Contributions to the Chemistry of Boron, 205¹⁾



Formation of Phosphinoborane Rings. A Reinvestigation of the Reaction of $[(CH_3)_3Si]_3P$ with Borane(3)

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Combination of $(Me_3Si)_3P$ and $H_3B \cdot THF$ results in the formation of the known adduct $(Me_3Si)_3P \cdot BH_3$ (1). The complex undergoes dehydrosilylation above 100°C, and two ring compounds,

The reactions of phosphanes, PX₃, with boranes, BY₃, have been studied over the last fifty years^{2, 3)}, 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 oligometric species that are poorly defined. As an illustration, Parshall and Lindsey⁴ 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°C and rapidly decompose at its melting point, 100-107°C. Leffler and Teach⁵ identified one coproduct of the thermal decomposition reaction as Me₃SiH. 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 Schrägle⁶⁾ found that Me₃SiH 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 $[(Me_3Si)_2PBH_2]_m$ and the second, yellow-brown polymeric product was [Me₃SiPBH]_n. No further studies of this system have appeared, but in related work Nöth and Schrägle⁷⁾ studied the thermal decompositions of $(Me_3Si)Et_2P \cdot BH_3$ and $(Me_3Si)Bu_2P \cdot BH_3$. At temperatures above 200°C, Me₃SiH was rapidly evolved, and according to elemental analysis data and cryoscopic molecular weight measurements, it was concluded that trimeric ring compounds, $(Et_2P \cdot BH_2)_3$ and $(Bu_2P \cdot BH_2)_3$, were formed.

We have used Me₃SiX elimination reactions to prepare a number of new phosphinoborane ring and cage compounds⁸⁻¹¹, and in the course of that work we have reinvestigated the complex pyrolysis of $(Me_3Si)_3P \cdot BH_3$ (1). The $[(Me_3Si)_2PBH_2]_3 (2) \text{ and } P[(\mu-H-B_2-H_2)]\{(BH_2)_2[P(SiMe_3)_2]_2\}_2 (3), are isolated. The crystal structures of the compounds are compared with those of other phosphinoboranes.$

adduct undergoes a small degree of decomposition even at 25°C in benzene solution, as evidenced by the appearance of several low-intensity resonances in the ³¹P-NMR spectrum: $\delta^{31}P{}^{1}H{}(C_6D_6) = -251, -203, -197, -191, -186, -182, -140, -129, -118, -106.$ The ³¹P{ $^{1}H{}$ - and ¹¹B-NMR spectra for a pure sample of 1 in C₆D₆ 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 H₃B·THF are present in the initial reaction mixture.

Pyrolysis of 1 under nitrogen in a closed vessel at 100°C slowly produces Me₃SiH, as indicated by gas-phase infrared and mass spectra. For a 0.5-g sample of 1, gas evolution ceases after ≈ 12 hours, and $\approx 50\%$ of the Me₃SiH expected from the reaction shown in equation (1) is isolated.

$$n (\mathrm{Me}_{3}\mathrm{Si})_{3}\mathrm{P} \cdot \mathrm{BH}_{3} \xrightarrow{\Delta T} [(\mathrm{Me}_{3}\mathrm{Si})_{2}\mathrm{P} \cdot \mathrm{BH}_{2}]_{n} + n \mathrm{Me}_{3}\mathrm{SiH} \quad (1)$$

$$1$$

The ³¹P{¹H}- and ¹¹B{¹H}-NMR spectra of the resulting oil suggest the formation of several products with major resonances¹² found at δ^{31} P{¹H} (C₆D₆) = -251, -208, -205, -203, -198, -161, -142, and -29. The resonance at δ = -251 may be assigned to free (Me₃Si)₃P. The ¹¹B{¹H}-NMR spectrum for this sample shows relatively broad, strong resonances centered at δ = -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 Me₃SiH 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 ${}^{31}P{}^{1}H$ -NMR spectrum (C₆D₆) shows major resonances centered at $\delta = -251, -208,$ -203, -198, -142, and -29^{13} , and the ${}^{11}B{}^{1}H{}$ -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 Me₃SiH, NMR spectra were recorded for the resulting yellow oil: ${}^{31}P{}^{1}H{}\delta = -251$, -236, -208, -203, -142; ${}^{11}B{}^{1}H{}\delta = -40.7$. A weak resonance remains in the ³¹P{¹H} spectrum at $\delta = -198$. The resonance at $\delta = -236$ may be assigned to (Me₃Si)₂PH¹⁴). Finally, a sample of 1 was heated at 210°C for 12 hours, and NMR spectra were obtained for the remaining yellow-orange oil: ${}^{31}P{}^{1}H{}\delta = -251, -236,$ $-203, -142; {}^{11}B{}^{1}H{}\delta = -40.1$. Very weak resonances remain in the ³¹P $\{^{1}H\}$ spectrum at $\delta = -208$ and -198. Variable-temperature (+60 to -70° C) ¹¹B-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 $[(Me_3Si)_2PBH_2]_3$ (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%) thermal ellipsoides). Selected bond distances (Å): P(1)-B(1) 1.966(10), P(2)-B(1) 1.974(6), P(2)-B(2) 1.991(6), P(1)-Si(1) 2.254(2), P(2)-Si(2) 2.259(4), P(2)-Si(3) 2.255(2). Selected bond angles (°): B(1)-P(1)-B(1') 124.4(4), B(1)-P(2)-B(2) 124.6(4), P(1)-B(1)-P(2) 115.2(5), P(2)-B(2)-P(2') 115.3(6)

The ring in 2 is drastically flattened¹⁵⁾ 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 [range 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 boraphosphabenzenes¹⁹ [MesBPPh]_3,

1.842 Å, and [MesBPC₆H₁₁]₃, 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 [Me₂PBH₂]₃ and [Ph₂PBH₂]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]₃ are 124.5 and 114.9°, respectively. The average Si-P-Si bond angle, 105.8°, on the other hand, is only slightly greater than the C-P-C angles in [Me₂PBH₂]₃, 100.4(9), and [Ph₂PBH₂]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.

$[(Me_{3}Si)_{2}PBH_{2}]_{3} P[(\mu-H-B_{2}H_{2})]\{(BH_{2})_{2}[P(SiMe_{3})_{2}]_{2}\}_{2}$ 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)₃ 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'), $61.7(2)^{\circ}$, is considerably compressed relative to the angles B(1) - P(1) - B(1'), 123.4(3)°, 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)°. 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) Å, than the remaining distances that fall in an order $P(1) - B(3) \ll P(1) - B(1) \simeq (2) - B(1) \simeq P(3) - B(3) < P(2) - B(3) < P(3) < P(3) - B(3) < P(3) - B(3) < P(3) < P$ 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 m/z 817; however, the highest mass ions detected from a mixture of 2 and 3 appear at m/z 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 ¹¹B spectra. Two resonances in the ³¹P{¹H} spectra, $\delta =$ -251 and -236, are present in several samples, and these correspond to (Me₃Si)₃P and (Me₃Si)₂PH. Very small amounts of (Me₃Si)PH₂ are also detected at $\delta =$ -235.3. The ³¹P{¹H}-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), P(2)-B(1) 1.959(4), P(1)-B(3) 1.918(4), B(2)-P(3) 2.000(5), P(2)-B(2) 1.974(5), P(3)-B(3) 1.961(4). Selected angles (°): 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), P(1)-B(3)-P(3) 118.9(2), P(2)-B(2)-P(3) 112.8(2), B(2)-P(3)-B(3) 118.4(2)



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° C. Above 175° C, the material apparently decomposes since the resonance disappears. The resonance is slightly upfield of the ³¹P resonance for 1, -193.8, and these shifts may be compared with data for Me₃P·BH₃, $\delta = -36.5$, $J_{BP} = 61$ Hz, and (Me₂PBH₂)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 ³¹P-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 ³¹P

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 lower-field 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 Me₂(H)P · BH₃ produces an analogous trimer, $(Me_2PBH_2)_3^{22}$. 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 ³¹P-NMR spectra of reaction mixtures, and Me₃SiH. 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 studies²³⁾.

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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. ¹¹B- and ³¹P-NMR spectra were used to monitor the progress of the reaction. – Single crystal X-ray diffraction data were obtained by using a Syntex P3/R3 automated diffractometer and structure solution system.

Tris(trimethylsilyl)phosphane - Borane(3) (1): Samples of the adduct (Me₃Si)₃P · BH₃ were prepared by addition of a hexane solution of 2.5 g (10 mmol) of (Me₃Si)₃P²⁴⁾ to a hexane solution of H₃B · THF (10 mmol).

The mixture was stirred for 1 h at 0°C and the solvent evaporated, leaving a colorless crystalline mass. The solid was purified by careful sublimation at 60°C, leaving 2.4 g of 1 (91%), m.p. $100-105^{\circ}C$ (dec). $-\delta^{11}B$ (benzene): -39.3, ${}^{1}J(BH) = 104$ Hz. $-\delta^{31}P\{{}^{1}H\}$: -193.8. $-\delta^{1}H$: 0.23, ${}^{3}J(PH) = 5$ Hz. $-\delta^{13}C\{{}^{1}H\}$: 0.63, ${}^{2}J(CP) = 7.6$ Hz. - MS: m/z = 264 [M⁺].

Pyrolysis Chemistry: Samples (0.50 g) of 1 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 by-products 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 spectrometry. 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: $C_{18}H_{60}B_3P_3Si_6$, M = 570.5, space group C2/c, a = 20.778(8), $b = 11.100(3), c = 19.822(7) \text{ Å}, \beta = 123.17(2)^{\circ}, V = 3827(2) \text{ Å}^{3},$ $d_{\rm c} = 0.99 \text{ g cm}^{-3}, Z = 4, \, \mu(\text{Mo-}K_{\alpha}) = 3.44 \text{ cm}^{-1}, \, F(000) = 1248.$ Details of data collection (20°C): crystal size 0.18 \times 0.39 \times 0.40 mm; ω scan; scan speed $4-30^{\circ}$ min⁻¹; 2Θ range $2-50^{\circ}$; semiempirical absorption correction, ψ 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 atoms²⁵⁾.

Table 1. Atomic coordinates (\times 10⁴) and equivalent isotropic thermal parameters U_{eq} (× 10³ Å²) for 2

	x	У	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(1)
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 U_{ij} tensor: B. T. M. Willis, A. W. Pryor, *Thermal Vibrations in Crystallography*, pp. 101–102, Cambridge University Press, Cambridge 1975.

3: $C_{24}H_{83}B_6P_5Si_8$, M = 816.4, space group C2/c, a = 26.986(5), b = 12.403(3), c = 17.211(3) Å, $\beta = 113.04(1)^{\circ}, V = 5301(2)$ Å³, $d_{\rm c} = 1.02 \text{ g cm}^{-3}, Z = 4, \ \mu(\text{Mo-}K_{\alpha}) = 3.6 \text{ cm}^{-1}, \ F(000) = 1776.$ Details of data collection (20°C): crystal size $0.2 \times 0.45 \times 0.1$ mm, ω scan, scan speed 4-30° min⁻¹; 2 Θ range 2-50°; semi-empirical absorption correction, ψ 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 atoms²⁵⁾.

Table 2. Atomic coordinates and equivalent isotropic thermal parameters U_{eq} (Å²) for **3**

ATOM	x/a	y/b	z/c	U
P(1)	.0000	.5737 (1)	.7500	.0466 (5)*
8(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 (5)*
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)	.8205 (1)	.0666 (5)*
C(4)	.2517 (2)	.4167 (3)	.9142 (3)	.100 (2)*
C(5)	.1710 (2)	.2591 (3)	.7945 (3)	.100 (3)*
C(6)	.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)	.9195 (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.

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1: 17478-11-4 / 2: 125685-61-2 / 3: 125685-62-3 / $(Me_{3}Si)_{3}P\colon$ 15573-38-3 / H₃B · THF: 14044-65-6

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