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Isolation of a New Nonaborane Cluster Form: *arachno*-$B_9H_{11}\cdot(PPh_3)_2$

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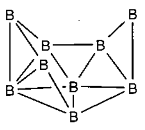
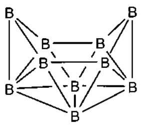
Introduction

The nine vertex, nonclosed polyhedral boranes have been the subject of much interest and activity for many years.[1] The structures of the *arachno*-nonaboranes provide interesting, and consistent, deviations from the coordination number pattern recognition theory for boranes and carbaboranes, as described by Williams in 1976.[2] The theory requires that, to generate arachno clusters from nido systems, a highest connectivity vertex, adjacent to the open face, is removed. The predicted cluster framework for an arachno nine-vertex system is illustrated by structure **I** and recognized as *n-arachno*-B_9H_{15}.[3] It is obtained by the removal of a five-connected vertex from *nido*-$B_{10}H_{14}$ (structure **II**). In contrast, the more commonly encountered nine-vertex arachno species are derived by removal of a low connectivity vertex from *nido*-$B_{10}H_{14}$ to generate derivatives of what are referred to as *i*-B_9H_{15} (structure **III**)[4] and *i*-$C_2B_7H_{13}$.[5]


I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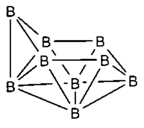
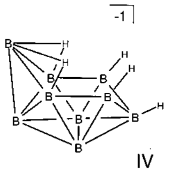
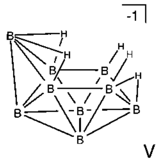

III

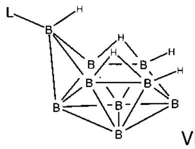
Nonaborane adducts and anions in this class also show the same tendency. Thus, the well-known arachno anion $[B_9H_{14}]^-$ (**IV**),[6] and the adducts 4-L-*arachno*-B_9H_{13} (**VI**)[7] and 5-L-*arachno*-B_9H_{13} (**VIII**),[8] all adopt the *i*-B_9H_{15} structure, as does a reported borane **VII**,[9] which is an isomer of **VIII**. It appears that the positions of the endo and bridging H atoms in $[B_9H_{14}]^-$ are not satisfactorily resolved in the literature. The result of the original structural study reported by Greenwood[6] is shown as structure **IV**, but recent calculations[10,11] and two unpublished structural studies[11] suggest that the structure shown as **V** is correct.



IV



V



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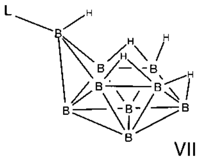
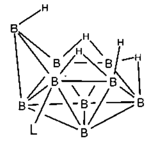
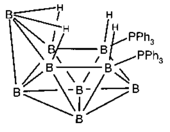


VII



VIII



IX

Herein, we add to the series of known nonaborane species by describing the new species $B_9H_{11}\cdot(PPh_3)_2$, which is formed in the oxidative fusion of B_5H_9 in the presence of Cp_2ZrCl_2/*n*-BuLi and PPh_3.

Experimental Section

Reactions were carried out under high vacuum or a dry nitrogen atmosphere. Solvents were reagent grade. THF and CH_2Cl_2 were dried and distilled from sodium/benzophenone and CaH_2, respectively, prior to use. PPh_3 and *n*-BuLi 1.6 M hexane solutions were commercially purchased from Aldrich and used as received. Cp_2ZrCl_2 (Alfa Aesar) was used as received. Column chromatography was done on a 2 cm^2 x 12 cm column using 200−400 mesh silica gel (Natland International). NMR spectra were recorded on a Varian Unity Plus 300 spectrometer and a Bruker ARX 500 spectrometer. ^1H, ^{31}P, and ^{11}B chemical shifts are referenced to $SiMe_4$ (0.0 ppm), $BF_3\cdot Et_2O$ (0.0 ppm), and 85% H_3PO_4 (0.0 ppm), respectively, and reported in ppm, with a negative sign indicating an upfield shift. The IR spectrum was recorded on a Perkin−Elmer 1600 FTIR spectrometer. The mass spectrum was obtained in the FAB mode on a JEOL MStation JMS-700 spectrometer using 3-nitrobenzyl alcohol (3-NBA). Atlantic Microlabs Inc., Norcross, GA performed elemental analysis.

Synthesis of *arachno*-$B_9H_{13}(PPh_3)_2$ (1). To a 50 mL three-neck flask equipped with a stir bar, stoppers, and a high-vacuum stopcock, was added Cp_2ZrCl_2 (293 mg, 1.0 mmol). The flask was evacuated on the vacuum line, and THF (3 mL) was condensed in at −196 °C. After nitrogen was introduced, a stopper was replaced with a septum, and *n*-BuLi (1.6 M hexane solution, 1.3 mL, 2.0 mmol) was added dropwise at −78 °C with vigorous stirring. The reaction mixture became a light yellow solution, and stirring was continued at −78 °C for 1h. The septum was replaced with the stopper, the flask was degassed at −196 °C, and B_5H_9 (0.94 mmol) was introduced. The reaction mixture was allowed to warm to room temperature and stirred for 1h, affording a red solution. Evaporation of all the volatiles at room temperature under high vacuum gave a deep red solid. PPh_3 (262 mg, 1.0 mmol) and CH_2Cl_2 (6 mL) were added to the open flask. Then air was bubbled into the reaction mixture with stirring at 0 °C for 1h. Evaporation of the solvent afforded an orange solid which contained $B_9H_{11}\cdot(PPh_3)_2$ (**1**), along with $B_9H_{14}^-$, $BH_3\cdot PPh_3$, and unidentified zirconocene species.

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Column chromatography using CH_2Cl_2/hexane = 1:1 as elute was carried out to afford **1** (R*f* 0.5) as white solid in up to 50% yield based on B_5H_9. However, because of partial decomposition on silica gel, it also included $BH_3\cdot PPh_3$. Further purification was effected by recrystallization from CH_2Cl_2/ether to afford a white crystalline solid (103 mg, 0.163 mmol, 35% based on B_5H_9). $^1H\{^{11}B\}$ NMR (300 MHz, $CDCl_3$): δ 7.8−7.3 (m. 30H, *Ph*), 2.85 [br, s, 2H, B*H(7,9)*], 2.64 [br, s, 1H, B*H(5)*], 2.43 [br, s, 1H, B*H(8)*], 1.76 [br, s, 2H, B*H(1,2)*], −0.04 [br, s, 2H, B*H(4,6)*], −0.59 [br, s, 1H, B*H(3)*], −1.88 [br, s, 2H, $H\mu_{7,8}$, $H\mu_{8,9}$] ppm. $^{11}B\{^1H\}$ NMR (96.2 MHz, $CDCl_3$): 0 [br, 2B, *B(7,9)*], −2.25 [br, 1B, *B(5)*], −9.72 [br, 2B, *B(1,2)*], −15.43 [br, 1B, *B(8)*], −41.42 [br, 2B, *B(4,6)*], −51.67 [br, 1B, *B(3)*] ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): 18.5 (br, m) ppm. IR (KBr): ν (BH) = 2546 (m), 2420 (m), 2471 (w) cm^{-1}. Mass spectral data for **1**: LRMS, FAB with 3-NBA. Calc. for $[M + H]^+$ $C_{36}H_{41}B_9P_2$ max: 634, obs. 634. The mass envelope in this region for the measured spectrum matches that calculated from the known isotopic abundances of the constituent elements. The observed *m*/*q* values (relative intensity) for the protonated molecular ion cluster were 629 (5.9); 630 (12.0); 631 (27.5); 632 (58.0), 633 (91.9); 634 (100.00); 635 (64.00); 636 (20.2); 637 (4.6). The calculated *m*/*q* data are 629 (0.63); 630 (3.92); 631 (16.32); 632 (45.97); 633 (85.77); 634 (100.00); 635 (64.68); 636 (20.2); 637 (3.25). Elemental Anal. Calcd for $C_{36}H_{41}B_9P_2$: C, 68.31; H, 6.53. Found: C, 68.08; H, 6.54.

Crystal Structure Determination.[12] Data collection was carried out using a Bruker CCD diffractometer. The structure was solved at −50 °C using direct methods and refined by full matrix least squares refinement to convergence. The hydrogen atoms on boron were located and refined freely. All other hydrogen atoms were treated using an appropriate riding model.

Results and Discussion

Treatment of Cp_2ZrCl_2 with *n*-BuLi at dry ice temperature and stirring for 1 h followed by addition of B_5H_9 afforded a red solid which contained boron but decomposed before we could identify it. These experiments were done in order to try to obtain Cp_2Zr derivatives of B_5H_9. Cp_2ZrCl_2/*n*-BuLi combinations are commonly used in organic synthesis.[13] When a suspension of Cp_2ZrCl_2 in THF is treated with 2 equiv of *n*-BuLi at −78 °C, metathesis occurs to give Cp_2ZrBu_2. This complex affords $Cp_2Zr(CH_2{=}CHEt)$ and BuH, via β-hydride elimination on warming to 0 °C, and serves as a convenient precursor to zirconocene "Cp_2Zr" due to the lability of the π ligand. Thus, we thought that "Cp_2Zr" might be incorporated into the B_5 cage as a vertex, since as a 14e metal fragment, it should supply two skeletal electrons, as does the BH fragment. To stabilize the metallaborane product, we added PPh_3. This also afforded no identifiable product, but accidental exposure to air formed a white solid soluble in CH_2Cl_2, $CHCl_3$, and only sparingly soluble in ethers. These observations led to a modified preparative procedure in which air was bubbled through the solution. This procedure is related to the well known oxidative fusion used in many laboratories but pioneered in polyhedral borane chemistry by Grimes.[14] This allowed for convenient isolation of the white solid which, on recrystallization from CH_2Cl_2/ether, afforded a pure white microcrystalline solid $B_9H_{11}(PPh_3)_2$ (**1**) in 35% yield.

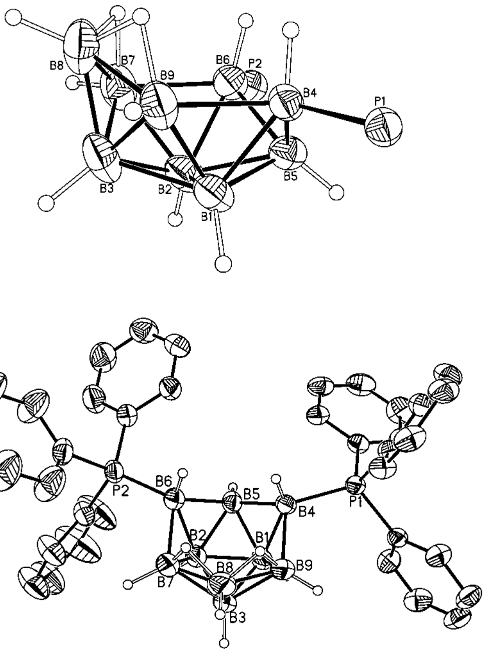

Figure 1. Two views of the molecular structure of *arachno*-B_9H_{13}-$(PPh_3)_2$ with 50% thermal ellipsoids. One has the phenyl groups omitted for clarity.

Table 1. Crystal Data and Structure Refinement for Compound **1**

chem formula	$B_9H_{11}(PPh_3)_2$	empirical formula	$C_{36}H_{41}B_9P_2$
temp/K	223(2) K	fw	632.92
D(calcd) Mg/m^3	1.182	radiation (λ, Å)	Mo Kα (0.71073)[a]
a/Å	9.3251(3)	space group	$P2_1/c$
c/Å	28.3923(9)	*b*/Å	13.5243(4)
V/Å^{-3}	3557.3(2)	β/°	96.556(2)°
Z	4	abs coeff mm^{-1}	0.148
final *R* indices [$I > 2\sigma(I)$]	R1[b] = 0.0464	*R* indices (all data)	wR2[c] = 0.1265

[a] Graphite monochromator. [b] $R1 = \sum||F_o| - |F_c|| / \sum|F_o|$. [c] $wR2 = [\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]]^{1/2}$.

The ^{11}B NMR spectrum of **1** exhibited six resonances in a 2:1:2:1:2:1 area ratio suggesting a symmetrical cluster containing nine boron atoms. The observation of the broad phosphine resonance at 18.5 ppm confirmed the presence of a phosphine−borane type moiety.[15] The ^1H NMR spectrum afforded resonances in a 2:1:1:2:2:1 ratio assigned to terminal H atoms on boron and a resonance at −1.82 ppm of area 2 assigned to the two bridging H atoms. The individual assignments of the NMR spectra, obtained from 2D ($^1H-^{11}B$) COSY experiments run on the Bruker 500 MHz spectrometer, are given in the Experimental Section. These results suggested that the cluster contained 9 boron atoms, 11 hydrogen atoms, and 2 phosphines associated with 2 of the boron atoms.

Crystals suitable for X-ray diffraction were grown very slowly from CH_2Cl_2/ether solutions at 23 °C, and the resultant structure is given in two views in Figure 1; crystal data and structure refinement for **1** are given in Table 1. The structure is that derived from *iso*-*arachno*-nonaborane(15), with the phosphine ligands symmetrically disposed in the prominent 6,8 positions. This is quite novel for this class of species, as is clear from an examination of the known *arachno*-nonaborane cluster motifs illustrated as structures **IV**−**IX**. The bond distances and angles

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[12] (a) *SHELXTL* Software Package; Bruker Analytical X-ray Division: Madison, WI, 2001. (b) For further details see Experimental Section in: McQuade, P.; Hupp, K.; Bould, J.; Fang, H.; Rath, N. P.; Thomas, R. Ll.; Barton, L. *Inorg. Chem.* **1999**, *38*, 5415.

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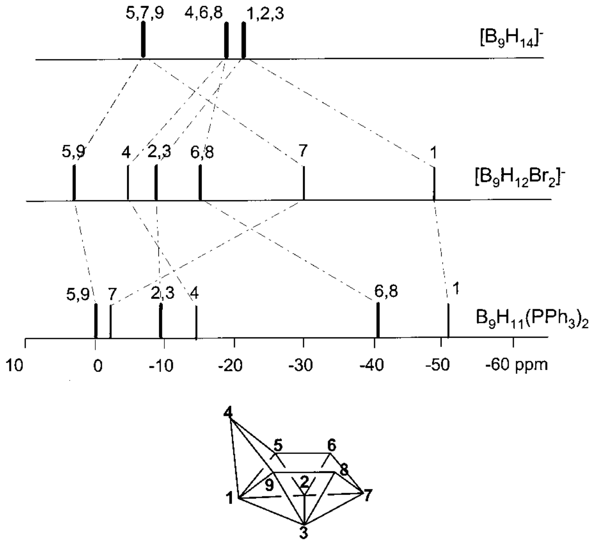

Figure 2. Correlation diagram comparing the ^{11}B NMR spectra of $[B_9H_{14}]^-$, $[B_9H_{12}Br_2]^-$, and $B_9H_{11}(PPh_3)_2$. Note that the numbering scheme for **1** has been modified to correlate with those for $[B_9H_{14}]^-$ and $[B_9H_{12}Br_2]^-$ and is given.

Table 2. Selected Interatomic Distances [Å] and Angles [deg] for **1**

B(4)−B(5)	1.817(3)	B(6)−B(7)	1.883(3)
B(4)−B(9)	1.864(3)	B(7)−B(8)	1.826(4)
B(5)−B(6)	1.818(3)	B(8)−B(9)	1.829(4)
B(5)−B(4)−B(9)	106.9(2)	B(5)−B(6)−P(2)	119.8(2)
B(5)−B(4)−P(1)	125.4(1)	B(7)−B(6)−P(2)	117.1(1)
B(9)−B(4)−P(1)	112.9(1)	B(8)−B(7)−B(6)	116.7(2)
B(4)−B(5)−B(6)	105.1(2)	B(9)−B(8)−B(7)	104.1(2)
B(5)−B(6)−B(7)	106.2(2)	B(8)−B(9)−B(4)	117.9(2)

do not differ much from those of related *arachno*-nonaboranes, Table 2. The long distances in $B_{10}H_{14}$[3b] and in $[B_9H_{14}]^-$,[11] corresponding to B(6)−B(7) and B(4)−B(9) in **1**, are ca. 0.1 Å longer in **1** than the analogous distances in $[B_9H_{14}]^-$, reflecting the increased electron density on B(4) and B(6). Also, the angle B(4)−B(5)−B(6) is about 10 ° less in **1**, clearly suggesting that electronic rather than steric factors influence the structure.

It is pertinent to compare the ^{11}B NMR spectra of **1** with the other *arachno*-nonaboranes, and we have chosen to include only $[B_9H_{14}]^-$, the unpublished $[B_9H_{12}Br_2]^-$,[11c] and none of the monoadducts of the type illustrated by structures **VI** and **VII**. A correlation diagram is given as Figure 2. The effects of the shielding of B(6,8) by donation of electron density by the phosphine moieties and the opposite effect on B(7) are the major features noted. Otherwise, the spectra of the three related species correlate very well. Note the numbering scheme for **1** is modified in order to facilitate the comparison. Since the numbering is detemined by the placement of substituents, those for illustrations **VI** and **XI** are necessarily different.

Compound **1** is only the second member of the important class of *arachno*-borane clusters to which belongs the species *arachno*-$B_{10}H_{12}L_2$, where L is a Lewis base such as CH_3CN or Me_2S. Such species, which are described by the formula $L_2B_nH_{n+2}$, are rare and are not known for any other borane clusters.[16] Probably no boron hydride cluster has seen more applications than the series of compounds described by the general formula $B_{10}H_{12}L_2$ and the species for which they are precursors.[17] It is reasonable to expect similar chemistry for **1**. The species $B_{10}H_{12}L_2$ is the precursor to the best known of the carboranes, $C_2B_{10}H_{12}$,[18] and also may be converted to *closo*-$[B_{10}H_{10}]^{2-}$.[19] Thus, $B_9H_{11}L_2$ could be a very useful synthon in polyhedral borane chemistry, perhaps not as the stable PPh_3 adduct, but involving a weaker donor base, such as Me_2S or $Me_2NC_6H_5$.

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Supporting Information Available: Crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Of course there is another borane species which belongs to this class, $B_2H_4L_2$, which, however, we do not define as a cluster. See (a) Hertz, R. K.; Denniston, M. L.; Shore, S. G. *Inorg. Chem.* **1978**, *17*, 2673. (b) DePoy, R.; Kodama, G. *Inorg. Chem.* **1985**, *24*, 2871.

(17) For example see: (a) Hawthorne, M. F. *Spec. Publ. R. Soc. Chem.* **1997**, *201*, 261. (b) Hawthorne, M. F. *Spec. Publ. R. Soc. Chem.* **2000**, *253*, 197.

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