Contributions to the Chemistry of Boron, **205')** 



## **Formation of Phosphinoborane Rings. A Reinvestigation of the Reaction of**   $\lceil$ (CH<sub>3</sub>)<sub>3</sub>Si]<sub>3</sub>P with Borane(3)

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Combination of  $Me<sub>3</sub>Si<sub>3</sub>P$  and  $H<sub>3</sub>B$   $THF$  results in the formation of the known adduct (Me,Si),P-BH, **(1).** The complex undergoes dehydrosilylation above lOO"C, and two ring compounds,

The reactions of phosphanes,  $PX_3$ , with boranes,  $BY_3$ , have been studied over the last fifty years<sup>2, 3)</sup>, but for many combinations, the products and reaction mechanisms remain incompletely characterized. For example, it is wellknown that most acid-base pairs produce isolable compounds  $X_3P \cdot BY_3$ . In turn, many of these simple compounds undergo subsequent **XY** elimination reactions with formation of a host of different boron-phosphorus ring compounds,  $[X_2PBY_2]_n$ , or oligomeric species that are poorly defined. As an illustration, Parshall and Lindsey<sup>4)</sup> reported the reaction of  $(Me_3Si)_3P$  with  $B_2H_6$  in tetrahydrofuran and the isolation of crystalline  $(Me_3Si)_3P\cdot BH_3$  (1). The adduct was reported to slowly decompose at  $25^{\circ}$ C and rapidly decompose at its melting point,  $100-107$ °C. Leffler and Teach') identified one coproduct of the thermal decomposition reaction as Me<sub>3</sub>SiH. They also noted that heating the adduct at 135°C for 14 hours produced a yellow liquid that was suggested to contain several products. Noth and Schrägle<sup>6)</sup> found that Me<sub>3</sub>SiH was evolved in two stages when the adduct was heated at 125 and then at 200°C. On the basis of the amount of Me3SiH evolved, it was suggested that the first product formed was  $[(Me<sub>3</sub>Si)<sub>2</sub>PBH<sub>2</sub>]<sub>m</sub>$  and the second, yellow-brown polymeric product was  $[Me_3SiPBH]_n$ . No further studies of this system have appeared, but in related work Nöth and Schrägle<sup>7)</sup> studied the thermal decompositions of  $(Me_3Si)Et_2P·BH_3$  and  $(Me_3Si)Bu_2P·BH_3$ . At temperatures above 200 $^{\circ}$ C, Me<sub>3</sub>SiH was rapidly evolved, and according to elemental analysis data and cryoscopic molecular weight measurements, it was concluded that trimeric ring compounds,  $(Et_2P\cdot BH_2)$ <sub>3</sub> and  $(Bu_2P\cdot BH_2)$ <sub>3</sub>, were formed.

We have used  $Me<sub>3</sub>SiX$  elimination reactions to prepare a number of new phosphinoborane ring and cage compounds<sup>8-11</sup>, and in the course of that work we have reinvestigated the complex pyrolysis of  $(Me<sub>3</sub>Si)<sub>3</sub>P·BH<sub>3</sub>(1)$ . The

 $[(Me<sub>3</sub>Si)<sub>2</sub>PBH<sub>2</sub>]$ <sub>3</sub> (2) and  $P[(\mu-H-B<sub>2</sub>-H<sub>2</sub>)]$  $\{(BH<sub>2</sub>)<sub>2</sub>[P(SiMe<sub>3</sub>)<sub>2</sub>]\frac{1}{2}$ <sub>2</sub> (3), are isolated. The crystal structures of the compounds are compared with those of other phosphinoboranes.

adduct undergoes a small degree of decomposition even at  $25^{\circ}$ C in benzene solution, as evidenced by the appearance of several low-intensity resonances in the  $31P-NMR$  spec- $-182$ ,  $-140$ ,  $-129$ ,  $-118$ ,  $-106$ . The <sup>31</sup>P{<sup>1</sup>H}- and <sup>11</sup>B-NMR spectra for a pure sample of 1 in  $C_6D_6$  recorded immediately after sample preparation show resonances at  $\delta =$  $-193.8$  and  $-38.7$  ( $J_{BH} = 108$  Hz), respectively. As might be expected, the formation of impurities or secondary reaction products is enhanced when small excesses of  $H_3B$ . THF are present in the initial reaction mixture. trum:  $\delta^{31}P_1^{\{1\}}(C_6D_6) = -251, -203, -197, -191, -186,$ 

Pyrolysis of **1** under nitrogen in a closed vessel at 100°C slowly produces Me<sub>3</sub>SiH, as indicated by gas-phase infrared and mass spectra. For a 0.5-g sample of **1,** gas evolution ceases after  $\approx$  12 hours, and  $\approx$  50% of the Me<sub>3</sub>SiH expected

from the reaction shown in equation (1) is isolated.  
\n
$$
n \left(Me_3Si\right)_3 P \cdot BH_3 \xrightarrow{\Delta T} \left[(Me_3Si)_2 P \cdot BH_2\right]_n + n \text{ Me}_3 SiH
$$
 (1)

The <sup>31</sup>P ${^1H}$ - and <sup>11</sup>B ${^1H}$ -NMR spectra of the resulting oil suggest the formation of several products with major resonances<sup>12)</sup> found at  $\delta^{31}P_1^{1}H_1^{1}(C_6D_6) = -251, -208,$  $-205, -203, -198, -161, -142,$  and  $-29$ . The resonance at  $\delta = -251$  may be assigned to free (Me<sub>3</sub>Si)<sub>3</sub>P. The  $^{11}B$ <sup>{1</sup>H}-NMR spectrum for this sample shows relatively broad, strong resonances centered at  $\delta = -40, -35, -30.6,$  $-30.0$  and 18. Restoration of proton coupling only results in apparent broadening of the resonances. Under these conditions, it appears that a majority of **1** is consumed.

**A** fresh sample of **1** was heated at 150°C for 12 hours in a sealed tube. Decomposition coproduct Me<sub>3</sub>SiH was rapidly formed, and it was vacuum-evaporated after cooling the reaction mixture to 20°C. NMR spectra for the remaining yellow oil show some simplification compared to spectra obtained at 100°C. The <sup>31</sup>P{<sup>1</sup>H}-NMR spectrum  $(C_6D_6)$ shows major resonances centered at  $\delta = -251, -208,$  $-203$ ,  $-198$ ,  $-142$ , and  $-29^{13}$ , and the  $^{11}B$ <sup>[1</sup>H]-NMR spectrum contains major resonances at  $\delta = -40, -35.7,$ and 18. Another fresh sample of **1** was heated at 175°C for 12 hours, and after removal of Me<sub>3</sub>SiH, NMR spectra were recorded for the resulting yellow oil: <sup>31</sup>P{<sup>1</sup>H}  $\delta = -251$ ,  $-236$ ,  $-208$ ,  $-203$ ,  $-142$ ;  $^{11}B$ {<sup>1</sup>H}  $\delta = -40.7$ . A weak resonance remains in the <sup>31</sup>P ${^1H}$  spectrum at  $\delta = -198$ . The resonance at  $\delta = -236$  may be assigned to  $(Me<sub>3</sub>Si)<sub>2</sub>PH<sup>14</sup>$ . Finally, a sample of 1 was heated at 210<sup>°</sup>C for 12 hours, and NMR spectra were obtained for the remaining yellow-orange oil:  ${}^{31}P{^1H} \delta = -251, -236,$  $-203$ ,  $-142$ ;  $^{11}B$ <sup>1</sup>H<sub>i</sub>  $\delta = -40.1$ . Very weak resonances remain in the <sup>31</sup>P ${}^{31}$ P ${}^{11}$  spectrum at  $\delta = -208$  and  $-198$ . Variable-temperature  $(+ 60 \text{ to } -70^{\circ}\text{C})$  <sup>11</sup>B-NMR spectra were recorded for the last two samples, but no evidence was gained on boron-hydrogen coupling patterns.

During the course of the **NMR** analyses of the pyrolysis products from **1,** colorless single crystals formed in the oil produced at 150°C. Microscopic examination revealed two habits, and the structures of both were studied by singlecrystal X-ray diffraction analysis. Crystals that formed as relatively thin parallelepipeds were found to have a composition  $[(Me<sub>3</sub>Si)<sub>2</sub>PBH<sub>2</sub>]<sub>3</sub>$  (2). The structure displays a planar, six-membered ring geometry, and a view of the molecule is shown in Figure 1.



Figure 1. Molecular structure and atom labeling scheme for **2** (20% Figure 1. Molecular structure and atom labeling scheme for 2 (20%<br>thermal ellipsoides). Selected bond distances (Å):  $P(1) - B(1)$ <br>1.966(10),  $P(2) - B(1)$  1.974(6),  $P(2) - B(2)$  1.991(6),  $P(1) - Si(1)$ <br>2.254(2),  $P(2) - Si(2)$  2

The ring in 2 is drastically flattened<sup>15)</sup> compared to the six-membered rings in  $(Me_2PBH_2)_3^{16}$  and  $(Ph_2PBH_2)_3^{17}$  that display chair-type cyclohexane-like conformations. The average  $P - B$  bond length in 2, 1.972 Å  $\int$ 1.984(11) $- 1.957(7)$  Å], is longer than the average P-B bond lengths in  $[Me_2PBH_2]_3$ , 1.935 Å,  $[Ph_2PBH_2]_3$ , 1.948 Å, and in the decalin analog,  $C_9H_{35}B_5P_5Br^{18}$ , 1.942 Å. As expected, the  $P - B$  bond distances in these compounds are much longer than the average  $P - B$  distances in the recently reported planar boraphosphabenzenes<sup>19)</sup> [MesBPPh]<sub>3</sub>,

1.842 Å, and  $[MesBPC<sub>6</sub>H<sub>11</sub>]<sub>3</sub>$ , 1.839 Å. The flattening of the ring in **2** results in significant differences between average internal  $B - P - B$ , 122.4°, and  $P - B - P$ , 117.3°, ring angles. The corresponding average  $B - P - B$  and  $P - B - P$  angles in  $[\text{Me}_2\text{PBH}_2]$ <sub>3</sub> and  $[\text{Ph}_2\text{PBH}_2]_3$  are 118 and 112.2, and 114.3 and 112.2°. The  $B - P - B$  and  $P - B - P$  angles in the planar borophosphabenzene [MesBPPh]<sub>3</sub> are 124.5 and 114.9°, respectively. The average  $Si-P-Si$  bond angle,  $105.8^\circ$ , on the other hand, is only slightly greater than the  $C - P - C$  angles in  $\text{[Me}_2\text{PBH}_2\text{]}_3$ , 100.4(9), and  $\text{[Ph}_2\text{PBH}_2\text{]}_3$ , 103.1'. Clearly, the geometry about the phosphorus atoms in *2* deviates considerably from the ideal tetrahedral condition, and these atoms absorb the flattening effect.

## $[(Me<sub>3</sub>Si)<sub>2</sub>PBH<sub>2</sub>]$ ,  $P[(\mu-H-B<sub>2</sub>H<sub>2</sub>)]{(BH<sub>2</sub>)<sub>2</sub>[P(SiMe<sub>3</sub>)<sub>2</sub>]}<sub>2</sub>$  $\overline{2}$ 3

The second habit formed as needles, and they were found to have the composition **3. A** view of the molecule is shown in Figure 2. The structure of **3** is unique. It may be looked at as two distorted (PB)<sub>3</sub> cyclohexane rings in boat conformation sharing a common phosphorus atom. Planes defined by  $B(1)$ ,  $B(2)$ ,  $B(3)$  and  $B(1')$ ,  $B(2')$ , and  $B(3')$  are twisted with respect to each other by 74.5°, and view of this distortion is shown in Figure 3. Further, the two adjacent boron atoms  $B(3)$  and  $B(3')$  each possess *one* terminal  $B - H$  bond, and they share a single bridging hydrogen atom. The internal angle  $B(3) - P(1) - B(3')$ , 61.7(2)°, is considerably compressed relative to the angles  $B(1)-P(1)-B(1')$ , 123.4(3)<sup>o</sup>,  $B(1) - P(1) - B(3)$ , 114.7(2)°, and  $B(1) - P(1) - B(3')$ , 113.4(2)°. The angles  $P(1)-B(1)-P(2)$ , 109.6(2), and  $P(2)-B(2)-P(3)$ , 112.8(2)°, are significantly more acute than  $P(1) - B(3) - P(3)$ , 118.9(2)<sup>o</sup>. The P-B bond distances are very irregular, with  $P(1) - B(3)$  in the  $P[\mu - H(B_2H_2)]$  fragment much shorter, 1.918(4) **A,** than the remaining distances that fall in an order  $P(1) - B(3) \le P(1) - B(1) \simeq (2) - B(1) \simeq P(3) - B(3) < P(2) B(2) < P(3) - B(2)$ .

It has not been possible to cleanly separate **2, 3,** and the yellow oil in significant quantities, and this has hindered the interpretation of some of the spectroscopic data. Nonetheless, given the results of the structural studies, some assignments are possible. The mass spectrum *(55* eV) of a sample rich in 2 shows ions at  $m/z$  570-567 that may be assigned to the parent ion envelope of the trimer. Several reasonable fragment ion envelopes for such a molecule are also observed. The parent envelope for **3** should begin at *mJz* 817; however, the highest mass ions detected from a mixture of **2** and **3** appear at *mlz* 799-794. Attempts to detect the parent ion at lower ionization voltages were not successful.

The NMR spectra are particularly difficult to unambiguously interpret due to the large number of phosphorus resonances and the lack of resolution of  $B - H$  coupling in the <sup>11</sup>B spectra. Two resonances in the <sup>31</sup>P ${^1H}$  spectra,  $\delta$  =  $-251$  and  $-236$ , are present in several samples, and these correspond to  $(Me_3Si)_3P$  and  $(Me_3Si)_2PH$ . Very small amounts of (Me<sub>3</sub>Si)PH<sub>2</sub> are also detected at  $\delta = -235.3$ . The  ${}^{31}P_1^{\{1\}}$ -NMR spectrum of 2 should show a single res-



Figure 2. Molecular structure and atom labeling scheme for 3 (20% thermal ellipsoids). Selected bond distances (Å):  $P(1) - B(1)$  1.948(5), Figure 2. Molecular structure and atom labeling scheme for 3 (20%<br>thermal ellipsoids). Selected bond distances (A): P(1) - B(1) 1.948(5),<br>P(2) - B(1) 1.959(4), P(1) - B(3) 1.918(4), B(2) - P(3) 2.000(5). <br>  $B(1) - P(1) - B(3)$  114.7(2),  $B(3) - P(1) - B(1)$ , 113.4(2),  $B(3)-P(1)-B(3')$  61.7(2),  $B(1)-P(1)-B(1')$  123.4(3),  $P(1)-B(1)-P(2)$  109.6(2),  $B(1)-P(2)-B(2)$  116.0(2),  $\overrightarrow{P(1)} - \overrightarrow{B(3)} - \overrightarrow{P(3)}$  118.9(2),  $\overrightarrow{P(2)} - \overrightarrow{B(2)} - \overrightarrow{P(3)}$  112.8(2),  $\overrightarrow{B(2)} - \overrightarrow{P(3)} - \overrightarrow{B(3)}$  118.4(2)  $P(2) - B(2)$  1.974(5),  $P(3) - B(3)$  1.961(4). Selected angles (°):



Figure 3. View of molecule **3** showing the twist of the two sixmembered rings

onance at high field, and the resonance at  $\delta = -208$  is tentatively assigned to the trimer. This peak appears even in very small amounts in unheated samples, and it appears in significant concentration after heating samples at 100 to 175 $\degree$ C. Above 175 $\degree$ C, the material apparently decomposes since the resonance disappears. The resonance is slightly upfield of the <sup>31</sup>P resonance for 1,  $-193.8$ , and these shifts may be compared with data for  $Me_3P \cdot BH_3$ ,  $\delta = -36.5$ ,  $J_{\text{BP}} = 61 \text{ Hz}$ , and  $(\text{Me}_2 \text{PBH}_2)_{3}^{20, 21}$ ,  $\delta = -48.2$ . The boron-11 shift for 2 is tentatively assigned to the resonance at  $\delta =$ **-35.7,** which **is** reduced in intensity in the 175°C sample and disappears from samples heated above 175°C.

The <sup>31</sup>P-NMR spectrum of **3** should display three resonances in a 2:2:1 ratio. No such pattern is obvious in the spectra from any of the samples; however, this species may be present in only relatively small amounts given the small population of the material in crystalline samples. Two  $^{31}P$  resonances at  $\delta = -203$  and  $-142$  are present with significant intensity in all heated samples. Assignment of these resonances has not been accomplished, although the lowerfield resonance is a doublet in the proton-coupled spectrum, so the species clearly contains a  $P-H$  unit.

The specific mechanism for formation of **2** and **3** was not studied; however, the formation of trimeric 2 in the pyrolysis of 1, as shown in equation (1)  $(n = 3)$ , is not unexpected. For example, pyrolysis of  $Me<sub>2</sub>(H)P·BH<sub>3</sub>$  produces an analogous trimer,  $(Me_2PBH_2)$ <sup>22</sup>. The generation of 3, on the other hand, has no precedent. However, its formation may be considered to arise from interaction of two trimeric rings with elimination of  $(Me_3Si)_3P$ , which is identified in  $^{31}P$ -NMR spectra of reaction mixtures, and  $Me<sub>3</sub>SiH$ . The formation process is schematically described in equation *(2).* 



Precedence for elimination reactions of  $(Me_3Si)_3P$  from condensation reactions of [(trimethylsilyl)phosphino]boranes may be found in several other studies<sup>23)</sup>.

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## **Experimental**

All manipulations of the reagents were performed under dry nitrogen or in vacuo.  $-$  MS: Finnegan GC/MS spectrometer.  $-$ NMR: Varian FT-80 and JEOL GSX-400 spectrometers. <sup>11</sup>B- and **3'P-NMR** spectra were **used to** monitor the progress of the reac $tion. - Single crystal X-ray diffraction data were obtained by using$ a Syntex P3/R3 automated diffractometer and structure solution system.

 $Tris (trimethylsilyl) phosphane - Borange(3)$  (1): Samples of the adduct (Me<sub>3</sub>Si)<sub>3</sub>P  $\cdot$  BH<sub>3</sub> were prepared by addition of a hexane solution of 2.5 g (10 mmol) of  $(Me_3Si)_3P^{24}$  to a hexane solution of  $H_3B \cdot THF$ (10 mmol).

The mixture was stirred for 1 h at  $0^{\circ}$ C and the solvent evaporated, leaving a colorless crystalline mass. The solid was purified by careful sublimation at  $60^{\circ}$ C, leaving 2.4 g of 1  $(91\%)$ , m.p.  $100-105\text{°C}$  (dec).  $- \delta^{11}B$  (benzene):  $-39.3$ ,  $^{1}$ *J*(BH) = 104 Hz.  $\delta^{31}P{\{^1H\}}$ : -193.8. -  $\delta^{1}H$ : 0.23,  $\delta J(PH) = 5 Hz$ . -  $\delta^{13}C{\{^1H\}}$ : 0.63,  $^{2}$ *J*(CP) = 7.6 Hz. - MS: *m*/z = 264 [M<sup>+</sup>].

C9H3"BSi3P (264.4) Calcd. *C* 40.88 **H** 11.44 Found C 40.26 H 10.97

*Pyrolysis Chemistry:* Samples *(0.50* g) of **I** were pyrolyzed under nitrogen in heavy-walled glass tubes sealed with a stopcock. After pyrolysis, the samples were cooled to 20°C and the volatile byproducts removed. The primary gaseous product obtained was Me3SiH, and it was identified by infrared and mass spectroscopic analysis. The oily and solid residues were collected and analyzed by NMR spectroscopy and mass spectromctry. Four pyrolysis temperatures were employed (100, 150, 175, and 210"C), and samples were typically heated for 12 h. Attempts to cleanly separate the several products by distillation and recrystallization were unsuccessful.

*X-ray Crystallographic Analyses:* Crystals of *2* and **3** slowly formed from the yellow oil obtained from pyrolysis of **1** at *200"C,*  and suitable crystals were sealed in glass capillaries under nitrogen.

**2**:  $C_{18}H_{60}B_3P_3S_i$ ,  $M = 570.5$ , space group  $C_2/c$ ,  $a = 20.778(8)$ ,  $b = 11.100(3)$ ,  $c = 19.822(7)$  Å,  $\beta = 123.17(2)$ °,  $V = 3827(2)$  Å<sup>3</sup>,  $d_c = 0.99$  g cm<sup>-3</sup>, Z = 4,  $\mu$ (Mo- $K_{\alpha}$ ) = 3.44 cm<sup>-1</sup>,  $F(000) = 1248$ . Details of data collection (20°C): crystal size  $0.18 \times 0.39 \times 0.40$ mm;  $\omega$  scan; scan speed  $4-30^{\circ}$  min<sup>-1</sup>; 2 $\Theta$  range  $2-50^{\circ}$ ; semiempirical absorption correction,  $\psi$  scans, *R* (before) = 0.0165, *R* (after) =  $0.0162$ , max/min transmissions  $0.902/0.986$ ; measured reflections 13714, averaged to give 3767 unique space-group-allowed reflections and 2575 with  $F > 3\sigma(F)$ . The structure was solved by direct methods. Isotropic refinement on all nonhydrogen atoms gave  $R_f = 0.21$ . Full-matrix anisotropic least squares refinement, H atoms in fixed positions,  $U_i = 1.2$   $U_{eq}$ ,  $R_f = 0.127$ ,  $R_{wF} = 0.06$ . Table 1 contains a list of atom coordinates for the nonhydrogen atoms **25).** 

Table 1. Atomic coordinates ( $\times$  10<sup>4</sup>) and equivalent isotropic thermal parameters  $U_{\text{eq}}$  ( $\times$  10<sup>3</sup> Å<sup>2</sup>) for 2

	x	y	z	U(eq)
P(1)	0	804(2)	2500	44(1)
P(2)	138(1)	$-1811(1)$	1739(1)	53(1)
B(1)	238(5)	$-55(6)$	1784(5)	72(6)
B(2)	0	$-2724(10)$	2500	156(16)
Si(1)	1020(1)	2027(2)	3242(1)	82(1)
C(1)	1007(5)	2670(7)	4101(4)	154(7)
C(2)	1910(4)	1154(7)	3639(5)	146(6)
C(3)	1020(4)	3237(6)	2603(5)	129(6)
Si(2)	1224(1)	$-2461(2)$	1855(1)	91(1)
C(4)	1482(4)	-1445(6)	1298(4)	114(6)
C(5)	1083(5)	-4023(6)	1440(5)	141(8)
C(6)	2010(5)	$-2457(9)$	2920(5)	201(8)
Si(3)	$-832(1)$	-2306(2)	476(1)	77 <sub>(1)</sub>
C(7)	$-571(4)$	$-1965(6)$	$-260(3)$	106(5)
C(8)	$-1676(4)$	$-1369(6)$	223(4)	122(5)
C(9)	$-1079(4)$	$-3912(6)$	416(4)	143(7)

Equivalent isotropic *U* defined as one third **of** the trace of the orthogonalized Uij tensor: B. T. M. Willis, A. W. Pryor, *Thermal Vibrations in Crystallography,* pp. 101 - 102, Cambridge University Press, Cambridge 1975.

3:  $C_{24}H_{83}B_6P_5S_{18}$ ,  $M = 816.4$ , space group  $C_2/c$ ,  $a = 26.986(5)$ ,  $d_c = 1.02$  g cm<sup>-3</sup>, Z = 4,  $\mu$ (Mo- $K_{\alpha}$ ) = 3.6 cm<sup>-1</sup>,  $F(000) = 1776$ . Details of data collection (20°C): crystal size  $0.2 \times 0.45 \times 0.1$  mm,  $\omega$  scan, scan speed  $4-30^{\circ}$  min<sup>-1</sup>; 2 $\Theta$  range  $2-50^{\circ}$ ; semi-empirical absorption correction,  $\psi$  scans, *R* (before) = 0.0119, *R* (after) = 0.0113; max/min transmissions  $0.647/0.598$ ; 13042 measured reflections (8 rejected), averaged to give 4700 unique space-group-allowed reflections and 3518 with  $F > 3\sigma(F)$ . The structure was solved by direct methods. Isotropic refinement on all nonhydrogen atoms gave  $R_f = 0.136$ . Anisotropic refinement, H atoms with fixed  $U_i =$ 1.2  $U_{eq}$ ,  $R_f = 0.064$ ,  $R_{wF} = 0.042$ . Table 2 contains a list of atom coordinates for the nonhydrogen atoms $^{25}$ .  $b = 12.403(3), c = 17.211(3)$  Å,  $\beta = 113.04(1)^\circ$ ,  $V = 5301(2)$  Å<sup>3</sup>,

Table 2. Atomic coordinates and equivalent isotropic thermal parameters  $U_{eq}$  ( $\hat{A}^2$ ) for 3

<b>ATOM</b>	x/a	y/b	z/c	U
P(1)	.0000	.5737(1)	.7500	$.0466(5)*$
B(1)	.0595(2)	.4993(4)	.7359(3)	$.055(2)$ *
P(2)	.1199 (0)	.4860(1)	.8455(1)	.0501 (4)*
Si(1)	.1001(1)	.3809(1)	.9363(1)	$.0742(6)*$
C(1)	.0589(2)	.4599 (3)	.9797(2)	$.088(2)*$
C(2)	.0621 (2)	.2599(3)	.8799(3)	$.122(4)^*$
C(3)	.1647(2)	.3411(4)	1.0231 (3)	$.128(3)*$
Si(2)	,1870 (0)	.4042(1)	.8206 (1)	$.0666(5)*$
C(4)	.2517(2)	.4167(3)	.9142(3)	$.100(2)*$
C(5)	.1710 (2)	.2591 (3)	.7945 (3)	$.100(3)*$
C(5)	.1937(2)	.4741(4)	.7305(3)	$.115(3)^*$
8(2)	.1494(2)	.6225(4)	.9043(3)	$.065(2)*$
P(3)	.0958 (0)	.7428 (1)	.8699(1)	$.0478(4)*$
Si(3)	.1243(1)	.8593(1)	.7944 (1)	.0642 (5)*
C(7)	.1890 (2)	.9196(3)	.8663(3)	$.096(2)$ *
C(8)	.0739(2)	.9679(3)	.7459(3)	$.091(2)$ *
C(9)	.1348(2)	.7833(3)	.7099(3)	.099 (3)*
Si(4)	.1032 (1)	.8280 (1)	.9913(1)	.0629 (5)*
C(10)	. 1742 (2)	.8149(3)	1.0688 (2)	$.095(2)$ *
C(11)	.0577(2)	.7630(4)	1.0349(3)	$.096(3)*$
C(12)	.0837 (2)	.9715(3)	.9711(3)	.107 (3)*
B(3)	.0193(2)	.7065(3)	.8117(3)	.051 (2)*

\* Equivalent isotropic *U* defined as one third **of** the trace of the orthogonalized  $U_{ij}$  tensor.

## CAS Registry Numbers

1: 17478-11-4 / **2**: 125685-61-2 / **3**: 125685-62-3 / (Me<sub>3</sub>Si)<sub>3</sub>P: 15573-38-3 / H3B ' THF: 14044-65-6

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- <sup>12)</sup> **Additional low-intensity resonances appear centered at**  $\delta^{31}P$  **=**  $-206, -184, -173, -169, -158, -142, -24.$
- <sup>13)</sup> Additional low-intensity resonances appear centered at  $\delta^{31}P =$  $-204, -194, -190, -173, -160, -156, -136, -108.$
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- *25)* Additional information cencerning the X-ray structure determinations are deposited at the Fachinformationszentrum Karlsruhe Gesellschaft fur **wissenschaftlich-technische** Information mbH, D-7514 Eggenstein-Leopoldshafen 2 **(W.** Germany), and can be requested by quoting the registry number CSD-54349, the authors and the reference to this publication.