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Journal of Organometallic Chemistry 680 (2003) 61–65

www.elsevier.com/locate/jorganchem

Synthesis and structural characterization of an 11-vertex *nido*-diphosphaborane, 7,9-Ph_2-*nido*-7,9-$P_2B_9H_9$

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Received 14 February 2003; received in revised form 11 March 2003; accepted 11 March 2003

Dedicated to Professor M. Fred Hawthorne on the occasion of his 75th birthday.

Abstract

The new 11-vertex *nido*-diphosphaborane, 7,9-Ph_2-*nido*-7,9-$P_2B_9H_9$, has been synthesized by the reaction of Me_4N^+[*nido*-$B_9H_{12}^-$] with $PhPCl_2$ in the presence of NaH. A single crystal X-ray diffraction determination and DFT/GIAO/NMR methods have both established that the compound has an open cage structure containing the phosphorus atoms in non-adjacent positions on the open face.

Keywords: Diphosphaborane; Heteroborane; DFT/GIAO; Boron

1. Introduction

Although there are now a variety of monophosphaboranes and monophospha-carbaboranes, [1] it has been only relatively recently that methods have become available for the syntheses of diphosphadicarbaboranes [2], including *nido*-7,8,9,11-$P_2C_2B_7H_9$, 3-Cl-*nido*-7,8,9,-11-$P_2C_2B_7H_8$, *nido*-7,9,8,10-$P_2C_2B_7H_9$, *nido*-7,8,9,10-$P_2C_2B_7H_9$, and 11-Cl-*nido*-7,8,9,10-$P_2C_2B_7H_8$; triphosphamonocarbaboranes [3], 4-Me-*nido*-7,8,9,10-$P_3CB_7H_7$ and 4-Me-11-Cl-*nido*-7,8,9,10-$P_3CB_7H_6$; and a small number of diphosphaboranes, 2,3,4-($i$$Pr_2N)_3$-1,5-$P_2B_3$ [4], *closo*-1,2-$P_2B_{10}H_{10}$, [5,6] *closo*-1,7-$P_2B_{10}H_{10}$ [5], *nido*-7,8-$P_2B_9H_{10}^-$ [7], *closo*-1,2-$P_2B_4X_4$ (X = Cl [8] or Br [9]) and *closo*-1,7-$P_2B_{10}Cl_{10}$ [10]. In all of the diphospha- and triphosphapolyboranes that have been reported to date, the phosphorous cage atoms do not have an *exo*-substituent, but rather have an *exo*-polyhedral lone pair of electrons. In this communication, we report the synthesis and structural characterization of the first neutral 11-vertex *nido*-diphosphaborane 7,9-Ph_2-*nido*-7,9-$P_2B_9H_9$ that is also the first diphosphaborane to have *exo*-substituents at the phosphorus cage atoms.

2. Results and discussion

We have previously prepared a wide variety of monophosphacarbaboranes and monophosphaboranes via in situ dehydrohalogenation/phosphorus-insertion reactions of $RPCl_2$ reagents with polyboranes in the presence of Proton Sponge [11]. During our attempt to employ similar methods to produce the previously unknown 10-vertex R-*nido*-PB_9H_{11} compound, we surprisingly found that the reaction of Me_4N^+[*nido*-$B_9H_{12}^-$] [12] with $PhPCl_2$ in the presence of NaH (instead of Proton Sponge, where no reaction was observed) does not produce the monophosphaborane Ph-*nido*-PB_9H_{11}, but instead yields the diphosphaborane 7,9-Ph_2-*nido*-7,9-$P_2B_9H_9$ (**1**). Better yields were obtained when two equivalent of $PhPCl_2$ were used (Eq. (1)), but even in reactions employing 1.0 equivalent of $PhPCl_2$, only the formation of **1** was observed.

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0022-328X/03/$ - see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0022-328X(03)00165-7

$$\mathrm{Me_4N^+[B_9H_{12}^-] + 2PhPCl_2} \xrightarrow[-3\mathrm{NaCl},\ 3\mathrm{H_2},\ \mathrm{Me_4NCl}]{3\mathrm{NaH}} \mathrm{7,9\text{-}Ph_2\text{-}}nido\mathrm{\text{-}7,9\text{-}P_2B_9H_9}\,\mathbf{1} \qquad (1)$$

The composition of **1** was confirmed by elemental analysis and mass spectroscopy. If each R–P unit donates four skeletal-electrons, then a compound of composition 7,9-Ph$_2$-*nido*-7,9-P$_2$B$_9$H$_9$ would contain a total of 26 skeletal electrons, and be expected to adopt the normal 11-vertex *nido*-deltahedral structure, an icosahedron missing one vertex, that has been observed for such systems [13]. Consistent with this prediction, a single crystal X-ray diffraction study of **1** established the structure shown in Fig. 1.

To our knowledge, **1** is the first crystallographically characterized *nido*-class diphosphaborane. In **1**, the phosphorus atoms are located in non-adjacent positions, separated by boron atoms in the open pentagonal face. There is a crystallographic mirror plane coincident with the B8–B5–B1 plane that equates the two halves of the structure. Unlike in the isoelectronic 7-Me-*nido*-7-PB$_{10}$H$_{12}$ phosphaborane, where all the P–B distances have similar values (1.978(6)–2.001(6) Å) regardless of their locations in the cluster [14], the P9–B8 (1.917(2) Å) and P9–B10 (1.923(3) Å) distances in the open face of **1** are significantly shorter than distances between the phosphorus atoms and the borons in the lower ring, P9–B3 (2.061(3) Å) and P9–B4 (2.028(3) Å). The phosphorus atoms are also puckered (0.2160(5) Å) above the B8–B10–B10′ plane. As a result, the B8–P9–B10 and B3–B4–B5 planes are not parallel, but have an 11.8(4)° dihedral angle. This is probably a consequence of the fact that both of the large phosphorus atoms are located on the open face.

Consistent with its crystallographically established structure, the ^{11}B-NMR spectrum obtained for **1** shows a six-resonance pattern in 1:2:2:2:1:1 ratios, indicating C_s symmetry (Fig. 2). The DFT/GIAO calculated ^{11}B chemical shifts (B3LYP/6-311G*) [15], based on the C_s symmetric optimized geometry (B3LYP/6-311G*) of **1** (**I**) shown in Fig. 3, are congruous with the experimental data (Table 1). As expected based on its DFT/GIAO assignment to the B8 boron situated between the P7 and P9 atoms, the resonance at −28.6 ppm in the experimental NMR spectrum shows a broad triplet structure arising from boron–phosphorus coupling. In the ^{1}H-

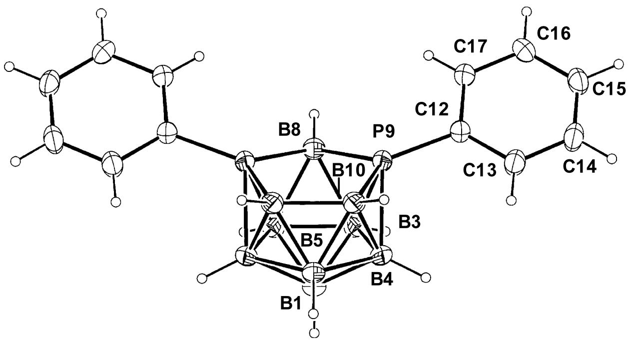

Fig. 1. ORTEP drawing of the structure of 7,9-Ph$_2$-*nido*-7,9-P$_2$B$_9$H$_9$ (**1**). Selected bond distances (Å): P9–B8, 1.917(2); P9–B10, 1.923(3); P9–C12, 1.796(2); P9–B4, 2.028(3); P9–B3, 2.061 (3); B1–B3, 1.758(4); B1–B4, 1.770(3); B1–B5, 1.785(5); B3–B3′, 1.748(5); B3–B4, 1.843(4); B3–B8, 1.875(4); B4–B5, 1.753(3); B4–B10, 1.860(4); B5–B10, 1.778(4); B10–B10′, 1.740(5).

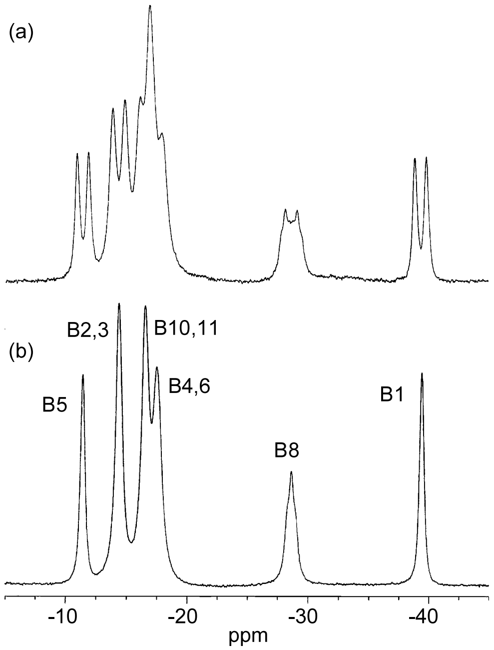

Fig. 2. ^{11}B-NMR spectra of 7,9-Ph$_2$-*nido*-7,9-P$_2$B$_9$H$_9$ (**1**), (a) ^{1}H-coupled (b) ^{1}H-decoupled.

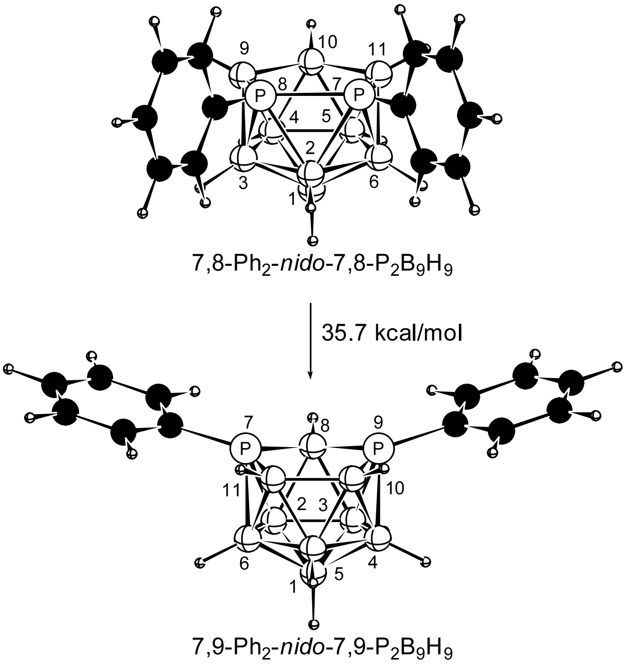

Fig. 3. Optimized geometries (B3LYP/6-311G*) of 7,9-Ph$_2$-*nido*-7,9-P$_2$B$_9$H$_9$ (**I**) and 7,8-Ph$_2$-*nido*-7,8-P$_2$B$_9$H$_9$ (**II**).

Table 1
NMR Data for 7,9-Ph_2-*nido*-7,9-$P_2B_9H_9$ (**1**) [a,b,c]

Nucleus	δ (multiplicity, assignment, J (Hz))
^{11}B	-11.4 (d, B5; $J_{BH}=148$), -14.4 (d, B2,3; $J_{BH}=159$), -16.6 (d, B10,11; $J_{BH}\sim 150$), -17.5 (d, B4,6; $J_{BH}\sim 150$), -28.6 (B8; $J_{BH}=159$, $J_{BP}\sim 70$), -39.4 (d, B1; $J_{BH}=154$)
^{11}B (Calc.) [d]	-12.3 (B5), -14.5 (B2,3), -16.9 (B10,11), -17.6 (B4,6), -30.3 (B8), -41.3 (B1)
$^{1}H\{^{11}B\}$	7.37–6.78 (m, 5, phenyl), 3.06 (t, 1, P_2BH; $J_{PH}=25$), 2.92 (2, BH), 2.84 (2, BH), 2.50 (1, BH), 2.39 (2, BH), 2.13 (1, BH)
$^{13}C\{^{1}H\}$	132.6–129.4 (phenyl)
^{13}C(Calc.)	137.2–133.1 (phenyl)
^{31}P	-69.2 (P7,9)
^{31}P(Calc.) [d]	-59.9 (P7,9)

[a] NMR shifts in ppm.

[b] ^{1}H-NMR (500.4 MHz), ^{11}B-NMR (160.5 MHz), ^{13}C-NMR (125.8 MHz), ^{31}P-NMR (145.8 MHz).

[c] C_6D_6.

[d] DFT/GIAO/NMR method (B3LYP/6-311G*//B3LYP/6-311G*).

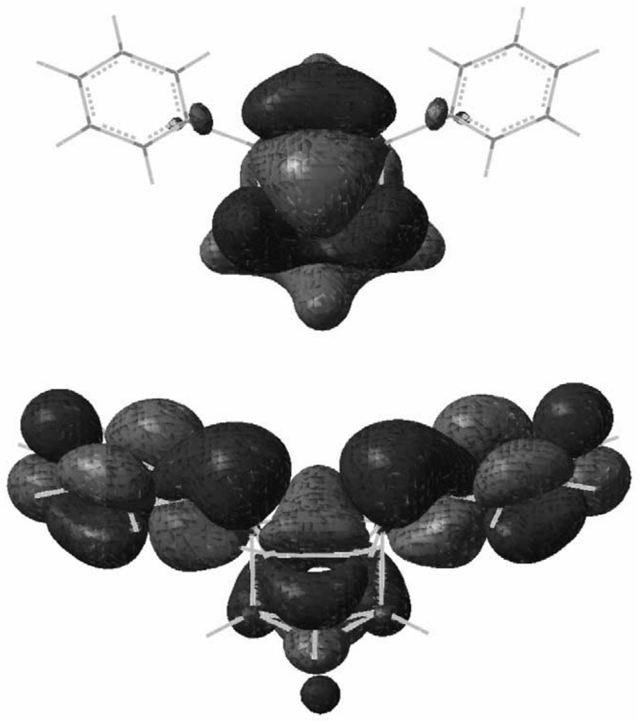

Fig. 4. HOMO (top) and LUMO (bottom) density surfaces (B3LYP/6-311G*) for 7,9-Ph_2-*nido*-7,9-$P_2B_9H_9$ (**I**).

NMR spectrum, **1** exhibited terminal BH hydrogen resonances in the predicted 1:2:2:1:2:1 intensity-ratios along with the phenyl ring resonances. Consistent with its assignment to the terminal BH hydrogen at B8, the resonance at 3.06 ppm showed a triplet structure ($J_{PH}=25$ Hz) arising from coupling to the two phosphorus atoms. The ^{31}P-NMR spectrum showed a single phosphorus resonance at -69.2 ppm, which, considering the large ^{31}P-NMR chemical shift range, is again close to the DFT/GIAO calculated value of -59.9 ppm.

In principle, phosphorus atom insertions into the starting *nido*-$B_9H_{12}^-$ anion could have produced either the observed 7,9-Ph_2-*nido*-$P_2B_9H_9$ product or its adjacent-phosphorus isomer 7,8-Ph_2-*nido*-$P_2B_9H_9$. However, electron-rich cage atoms, such as phosphorus, are known to favor both low-coordinate positions on an open face and positions in which maximum separation between heteroatoms can be attained [13c]. Indeed, although it has not been crystallographically characterized, the isoelectronic 9-Ph-*nido*-7,9-SPB_9H_9 [11a] cluster is proposed to adopt a structure similar to that established for **1**, in which the heteroatoms adopt non-adjacent positions on the open face. In agreement with this trend, the DFT calculations (B3LYP/6-311G*) showed that the adjacent-phosphorus isomer 7,8-Ph_2-*nido*-$P_2B_9H_9$ (**I**) is 35.7 kcal mol^{-1} higher in energy than the phosphorus non-adjacent isomer 7,9-Ph_2-*nido*-$P_2B_9H_9$ (**II**) (Fig. 3).

The HOMO and LUMO energy levels of the DFT optimized 7,9-Ph_2-*nido*-7,9-$P_2B_9H_9$ (**I**) geometry were calculated as -0.23955 and -0.06513 hartrees, respectively, which corresponds to a $\Delta E = 4.7$ eV (or 262 nm) for the HOMO–LUMO gap. Although the fluorescence emission of **1** was completely quenched, **1** did show strong absorption at 262 nm in a dichloromethane solution ($\varepsilon_{262} = 1.45 \times 10^4$ l mol^{-1} cm^{-1}) in agreement with the calculated HOMO–LUMO transition.

As shown in Fig. 4 [16], the HOMO of **I** is mainly derived from the diphosphaborane cage orbitals, with very little contribution from the two phenyl rings, and is largely localized on the five-membered open face of the structure. These results suggest that **1** should show strong donor properties facilitating the formation of 'π-arene'-type metal complexes where **1** functions as a neutral six-electron donor to a transition metal η^5-coordinated to the open face of the cluster. For the LUMO in **I**, the phenyl ring orbitals participate as much as the cage cluster orbitals. Thus, the HOMO–LUMO transition qualitatively corresponds to an electron excitation from cage to phenyl centered orbitals. Monoborane and polyborane compounds containing conjugated π systems have recently become of great interest because of the potential that HOMO–LUMO charge transfer transitions in these compounds could yield important photochemical [17], liquid crystalline [18], and/or nonlinear optical properties [19]. The HOMO/LUMO excitation observed for **1** suggests that compounds having π systems linked by diphosphaboranes might also have uses in these areas. Further investigations of the properties of **1**, as well as the syntheses and properties of related compounds are in progress.

3. Experimental

3.1. Preparation of 7,9-Ph_2-*nido*-7,9-$P_2B_9H_9$ (**1**)

A sample of 0.916 g (5.0 mmol) of Me_4N^+[*nido*-$B_9H_{12}^-$] [12] was dissolved in 30 ml of 1,2-dimethoxyethane with 0.268 g (11.2 mmol) of NaH and 1.37 ml (10.1 mmol) of $PhPCl_2$. The reaction mixture was heated at 80 °C for 39 h under an inert atmosphere. The product was purified by preparative TLC (hexanes:dichloromethane = 4:1, v/v) to yield 0.320 g (20%) of white solid **1**. Melting point (m.p.) 151 °C; Anal. Calc.: C, 44.69; H, 5.94. Found: C, 44.28; H, 6.23%. LRMS Calc. for $^{12}C^1_{12}H^{11}_{19}B^{31}_9P_2$, 247 ($m/e$, C_6H_5, parent envelope not observed). Found: 247; IR (CCl_4 sol, NaCl, cm^{-1}) 3100 (m), 2550 (s),1440 (s), 1420 (s), 1340 (m), 1200 (m), 1090 (s), 950 (s).

3.2. Crystal structure determination of 7,9-Ph_2-*nido*-7,9-$P_2B_9H_9$ (**1**)

Crystal data for $C_{12}H_{19}B_9P_2$: crystal dimensions 0.45 × 0.15 × 0.08 mm, $M = 322.50$, monoclinic ($P2_1/m$), $Z = 2$; $a = 7.5068(2)$ Å; $b = 15.4476(5)$ Å; $c = 7.5159(2)$ Å; $\beta = 97.592(2)°$; $V = 863.92(4)$ Å^3, $2\theta = 5.28–50.7°$; 1618 independent reflections, R_1 (wR_2) = 0.0478 (0.1183) for the 1535 reflections with $F > 4\sigma$. Data were collected at 210 K on a Rigaku R-AXIS IIc area detector employing Mo–K_α radiation ($\lambda = 0.71069$ Å). The structure was solved by direct methods (SIR92) and refined on F^2 using SHELXL-93.

3.3. Computational studies

The DFT/GIAO/NMR computations [20] employing the GAUSSIAN 98 program [15], were carried out in a manner similar to that which we have described previously [11]. The geometries of **I** and **II** were fully optimized at the B3LYP/6-311G* level within the specified symmetry constraints on a (4)-processor Origin 200 computer running IRIX 6.5.5. A vibrational frequency analysis was carried out on each optimized geometry at the B3LYP/6-311G* level with a true minimum found for each structure (i.e. possessing no imaginary frequencies).

4. Supplementary material

Crystallographic data for the structural analysis of compound **1** has been deposited with the Cambridge Crystallographic Data Center, CCDC no. 203302. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank the National Science Foundation for the support of this work.

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