C) = 42 Hz), 132.35 (d, ^1J(P,C) = 21 Hz), 133.20 (d, ^1J(P,C) = 10 Hz), 134.89 (s). $C_{26}H_{31}B_9O_2P_2$: Calcd: C, 58.40; H, 5.84. Found: C, 58.22; H, 5.78.

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(9) $[NMe_4]$[**2**]: To a solution of $[NMe_4][7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_{10}H_{10}]$, $[NMe_4]$[**3**] (0.5 g, 0.87 mmol) in acetone at 0 °C was added dropwise 12.4 mL (1.24 mmol) of a 0.1 M H_2O_2 solution. The mixture was stirred at room temperature for 4 h, and a white solid was precipitated. The addition of a $[NMe_4]Cl$ aqueous solution increases the precipitation of the solid. The solid was filtered off, washed with water, and dried in vacuo to obtain compound $[NMe_4]$[**2**] (yield: 74.1%).

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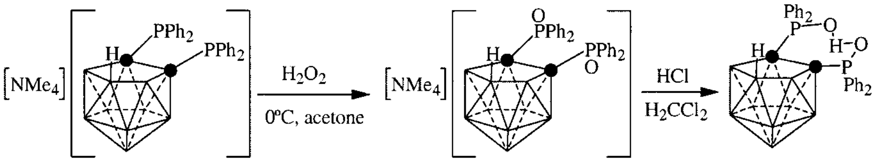
Scheme 2. Preparation of H[**2**] Using $[NMe_4][7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]$ as Starting Material



precise structure determination, crystals of H[**2**] were grown. An ethanol solution of this protonated species yielded adequate crystals for X-ray diffraction after standing for 2 months at 4 °C.[11] Figure 1 shows an ORTEP diagram and most relevant distances and angles of H[**2**]. Structure analysis confirmed the expected structure: both phosphorus atoms are oxidized, and the proton between the oxygen atoms balances out the negative charge of the *nido*-carborane cage. The proton lies approximately midway between the oxygen atoms, and the short O(1)···O(2) distance (2.421(4) Å), the O−H distances (1.21(5) Å), and the O−H−O angle (174(4)°) indicate an essentially centrosymmetric linear hydrogen bond. In $[({}^{i}Pr_3PO)_2H][I_3]$, which contains a centrosymmetric P−O−H−O−P hydrogen bond, the P−O distance of 1.530(6) Å is comparable with the distances in H[2] but the O···O distance of 2.386 Å is slightly shorter than that in H[**2**].[12]

The only reported structures containing a P−O−H−O−P array are $[(Me_3PO)_2H][AuI_2]$,[13] $[(Ph_3PO)_2H][ICl_4]$,[14] and $[({}^{i}Pr)_3PO)_2H][I_3]$[12] and one containing the moiety $PtPPh_2OHOPPh_2Pt$.[15] Surprisingly, none of them is chelating. Thus, H[**2**] is the first fully characterized proton chelated to two P−O moieties. Again, the singularity of the *nido*-$[C_2B_9]^-$ cluster with its intrinsic negative charge has permitted us to report for the first time the chelating P−O−H−O−P motif.

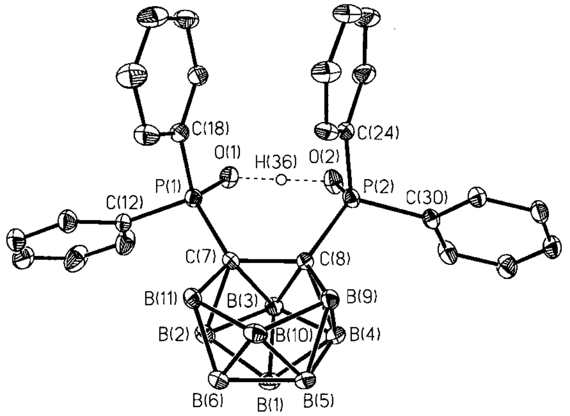


Figure 1. ORTEP drawing of compound H[**2**]. Hydrogen atoms, except H(36), have been omitted. Selected bond distances (Å) and angles (deg): P(1)−O(1) 1.523(3), P(1)−C(7) 1.810(3), P(2)−O(2) 1.534(3), P(2)−C(8) 1.808(3), C(7)−C(8) 1.609(5), O(1)−P(1)−C(7) 112.12(16), O(2)−P(2)−C(8) 112.58(15), C(8)−C(7)−P(1) 122.1(2), C(7)−C(8)−P(2) 121.4(2).

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. Additionally, crystallographic data for the structures reported in this paper have been deposited with the Cambridge Data Centre.

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(10) Selected spectroscopic and analytical data for $[NMe_4]$[**2**]: FTIR, (KBr, cm^{-1}) $\nu = 3019$ (C_{ar}−H), 2535 (B−H); $^{1}H\{^{11}B\}$ NMR (300.13 MHz, $((CD_3)_2CO)$, 25 °C, TMS) $\delta = -2.01$ (br s, 1 H, B−H−B), 3.45 (s, 12 H, CH_3), 7.24−7.92 (m, 20 H, C_6H_5); ^{11}B NMR (96.29 MHz, $((CD_3)_2CO)$, 25 °C, $Et_2O{\cdot}BF_3$) $\delta = -5.6$ (d, 2 B, $^{1}J(B,H) = 119$ Hz), −11.1 (d, 3 B, $^{1}J(B,H) = 133$ Hz), −19.0 (d, 2 B, $^{1}J(B,H) = 111$ Hz), −32.2 (d, 1 B, $^{1}J(B,H) = 142$ Hz), −33.9 (d, 1 B, $^{1}J(B,H) = 150$); $^{31}P\{^{1}H\}$ NMR (121.48 MHz, $((CD_3)_2CO)$, 25 °C, 85% H_3PO_4) $\delta = 29.3$ (s); $^{13}C\{^{1}H\}$ NMR (75.47 MHz, $((CD_3)_2CO)$, 25 °C, TMS) $\delta = 55.1$ (s), 126.8 (d, $^{1}J(P,C) = 37.4$ Hz), 129.9 (d, $^{1}J(P,C) = 26$ Hz), 132.4 (d, $^{1}J(P,C) = 33$ Hz), 135.89 (s), 137.2 (d, $^{1}J(P,C) = 18$ Hz), 138.5 (s). $C_{30}H_{42}B_9NO_2P_2$: Calcd: C, 59.27; H, 6.96; N, 2.30. Found: C, 58.95; H, 7.00; N, 2.45.

(11) Crystal structure analysis for H[**2**]: $C_{26}H_{31}B_9O_2P_2$, $M = 534.74$, triclinic, $a = 11.638(3)$ Å, $b = 13.124(3)$ Å, $c = 11.480(3)$ Å, $\alpha = 108.66(2)°$, $\beta = 110.25(2)°$, $\gamma = 103.25(2)°$, $V = 1440.1(6)$ Å^3, $T = 294(2)$ K, space group $P\bar{1}$ (No. 2), $Z = 2$, λ (Mo Kα)= 0.175 mm^{-1}, 5343 reflections measured, 5069 unique ($R_{int} = 0.0293$) which were used in all calculations. The final $R1(F^2) = 0.0547$ (observed data), $wR2(F^2) = 0.1110$ (observed data). Solution and refinement were by SHELX-97. Non-hydrogen atoms were refined anisotropically. H-atoms were in calculated positions as riding atoms, except H(36), which was refined isotropically with fixed *U*.

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