

# Synthesis and Molecular and Crystal Structure of Bis(borane)cyclenphosphorane. First Stable Compound with a Bipyramidally Surrounded Element Having Two Quaternarized Apical Nitrogen Atoms

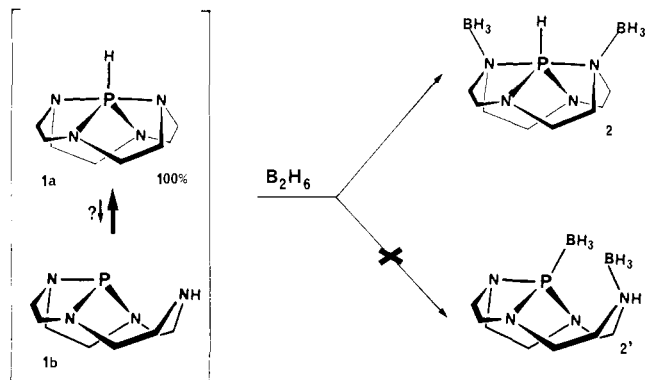
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**Abstract:** Cyclenphosphorane reacts with diborane at 0 °C to afford bis(borane)cyclenphosphorane, (C<sub>8</sub>H<sub>17</sub>N<sub>4</sub>P)(BH<sub>3</sub>)<sub>2</sub> (**2**), in close to quantitative yield. No evidence for the formation of an adduct of the open-form tautomer, as from cyclamphosphorane, was found. **2** provides the first example of a stable H<sub>3</sub>B-N-P-N-BH<sub>3</sub> sequence (dec 200 °C). It crystallizes in the orthorhombic space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> with *a* = 6.217 (2) Å, *b* = 12.557 (4) Å, *c* = 16.519 (6) Å, and *Z* = 4. The arrangement of the five bonds around phosphorus is close to that of a regular trigonal bipyramid (displaced 10.4% from the idealized trigonal bipyramid toward the square pyramid). Both BH<sub>3</sub> groups are coordinated to apical nitrogen atoms, but the B-N bonds do not lie in the same plane, which implies a slightly helical distortion of the molecule. The apical P-N bonds (1.872 (5), 1.864 (5) Å) are the longest reported for a phosphorane, and it is proposed that each of them is a single apical P(V)-N(III) bond. Among the derivatives of cyclenphosphorane whose structure is known, **2** also has the shortest equatorial P-N bonds (1.645 (5), 1.654 (5) Å), for which a compensatory mechanism is suggested. The P-H bond is short (1.25 (5) Å). The N-B bonds (1.597 (10), 1.604 (9) Å) lie in the usual range for amines, which implies unusual basicity for the apical P-bound nitrogen atoms.

Phosphoranes derived from macrocyclic tetraamines such as cyclen, cyclam, and their homologues are of considerable interest, since their polycyclic structures and high symmetry<sup>2</sup> engender original behavior.<sup>2,3</sup>

In solution these tetracyclic tetraaminophosphoranes are in equilibrium with open tricyclic phosphane tautomers, with the exception of cyclenphosphorane (**1**) for which the open tautomeric



form **1b** has never been detected. Under the action of transition-metal derivatives, adducts of the open form of cyclamphosphorane have been obtained, and the equilibrium was eventually completely displaced toward adducts of this form.<sup>4</sup> Similar behavior was observed with a series of bicyclic hydrophosphoranes, which yielded adducts of the corresponding, normally undetected, open phosphane tautomer.<sup>5</sup>

Attempts to reveal such an open form in cyclenphosphorane under the action of diborane failed.<sup>6</sup> Instead the unexpected quantitative formation of bis(borane)cyclenphosphorane (**2**) was observed. This compound is the first stable adduct in which phosphorus(V)-bound, triply coordinated nitrogen atoms display donor character. More generally, it is one of the very few reported examples of compounds in which a nitrogen atom bound to a  $\pi$ -accepting third-row element exhibits definite basicity<sup>7</sup> toward BH<sub>3</sub> to yield a stable adduct. We now report the detailed synthesis and complete structure analysis of **2** and discuss their significance.

## Experimental Section

**Preparation of Bis(borane)cyclenphosphorane (2).** One molar equivalent of B<sub>2</sub>H<sub>6</sub> (0.021 g, 0.76 mmol) was added on a vacuum line to a solution of 0.147 g (0.73 mmol) of cyclenphosphorane **1a** in 5 mL of toluene at 0 °C. A precipitate formed immediately. The solution was stirred 1 h at 0 °C and then filtered. The precipitate was dried, yielding 0.158 g (95%) of **2** as a white, air-stable powder, soluble in CHCl<sub>3</sub>; mp (sealed capillary) 200 °C (dec); mass spectrum (chemical ionization with NH<sub>3</sub>, *m/e*<sup>+</sup>), MH (1.6), [M - BH<sub>3</sub>]H (1.4), [M - 2BH<sub>3</sub>]H (100); <sup>1</sup>H NMR (CDCl<sub>3</sub>) 7.27 ppm (H-P, d, <sup>1</sup>J<sub>HP</sub> = 790 Hz); <sup>31</sup>P NMR (CDCl<sub>3</sub>) -28 ppm (upfield from 85% H<sub>3</sub>PO<sub>4</sub>, d, <sup>1</sup>J<sub>PH</sub> = 790 Hz); <sup>11</sup>B NMR (CDCl<sub>3</sub>) -15.7 ppm (upfield from Et<sub>2</sub>O·BF<sub>3</sub>, q, <sup>1</sup>J<sub>BH</sub> = 100 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) +41.2 (d, <sup>2</sup>J<sub>PC</sub> = 10 Hz), +50.2 ppm (d, <sup>2</sup>J<sub>PC</sub> = 7.5 Hz); IR (KBr) 2260 (s), 2300 (s), 2350 (shoulder), 2370 (shoulder), 2420 (m) cm<sup>-1</sup>. Anal. Calcd for C<sub>8</sub>H<sub>23</sub>B<sub>2</sub>N<sub>4</sub>P: C, 42.16; H, 10.17; B, 9.49; N, 24.58; P, 13.59. Found: C, 42.23; H, 10.31; B, 9.20; N, 24.12; P, 13.64.

When half a molar equivalent of B<sub>2</sub>H<sub>6</sub> is added to **1** under the same conditions, the same product is formed but in 47% yield; the filtrate then contains the remaining unconsumed cyclenphosphorane.

**X-ray Crystallographic Study of 2.** A suitable crystal of **2** was obtained by dissolving the above crystalline powder in dry chloroform and allowing the solution to evaporate very slowly at 0 °C under an argon

(1) (a) Université de Nice. (b) Université de Rennes.  
 (2) (a) Richman, J. E. *Tetrahedron Lett.* 1977, 559. Guggenberger, L. J., personal communication. (b) Richman, J. E.; Atkins, T. J. *Tetrahedron Lett.* 1978, 4333. (c) Atkins, T. J.; Richman, J. E. *Tetrahedron Lett.* 1978, 5149. (d) Richman, J. E.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* 1981, 20, 3378. (e) Richman, J. E.; Gupta, O. D.; Flay, R. B. *J. Am. Chem. Soc.* 1981, 103, 1291. (f) Richman, J. E.; Flay, R. B. *J. Am. Chem. Soc.* 1981, 103, 5265. (g) Richman, J. E.; Kubale, J. J. *J. Am. Chem. Soc.* 1983, 105, 749.  
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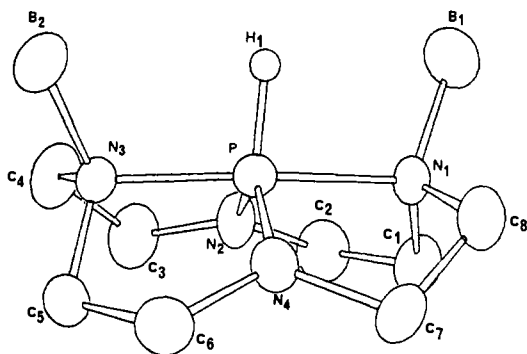


Figure 1. ORTEP view of the  $\text{HP}(\text{CH}_2\text{CH}_2\text{N})_4(\text{BH}_3)_2$  molecule (**2**).

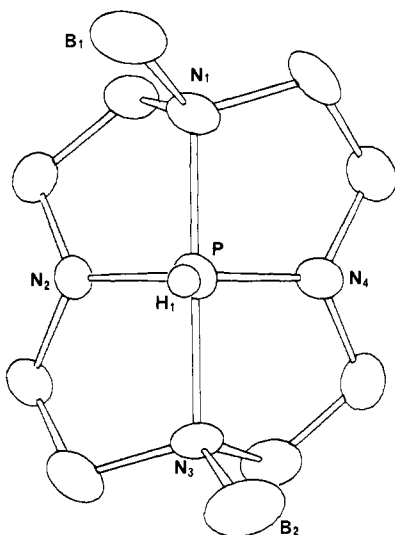


Figure 2. ORTEP view of **2** showing the skew position of the  $\text{BH}_3$  groups with respect to the P-H bond.

atmosphere. Crystals are air stable and colorless with various shapes.

Crystals of  $\text{C}_8\text{H}_{23}\text{B}_2\text{N}_4\text{P}$  ( $M_r = 227.9$ ) were found to be orthorhombic, with cell dimensions  $a = 6.217$  (2) Å,  $b = 12.557$  (4) Å, and  $c = 16.519$  (6) Å and  $V = 1289.6$  Å<sup>3</sup>. The space group is  $P2_12_12_1$  with  $Z = 4$  and a calculated density of  $1.17$  g·cm<sup>-3</sup>. The unit cell parameters were refined by using the angles of 20 reflections measured on a Nonius CAD4 automatic diffractometer.

The intensities of 1480 reflections were collected at room temperature, in the  $2^\circ < \theta < 26^\circ$  range, on a crystal of dimensions  $0.22 \times 0.13 \times 0.09$  mm. Owing to this small size and to the low value of the linear absorption coefficient ( $\mu = 1.8$  cm<sup>-1</sup>) for the Mo  $K\alpha$  radiations used ( $\lambda = 0.71073$  Å), absorption corrections were considered unnecessary.

The characteristics of diffractometer measurements were as follows: graphite monochromator;  $\omega - 2\theta$  scan technique; scan angle,  $S = 1.20 + 0.35 \tan \theta$  (deg); detector aperture,  $D = 1.40 + 0.50 \tan \theta$  (min). After corrections for Lorentz and polarization effects, reflections having  $\sigma(I)/I > 1$  were considered to be unobserved. Finally, 856 independent reflections were used for the structure analysis.

The structure was solved on a PDP 11/60 computer using the Enraf-Nonius SDP.<sup>8</sup> Atomic positions were obtained with program MULTAN and subsequent Fourier difference synthesis for the 15 nonhydrogen atoms of the molecule that constitute the asymmetric unit.

Least-squares refinement of coordinates and thermal parameters, first isotropic and then anisotropic, of these 15 atoms and a secondary extinction coefficient led to values of  $R = \sum(|F_o| - |F_c|) / \sum|F_o| = 0.094$  and  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.109$ . At this stage of refinement, a Fourier difference map showed the hydrogen atoms. They were introduced isotropically but not refined, with the exception of H1, bound to P, for which coordinates and isotropic thermal parameters were refined. Two last cycles of refinement of H1 and of the 15 non-hydrogen atoms (coordinates and anisotropic thermal parameters) significantly

Table I. Bond Lengths (Å) and Angles (deg) for **2**<sup>a</sup>

P-N1	1.872 (5)	N3-B2	1.604 (9)
P-N2	1.645 (5)	N3-C4	1.481 (7)
P-N3	1.864 (5)	N3-C5	1.486 (7)
P-N4	1.654 (5)		
		N4-C6	1.444 (7)
P-H1	1.25 (5)	N4-C7	1.442 (7)
N1-B1	1.597 (10)	C1-C2	1.489 (9)
N1-C1	1.485 (8)	C3-C4	1.514 (9)
N1-C8	1.496 (8)	C5-C6	1.532 (8)
		C7-C8	1.518 (9)
N2-C2	1.445 (8)		
N2-C3	1.452 (7)		
N1-P-N2	88.5 (2)	P-N2-C2	119.7 (4)
N1-P-N3	176.8 (3)	P-N2-C3	119.5 (4)
N1-P-N4	90.0 (2)	C2-N2-C3	120.5 (5)
N2-P-N3	89.7 (2)		
N2-P-N4	125.6 (3)	P-N3-C4	106.2 (4)
N3-P-N4	88.9 (2)	P-N3-C5	105.3 (4)
N1-P-H1	88 (2)	P-N3-B2	112.1 (4)
N2-P-H1	120 (2)	C4-N3-C5	111.5 (5)
N3-P-H1	95 (2)	C4-N3-B2	110.3 (5)
N4-P-H1	114 (2)	C5-N3-B2	111.3 (4)
P-N1-C1	105.3 (4)	P-N4-C6	119.1 (4)
P-N1-C8	106.3 (4)	P-N4-C7	118.8 (4)
P-N1-B1	110.8 (4)	C6-N4-C7	120.5 (5)
C1-N1-C8	111.3 (6)		
C1-N1-B1	112.3 (5)	N1-C1-C2	107.6 (6)
C8-N1-B1	110.6 (6)	N2-C2-C1	105.4 (6)
		N2-C3-C4	105.0 (5)
		N3-C4-C3	108.3 (5)
		N3-C5-C6	105.9 (4)
		N4-C6-C5	105.1 (4)
		N4-C7-C8	105.6 (5)
		N1-C8-C7	107.3 (5)

<sup>a</sup> Esd's are given in parentheses.

reduced  $R$  and  $R_w$  to their final values of 0.057 and 0.054, respectively. The esd of an observation of unit weight is 1.219. Interatomic distances and angles are given in Table I. The numeration is the same as in Figures 1 and 2, which show two ORTEP views of the molecule.

## Discussion

**Synthesis and Solution Data.** Cyclenphosphorane reacts readily with 1 equiv of diborane to give the bis(borane) adduct **2** in nearly quantitative yield. No evidence was found for the formation of phosphorus and/or nitrogen adducts of the open-form tautomer **1b**, such as **2'**. The same product was obtained in the presence of an excess or shortage of diborane, along with, in the latter case, unreacted starting material. The action of transition-metal derivatives such as  $[\text{RhCl}(\text{CO})_2]_2$  on **1a** has so far failed to provoke any tautomeric rearrangement of the initial phosphorane structure.

In solution, the <sup>31</sup>P NMR spectrum of **2** in  $\text{CDCl}_3$  exhibits a single sharp high-field doublet at  $-28$  ppm (from 85%  $\text{H}_3\text{PO}_4$ ), characteristic of five-connected phosphorus with  $J_{\text{PH}} = 790$  Hz. The <sup>11</sup>B spectrum consists of a single quartet at  $-15.7$  ppm (from  $\text{Et}_2\text{O} \cdot \text{BF}_3$ ;  $J_{\text{BH}} = 100$  Hz), a position usually found for N-coordinated  $\text{BH}_3$  groups.<sup>9</sup> The <sup>13</sup>C NMR spectrum displays only two  $\text{CH}_2$  signals, of equal intensity, at  $+41.2$  and  $+50.2$  ppm; this can only be consistent with the presence of the two  $\text{BH}_3$  groups on two nitrogen atoms symmetrically located in the macrocycle.

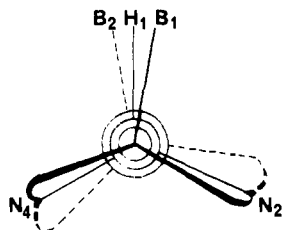
The remarkable stability of **2** is illustrated by its rather high decomposition point ( $\sim 200$  °C), which is much higher than the melting point of **1a** ( $112$ – $115$  °C).

**Crystal Structure.** The dominant structural features of **2** (Figure 1) are the preservation of the initial pentacoordinated phosphorus form, the coordination of its apical nitrogen atoms to  $\text{BH}_3$  groups, the closeness to a regular trigonal bipyramid of the arrangement of the five bonds around phosphorus, and the unusually long apical and short equatorial P-N bond distances.

The molecule has no crystallographic symmetry. The P, N1, N3, and H atoms are located in the same plane (plane 1). With respect to this reference plane, atoms B1 and B2 are located at about equal distances on both sides, their distances to plane 1 being respectively 0.65 and  $-0.53$  Å (Figure 2). The molecule displays

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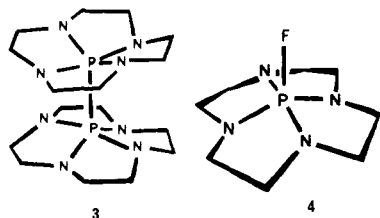


**Figure 3.** Schematic view along the N1-P-N3 axis showing the helical distortion of molecule **2**.

a slight helical distortion, as shown in Figure 3. The atoms N2 and N4, as well as the carbon atoms, hence exhibit comparably dissymmetrical positions with respect to plane 1. The P, N2, N4, and H atoms belong to the same plane (plane 2). Planes 1 and 2 are orthogonal (dihedral angle of  $90.7^\circ$ ). The absolute configuration of the helical, hence chiral, molecule could not be determined since the *R* and *R<sub>w</sub>* factors obtained for the two enantiomorphs did not differ significantly.

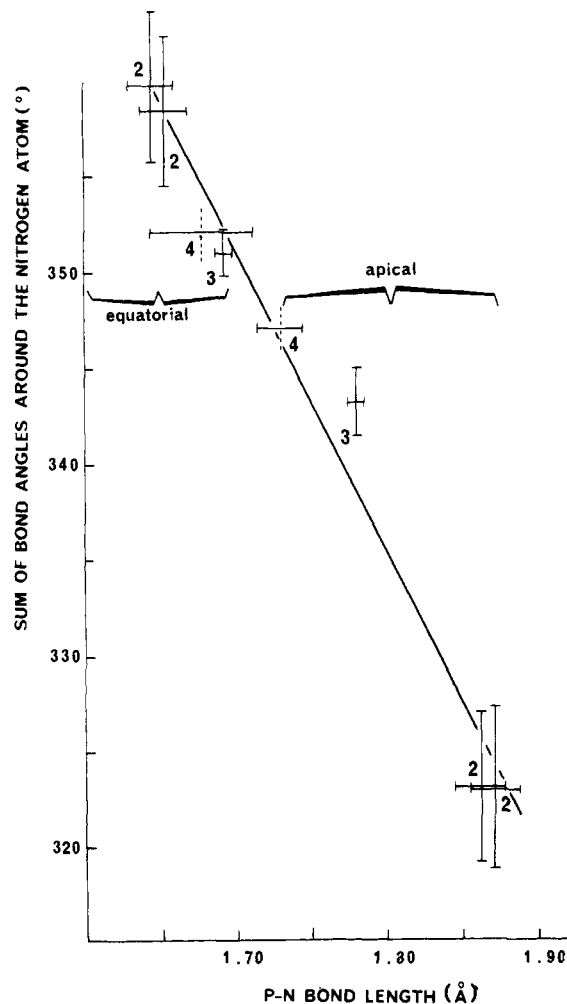
In spite of the presence in **2** of four five-membered rings, all in axial-equatorial position, the arrangement of the five bonds around phosphorus is remarkably close to that of a regular trigonal bipyramid (TP). The minute structural distortion from TP is reflected in the values of the axial and equatorial N-P-N angles of  $176.8(3)^\circ$  and  $125.6(3)^\circ$ , respectively.

By the use of the dihedral angle method<sup>10</sup> and unit bond lengths, it was estimated that the structure is displaced by 10.4% along the Berry coordinate<sup>11</sup> from the ideal TP toward the ideal square pyramid (SP), H1 being the pivotal atom in the pseudorotation process (on the Berry coordinate 0% represents the TP and 100% the SP structure).<sup>12</sup> For lack of structural data on cyclenphosphorane itself,<sup>13</sup> this distortion should be compared with that of 32.9% reported for bis(cyclenphosphorane) (**3**)<sup>2d</sup> whose geom-



etry at phosphorus is significantly more displaced toward the SP. For fluorocyclenphosphorane (**4**), another derivative of cyclenphosphorane, the geometrical configuration at the penta-coordinated phosphorus was stated to be essentially midway between the SP and TP geometries.<sup>2a</sup>

Structure **2** provides the first example of a bipyramidally surrounded element having two quaternarized apical nitrogens; this renders the discussion of the P-N bond lengths particularly worthwhile. The equatorial P-N bonds are much shorter, and the apical ones much longer, than the sum of Pauling's single-bond radii (1.80 Å for tetrahedral P(V) and N(III)<sup>14</sup>) or the value of 1.77 Å, as found in  $\text{Na}[\text{H}_3\text{N}-\text{PO}_2]$ ,<sup>15</sup> often proposed as a standard P(V)-N(III) single bond. The equatorial P-N bonds (1.654 (5) and 1.645 (5) Å) lie in the lower part of the usual range (1.62-1.71



**Figure 4.** Sum of bond angles around the nitrogen atom vs. P-N bond lengths in three derivatives of cyclenphosphorane: bis(borane)cyclenphosphorane (**2**); bis(cyclenphosphorane) (**3**);<sup>2d</sup> fluorocyclenphosphorane (**4**)<sup>2a</sup> (for this last, no esd's for the bond angles were reported by the authors).

Å)<sup>16</sup> for such bonds; their shortness with respect to the above "standards" can in part be assigned to the  $\text{sp}^2$  type hybridization of the planar nitrogens and in part to a  $\text{N}_p\pi-\text{P}_d\pi$  contribution to bonding.<sup>17</sup> The apical P-N bonds are remarkably longer (average 1.868 (5) Å), significantly longer in fact than all those as yet reported for phosphoranes (1.70-1.83 Å).<sup>16</sup> But the latter values involve either planar or strongly flattened tetrahedral nitrogen atoms; the change to a regular tetrahedral nitrogen atom and the involvement of its lone pair in bonding with boron, which prevents any significant  $\text{N}_p\pi-\text{P}_d\pi$  interaction from occurring, must account for the observed lengthening. The latter factor may in turn, by a compensatory mechanism, cause an enhancement of the phosphorus  $\pi$ -acceptor character in its equatorial plane, thus further contributing to increasing the difference between the two sets of P-N bonds. That this difference constitutes an extreme case is illustrated by comparing the ratios of the apical to equatorial bond lengths for compounds **2** (1.13 Å), **4** (1.04 Å), and **3** (1.05 Å). As no  $\pi$  contribution can be envisaged between phosphorus and the quaternarized nitrogen atoms, the bond distance of 1.87 Å can be proposed as an apical single bond between a bipyramidal P(V) and a tetrahedral N(III). By contrast, maximum  $\text{P}_d\pi-\text{N}_p\pi$  bonding is achieved with the planar equatorial nitrogen atoms (sums,  $\sum\text{N}$ , of the angles around N2

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(12) It was estimated, for **2**, that a Berry coordinate is strictly followed for structural distortions, since the deviation calculated from the dihedral angles<sup>10</sup> with respect to the most symmetrical low-energy apical-equatorial bending pathway is only  $0.6^\circ$ , a value that lies within the limit of experimental error.

(13) Hamerlinck et al. published the structure of cyclenphosphorane.<sup>3b</sup> Though the trigonal-bipyramidal configuration of the phosphorus is clearly proven, too much reliance could not be placed on the values of angles and bond distances as a result of the high *R* factor of 0.22 due to disorder in the crystals.

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(15) Hobbs, E.; Corbridge, D. E. C.; Raistrick, B. *Acta Crystallogr.* **1953**, *6*, 621.

(16) (a) Holmes, R. R. "Pentacoordinated Phosphorus"; American Chemical Society: Washington, DC, 1980; ACS Monogr. No. 175. (b) Day, R. O.; Schmidpeter, A.; Holmes, R. R. *Inorg. Chem.* **1982**, *21*, 3916. (c) Day, R. O.; Schmidpeter, A.; Holmes, R. R. *Inorg. Chem.* **1983**, *22*, 3696.

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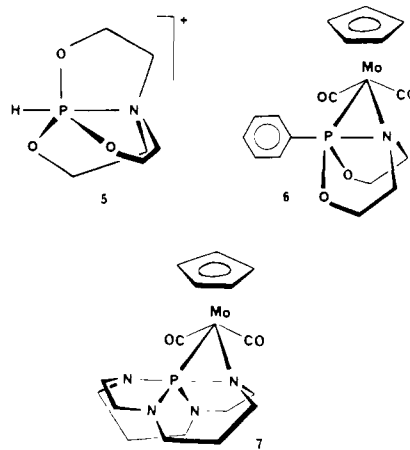
and N4 are  $359.7 \pm 3.9^\circ$  and  $358.4 \pm 3.9^\circ$ , respectively) which have their substituents favorably oriented perpendicular to the equatorial plane.<sup>18</sup>

Figure 4 shows the linear relation<sup>19</sup> that exists between the sums of the bond angles around the nitrogen atoms and the corresponding P–N bond lengths in **3**, **4**, and **2**. Again the case of **2** is extreme and exemplary: it combines the longest apical P–N bonds (with regular tetrahedral geometry about the nitrogen atoms and mean values of the six angles around N1 of  $109.4 (5)^\circ$  and around N3 of  $109.5 (4)^\circ$ ) with the shortest equatorial P–N bonds (with planar geometry about the nitrogen atoms). This compensatory apical lengthening/equatorial shortening phenomenon also explains that **2** can adopt a closer to TP structure than **3** or **4**.

The P–H bond in **2** ( $1.25 (5) \text{ \AA}$ ) is the shortest, or among the shortest, reported for a phosphorane. The range of previously known P–H bond lengths in phosphoranes extends from  $1.32 (2)$  to  $1.50 (6) \text{ \AA}$ .<sup>10</sup> The sum of Pauling's covalent radii, corrected for an  $sp^2$  hybridization of phosphorus in the equatorial plane, is  $1.31 \text{ \AA}$ .<sup>14</sup> The increased  $\pi$  character of the equatorial P–N bonds and the synergic increase in electroattracting character of the nitrogen atoms within the  $\sigma$ -bond frame, and resulting shrinkage of the phosphorus orbitals, may in turn explain the short P–H bond observed in **2**.

It is also remarkable that the N–B bond lengths in **2** ( $1.597 (10)$  and  $1.604 (9) \text{ \AA}$ ) lie well within the usual range reported for N–BH<sub>3</sub> bonds ( $1.56$ – $1.66 \text{ \AA}$ ),<sup>7a,20</sup> in spite of the nitrogen atoms being bound to a  $\pi$ -accepting third-row element. They are significantly shorter than that reported for (H<sub>3</sub>B)P(OCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>N–(BH<sub>3</sub>) ( $1.655 (8) \text{ \AA}$ ),<sup>7a</sup> which appears to be the first stable compound showing that a phosphorus-bound nitrogen atom may exhibit strong basicity. The N–B bond lengths in **2** thus further imply a definite basicity of the apical nitrogen atoms toward diborane. The closest related yet quite different situation is found

in atrane-type structures.<sup>21</sup> Four-coordinated nitrogens are present in Verkade's phosphatranes (**5**)<sup>22</sup> and Turley's silatranes,<sup>23</sup> in which



one, "transannular", nitrogen atom acts as a donor to form an intramolecular coordination bond with phosphorus or silicon. The resulting bond is particularly long, however ( $1.986 \text{ \AA}$  in **5**), which probably indicates a relatively weak interaction. Another case, also distinct, is that of the transition-metal phosphoranides (**6**, **7**)<sup>4a,24</sup> in which both the phosphorus and nitrogen atoms are coordinated to the metal.

**Registry No.** **1a**, 64317-97-1; **2**, 84237-90-1; B<sub>2</sub>H<sub>6</sub>, 19287-45-7.

**Supplementary Material Available:** Tables of atomic coordinates and thermal parameters, calculated and observed structure factors, and least-squares planes (7 pages). Ordering information is given on any current masthead page.

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