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Two Isomeric Phosphacarboranes 2,1- and 6,1-PCB_8H_9, the First Representatives of the 10-Vertex *closo* Phosphacarborane Series

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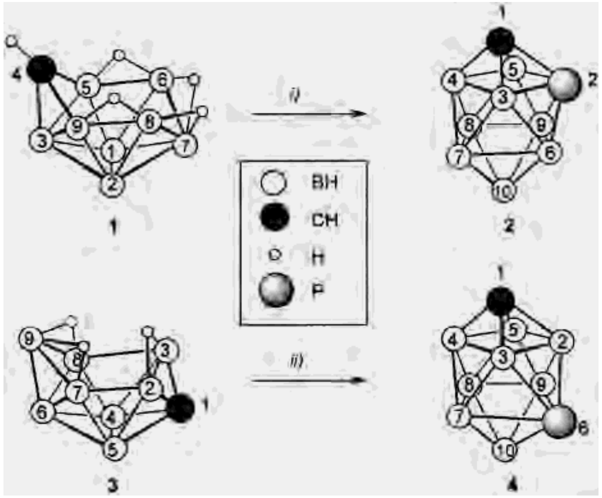
The reaction between *arachno*-4-CB_8H_{14} and PCl_3 in the presence of PS (PS = proton sponge = 1,8-dimethylamino naphthalene) (dichloromethane, rt, 24 h) produced the neutral phosphacarborane *closo*-2,1-PCB_8H_9 (35% yield), while a similar reaction of *nido*-1-CB_8H_{12} gave the isomeric compound *closo*-6,1-PCB_8H_9 (27% yield). The structures of both compounds were derived on the basis of the combined ab initio/GIAO/NMR (^1H, ^{11}B, ^{13}C) approach. The optimized structures at a correlated level of theory (MP2) with 6-31G* basis set were used as a basis for calculations of the ^{11}B and ^{13}C chemical shifts at GIAO-SCF/II and GIAO-MP2/II, the latter showing excellent agreement with experimental data.

Todd et al. found that reactions of PCl_3 or $RPCl_2$ (R = alkyl or aryl) with open structured (*nido* or *arachno*) boron-cluster substrates in the presence of deprotonation agents led to phosphaboranes or phosphacarboranes.[1] Thus, for example, all three isomers, 1,2-, 1,7-, and 1,12-$PCB_{10}H_{11}$, were prepared. These are analogous to the well-known 12-vertex dicarbaboranes $C_2B_{10}H_{12}$, CH and P units being isolobal. Recent work by Sneddon at al.[2] reported on a high-yield synthesis of the 11-vertex P-substituted phosphadicarbaboranes, 7-R-*nido*-7,8,9-$PC_2B_8H_{10}$ (R = alkyl or aryl), based on the reaction between *nido*-5,6-$C_2B_8H_{12}$[3] and $RPCl_2$ in the presence of PS (PS = proton sponge = 1,8-dimethylamino naphthalene); however, the same reaction with PCl_3 generated the unsubstituted phosphadicarbaborane *nido*-7,8,9-$PC_2B_8H_{11}$.[4] Reactions with some borane and carborane substrates may also result in multiple insertion of P-cluster units, as exemplified by the formation of 1,2-$P_2B_8H_{10}$,[5] isomeric compounds $P_2C_2B_7H_9$,[6] and the derivatives of $P_3CB_7H_8$[7] from reactions of PCl_3 with $B_{10}H_{14}$ and the two (4,6- and 4,5-) *arachno*-$C_2B_7H_{13}$ isomers. We report here our preliminary results on monophosphorus insertion reactions into the cages of the 9-vertex monocarboranes[8] *arachno*-4-CB_8H_{14} and *nido*-4-CB_8H_{12} which produced the first representatives of the 10-vertex *closo* phosphacarborane series, neutral compounds 2,1-PCB_8H_9 and 6,1-PCB_8H_9.

Scheme 1



As shown in Scheme 1 (path i), the reaction between *arachno*-4-CB_8H_{14} (**1**) and PCl_3 in the presence of PS in

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(1) (a) Little, J. L.; Whitesell, M. A.; Chapman, R. W.; Kester, J. G.; Huffman, J. C.; Todd, L. J. *Inorg. Chem.* **1993**, *32*, 3369−3372. (b) Todd, L. J.; Little, J. L.; Silverstein, H. T. *Inorg. Chem.* **1969**, *8*, 1698. (c) Todd, L. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E., Eds; Pergamon Press: Oxford, U.K., 1982, Part I, Chapter 5.6, pp 543−553. Todd, L. J. In *Metal Interactions with Boron Clusters*; Grimes, R. N., Ed.; Plenum: New York, 1982; pp 145−171.

(2) Shedlow, M.; Sneddon, L. G. *Inorg. Chem.* **1998**, *37*, 5269−5277.

(3) Štíbr, B.; Holub, J.; Jelínek, T.; Grüner, B.; Fusek, J.; Plzák, Z.; Teixidor, F.; Viñas, C.; Kennedy, J. D. *Collect. Czech. Chem. Commun.* **1997**, *62*, 1229−1238.

(4) Štíbr, B.; Holub, J.; Bakardjiev, M.; Tok, O. L.; Milius, W.; Hnyk, D.; Wrackmeyer, B. *Chem.*−*Eur. J.*, submitted.

(5) Little, J. L.; Kester, J. G.; Huffman, J. C.; Todd, L. J. *Inorg. Chem.* **1989**, *28*, 1087−1091.

(6) Holub, J.; Jelínek, T.; Hnyk, D.; Plzák, Z.; Císařová, I.; Bakardjiev, M.; Štíbr, B. *Chem.*−*Eur. J.* **2001**, *7*, 1546−1554.

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dichloromethane at ambient temperature for 24 h produced the neutral phosphacarborane *closo*-2,1-PCB_8H_9 (**2**) in 35% yield as the main product after LC separation of the reaction products.[9] Side products from the reaction seem to be consistent with $P_3CB_7H_8$ and $P_2CB_8H_{10}$ and will be characterized in the full paper after isolating pure substances. The formation of **2** is consistent with the stoichiometry as in eq 1 and with the insertion of the P-vertex into the area identified by the open-face cluster atoms C(4), B(5), B(6), B(8), and B(9) in structure **1** upon removal of all bridging and *endo* hydrogens as HCl (scavenged by PS) or H_2.

$$\underset{\mathbf{1}}{CB_8H_{14}} + PCl_3 + 3PS \rightarrow \underset{\mathbf{2}}{PCB_8H_9} + 3\ PSH^+Cl^- + H_2 \quad (1)$$

A similar reaction between *nido*-1-CB_8H_{12} (**3**) and PCl_3 in the presence of PS in dichloromethane at ambient temperature for 24 h produced the neutral phoshacarborane *closo*-6,1-PCB_8H_9 (**4**) in 27% yield as a single product, the rest of **3** or **4** being probably decomposed by hydrolysis.[10]

$$\underset{\mathbf{3}}{CB_8H_{12}} + PCl_3 + 3PS \rightarrow \underset{\mathbf{4}}{PCB_8H_9} + 3PSH^+Cl^- \quad (2)$$

Compound **4** is isomeric with **2**, and its formation is consistent with the simple stoichiometry of eq 2. The P-vertex is obviously incorporated into the area identified by the open-face cluster atoms B(2), B(3), B(6), B(7), and B(9) in structure **3** upon simultaneous removal of all bridging hydrogens.

The C_s symmetry 10-vertex *closo* structure with the CH vertex at the apical site of lowest coordination is a common feature of both isomeric compounds **2** and **4**. These structures are in agreement with the found molecular cutoffs in the mass spectra and multinuclear NMR data.[9,10] The ^{11}B NMR spectra of both compounds consist of 1:1:2:2:2 patterns of doublets and could be unabiguously assigned by two-dimensional [$^{11}B-^{11}B$] COSY experiments[11] combined with $^1H\{^{11}B(\text{selective})\}$ measurements.[12] A typical feature of their ^1H NMR spectra is the presence of a broader low-field CH resonance which is split into a doublet due to $^2J_{PH}$ coupling in the spectrum of **2** while the corresponding spectrum of **4** shows just a singlet CH resonance. The $^{13}C\{^{11}B, ^1H\}$ NMR spectrum of **2** displays one doublet due to $^1J_{PC}$ coupling, while the corresponding spectrum of **4** shows one singlet with a fine $^1J_{CB}$ splitting. The ^{31}P NMR spectra of both species exhibit one singlet resonance. It should be also noted that there are straightforward NMR similarities between compounds **2** and **4** and their dicarbaborane counterparts 1,2- and 1,6-$C_2B_8H_{10}$, which reflect the isolobality between CH and bare P vertices. Moreover, **2** and **4** resemble the 10-vertex-*closo* dicarbaboranes in their relative stabilities: **4** is favored over **2** by 17.8 kcal/mol [RMP2(fc)/6-31G* + ZPE (HF/6-31G*), zero point energy corrections are scaled by 0.89].[13]

The relatively high volatility and solubility in hydrocarbons precluded growing crystals suitable for X-ray diffraction analyses. The molecular geometries of compounds **2** and **4**

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(7) Jelínek, T.; Hnyk, D.; Holub, J.; Štíbr, B. *Inorg. Chem.* **2001**, *40*, 4512−4513.

(8) Jelínek, T.; Štíbr, B.; Holub, J.; Bakardjiev, M.; Hnyk, D.; Ormsby, D. L.; Kilner, C. A.; Thornton-Pett, M.; Schanz, H.-J.; Wrackmeyer, B.; Kennedy, J. D. *Chem. Commun.* **2001**, 1756−1757.

(9) A solution of compound **1** (500 mg, 4.44 mmol) in CH_2Cl_2 (20 mL) was cooled to 0 °C and treated with PS (2.87 g, 13.4 mmol) under stirring for 15 min. To this solution was added dropwise PCl_3 (825 mg, 6 mmol) over a period of 15 min, and the mixture was then stirred at ambient temperature for an additional 24 h. The mixture was then cooled again to 0 °C and treated with water (20 mL, dropwise) under stirring. The CH_2Cl_2 layer was separated and the solvent evaporated, and the residual materials were separated via chromatography on a silica gel column (30 cm × 2.5 cm) in hexane to collect a pure fraction of R_f 0.13. This was evaporated to dryness, and the residual materials were vacuum sublimed at 50 °C (bath) to give 215 mg (35%) of a white, air-sensitive solid which was identified as **2**. For **2**: R_f (hexane) 0.13; mp > 350 °C. ^{11}B NMR ($CDCl_3$): $\delta = 50.2$ (d, $^1J_{BH} = 173$ Hz, 1B, B_{10}), −5.0 (d, $^1J_{BH} = 169$ Hz, 1B, B_4), −17.5 (d, $^1J_{BH} = 173$ Hz, 2B, $B_{3,5}$), −24.4 (br d, $^1J_{BH} = 165$ Hz, 2B, $B_{6,9}$), −26.6 (d, $^1J_{BH} = 150$ Hz, 2B, $B_{7,8}$), all theoretical [$^{11}B-^{11}B$] COSY cross-peaks observed. ^{11}B NMR (calcd, GIAO-MP2/II//RMP2(fc)/6-31G*): $\delta =$ 51.9 (B_{10}), −4.7 (B_4), −17.3 ($B_{3,5}$), −26.0 ($B_{6,9}$), −28.2 ($B_{7,8}$).^1H-$\{^{11}B\}$ NMR ($CDCl_3$): $\delta = 6.94$ (s, 1H, H_{10}), 6.22 (d, $^2J_{PH} = 15.5$ Hz, 1H, H_1), 2.88 (s, 1H, H_4), 1.71 (d, $^2J_{PH} = 14.5$ Hz, 2H, $H_{3,5}$), 1.31 (s, 2H, $H_{7,8}$), 1.28 (d, $^2J_{PH} = 15.5$ Hz, 2H, $H_{6,9}$). $^{13}C\{^{11}B,^1H\}$ NMR ($CDCl_3$): $\delta = 54.4$ (d, $^1J_{PC} = 74.4$ Hz, 1C, C_1). $^{13}C\{^{11}B\}$ NMR ($CDCl_3$): $\delta = 54.4$ (d, $^1J_{CH} = 191$ Hz, 1C, C_1). ^{13}C NMR (calcd, GIAO-MP2/II//RMP2(fc)/6-31G*): $\delta = 63.6$. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = -129.9$ (s, 1P, P_2). IR (KBr): $\nu = 2576$ (B−H) cm^{-1}. MS (70 eV, EI), *m/z* (%): 140 (17) $[M]^+$, 137 (100) $[M - 3H]^+$ (± 5% agreement between observed and calcd intensities in the parent envelope). Anal. Calcd for CH_9B_8P (138.61): B, 62.45. Found: B, 60.71.

(10) A solution of compound **3** (352 mg, 3.18 mmol) in CH_2Cl_2 (20 mL) was cooled to 0 °C and treated with PS (2.057 g, 9.6 mmol) under stirring for 15 min. To this solution was added dropwise PCl_3 (550 mg, 4 mmol) over a period of 15 min, and the mixture was then stirred at ambient temperature for an additional 24 h. The mixture was then cooled again to 0 °C and treated with water (20 mL, dropwise) under stirring. The CH_2Cl_2 layer was separated and the solvent evaporated, and the residual materials were vacuum sublimed at 50 °C (bath) to give 119 mg (27%) of a white, air-sensitive solid which was identified as **4**. For **4**: R_f (hexane) 0.15; mp > 350 °C. ^{11}B NMR ($CDCl_3$): $\delta = 34.9$ (d, $^1J_{BH} = 181$ Hz, 1B, B_{10}), −11.6 (d, $^1J_{BH} = 154$ Hz, 1B, B_8), −13.6 (dd, $^1J_{BH} = 172$ Hz, $^1J_{BP} = 32$ Hz, 2B, $B_{2,3}$), −22.2 (d, $^1J_{BH} = 169$ Hz, 2B, $B_{4,5}$), −23.9 (br d, $^1J_{BH} = 162$ Hz, 2B, $B_{7,9}$), all theoretical [$^{11}B-^{11}B$] COSY cross-peaks observed. ^{11}B NMR (calcd, GIAO-MP2/II//RMP2(fc)/6-31G*): $\delta = 35.9$ (B_{10}), −11.4 (B_8), −12.7 ($B_{2,3}$), −21.9 ($B_{4,5}$), −24.0 ($B_{7,9}$). $^1H\{^{11}B\}$ NMR ($CDCl_3$): $\delta = 6.44$ (s, 1H, H_{10}), 6.05 (s, 1H, H_1), 2.53 (d, $^2J_{PH} = 21.5$ Hz, 2H, $H_{2,3}$), 2.34 (s, 1H, H_8), 1.76 (s, 2H, $H_{4,5}$), 1.00 (d, $^2J_{PH} = 21.5$ Hz, 2H, $H_{7,9}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 69.9$ (s, 1C, C_1). ^{13}C NMR (calcd, GIAO-MP2/II//RMP2(fc)/6-31G*): $\delta = 74.6$. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = -191.2$ (s, 1P, P_6). IR (KBr): $\nu = 2582$ (B−H) cm^{-1}. MS (70 eV, EI), *m/z* (%): 140 (17) $[M]^+$, 137 (100) $[M - 3H]^+$ (±5% agreement between observed and calcd intensities in the parent envelope). Anal. Calcd for CH_9B_8P (138.61): B, 62.45. Found: B, 60.30.

(11) Hutton, W. C.; Venable, T. L.; Grimes, R. N. *J. Am. Chem. Soc.* **1984**, *106*, 29−37.

(12) Fontaine, X. L. R.; Kennedy, J. D. *J. Chem. Soc., Dalton Trans.* **1987**, 1573.

(13) All calculations used the Gaussian94 program package (ref 14) and were performed on the Power Challenge XL computer of the Supercomputing Centrum of the Charles University in Prague. The structures of both compounds were optimized first at RHF/6-31G* within C_s symmetry proposed on the basis of experimental ^{11}B and ^1H NMR spectroscopy. Second derivative analysis, carried out at the same level, determined the nature of the stationary points and provided the zero point energies (ZPEs) (ref 16). Minima were characterized with zero imaginary frequency (NIMAG = 0). Final optimizations at RMP2(fc)/6-31G* included the effect of electron correlation and gave the relative energies of **2** and **4**. The chemical shieldings were calculated first at an SCF level with the GIAO (gauge-invariant atomic orbital) method and utilized a II Huzinaga basis set (ref 17) well-established for the calculations of magnetic properties (GIAO-SCF/II) (ref 18). The final level of the computations of chemical shieldings was GIAO-MP2 with the same Huzinaga basis set. Nucleus independent chemical shifts (NICS) (ref 15) were computed at GIAO-SCF with 6-31G* basis set.

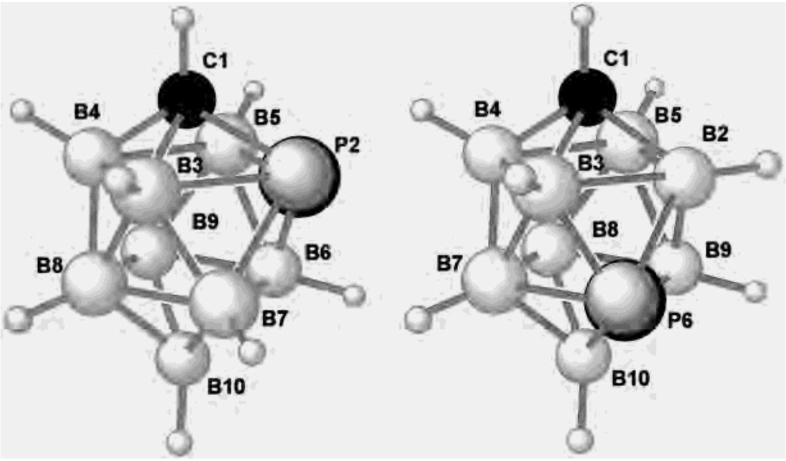

Figure 1. RMP2(fc)/6-31G* optimized geometrical parameters for (a) 2,1-PCB$_8$H$_{10}$ (**2**) and (b) 6,1-PCB$_8$H$_{10}$ (**4**). Selected bond distances (Å) and angles (deg) were (a) P(2)−C(1) 1.859, P(2)−B(3) 2.121, P(2)−B(6) 2.031, B(6)−B(9) 1.890, B(3)−P(2)−B(5) 76.8, P(2)−B(3)−B(4) 95.4, B(3)−B(4)−B(5) 92.4, B(7)−B(6)−B(9) 89.0; (b) P(6)−B(2) 2.077, P(6)−B(7) 2.104, B(2)−C(1) 1.592, B(3)−B(2) 1.953, B(7)−P(6)−B(9) 77.6, P(6)−B(7)−B(8) 94.8, B(7)−B(6)−B(9) 89.0, B(7)−B(8)−B(9) 92.6, B(2)−B(3)−B(4) 87.9.

were therefore derived computationally (Figure 1) at the RMP2(fc)/6-31G* level, and the calculated parameters were used for GIAO-SCF/II//RMP2(fc)/6-31G* and GIAO-MP2/II//MP2(fc)/6-31G* calculations of the ^{11}B and ^{13}C NMR shifts.[13−18] The GIAO-MP2/II//RMP2(fc)/6-31G* results were superior to the GIAO-MP2/II//MP2(fc)/6-31G* ones in terms of their relation to the experimental findings. There is an excellent agreement between the theoretical and experimental NMR spectra, which provide a good ground for believing that the RMP2(fc)/6-31G* geometries of **2** and **4** (maximum deviation ∼1.5 ppm at GIAO-MP2/II//RMP2-(fc)/6-31G*) are precise. The calculated nucleus independent chemical shifts (NICS)[15] (−28.9 ppm for **2**, -30.0 ppm for **4)** revealed these species to exhibit "three-dimensional aromaticity", which is, on the basis of this criterion, very similar to that for 1,2- and 1,6-C$_2$B$_8$H$_{10}$ (−29.7 ppm, −30.6 ppm,[15] respectively, at GIAO-SCF/6-31G*//RMP2(fc)/6-31G*).

The most significant feature of the computed molecular structures consists of considerable distortion of the Archimedean antiprismatic shape of the cages. In effect, the phosphorus atom is pushed away from the center of the cluster relative to the positions they would have in a regular bicapped square antiprism: this can clearly be seen in Figure 1. As a consequence, the B(3)P(2)B(5) and B(7)P(6)B(9) bond angles in **2** and **4**, respectively, are closed by ∼13° from the value of 90° in the parent $[B_{10}H_{10}]^{2-}$. The expanded B(6)P(2)B(9) and B(2)P(6)B(3) triangles in **2** and **4**, respectively, are another structural consequence of the presence of the phosphorus atoms (for example, B(6)−B(9) in **2** and B(2)−B(3) in **4** are the longest B−B separations).

The neutral compounds *closo* 2,1- and 6,1-PCB$_8$H$_9$ (**2** and **4**) described in this paper are the first representatives of the 10-vertex *closo* family of phosphacarboranes. Both compounds can be now easily prepared by phosphorus insertion from the readily available monocarboranes 4-CB$_8$H$_{14}$ (**1**) and 1-CB$_8$H$_{12}$ (**3**).[8] The constitutions of **2** and **4** are analogous to those of the corresponding *closo* dicarbaboranes 1,2- and 1,6-C$_2$B$_8$H$_{10}$ because the bare P vertex is isolobal with a cage CH group. We are now exploring various isomerization cluster expansion and substitution reactions of the phosphacarborane species outlined in this paper. Moreover, main-group element insertion reactions with other borane and carborane compounds are also studied with the aim of generating new types of chemically versatile heteroborane and heterocarborane cages.

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Supporting Information Available: Coordinates for the RMP2-(fc)/6-31G* calculated structures of the compounds **2** and **4** and the GIAO−SCF/II//RMP2/6-31G* results. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, revision B.2; Gaussian, Inc.: Pittsburgh, PA, 1995.

(15) (a) Schleyer, P. v. R.; Maercker, C.; Dransfeld, A.; Jiao, H.; Hommes N. J. R. *J. Am. Chem. Soc.* **1996**, *118*, 6317−6318. (b) Schleyer, P. v. R.; Najafian, K. *Inorg. Chem.* **1998**, *37*, 3454−3470.

(16) Scott, P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502 and references therein.

(17) Huzinaga, S. *Approximate Atomic Wave Functions*; University of Alberta: Edmonton, 1971.

(18) Kutzelnigg, S. W.; Schindler, M.; Fleischer, U. *NMR, Basic Principles and Progress*; Springer: Berlin, New York, 1990; Vol. 23.