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The crystal and molecular structure of tricyclohexylphosphine-(trimethylsilyl)borane $\text{Cy}_3\text{P} \cdot \text{BH}_2\text{SiMe}_3$ *

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Abstract

The crystal and molecular structures of the title compound have been determined by a single crystal X-ray diffraction study. This compound is one of the rare species with a discrete silicon–boron two-centre/two-electron bond involving tetra-coordinate boron. The B–P bond length, 1.913(4) Å, is therefore an important reference value. The conformations at the phosphorus, boron and silicon atoms can be described as fully staggered. The valence angle P–B–Si, 122.1(2)°, is rather large, indicating the presence of steric interactions between the bulky Me_3Si and Cy_3P groups.

1. Introduction

Compounds with a discrete silicon–boron two-centre/two-electron bond are very rare [1–3]. This is particularly the case for species containing coordinatively saturated tetra-coordinate boron. Of the few reasonably well characterized compounds with Si–B bonds mentioned in the literature, to the best of our knowledge only one has been structurally characterized, in which the boron atom is two-coordinate [3].

In the course of a study of boron-centred gold clusters [4] we became interested in the chemistry of the novel silylated phosphine-boranes recently reported by Imamoto *et al.* [5,6] that appeared to be promising precursors for poly-aurated boranes. By use of the preparative procedure described by those authors we were able to obtain single crystals of the title compound, and decided to determine its structure in order to facilitate reliable judgements of the geometry of phosphine-coordinated silylboranes. These studies extend our earlier work on the structural chemistry of phosphine-boranes [7–9], isoelectronic silylmethylphosphonium cations [10] and phosphonium-(silyl)methylides [11–13]. At the same time we have added to

the still somewhat limited spectroscopic data for the phosphine-(silyl)borane and its precursors. We also present a description of the synthetic work because we found that some of the details are critical, and may be different from those of the individual steps in the process used by Imamoto *et al.* [5,6].

2. Results and discussion

Tricyclohexylphosphine-borane (**1**) can be prepared by reaction of the tertiary phosphine with the tetrahydrofuran-borane complex in tetrahydrofuran, or with sodium borohydride and iodine in tetrahydrofuran [14,15]. It was obtained in high yield (85%) as a colourless, air-stable crystalline solid of m.p. 177°C, and was readily identified from its analytical and spectroscopic data (Experimental section).

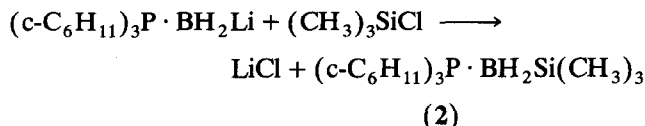
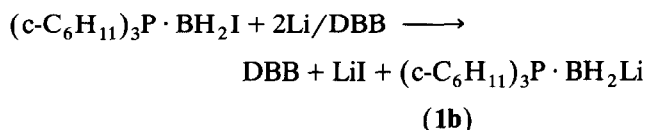
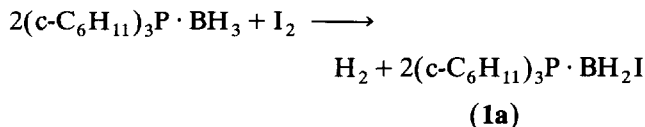
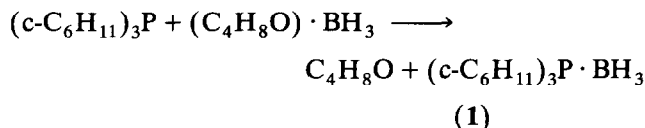
Compound **1** is converted into the mono-iodo derivative (**1a**) by reaction with elemental iodine in benzene [16]. The product can be isolated (in ca. 85% yield) as a light-brown microcrystalline powder of m.p. 153°C, which is, however, much more sensitive to air and moisture than compound **1**, and cannot be kept at room temperature for long periods.

Compound **1a** can be lithiated at the boron atom (to give the intermediate **1b**) by treatment with lithium-di-tert-butyl-biphenyl (LDBB) in tetrahydrofuran at –78°C [5,6] and was converted into the trimethylsilyl derivative **2** by treatment with chlorotrimethylsilane.

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* Dedicated to Professor Michael Lappert on the occasion of his 65th birthday.

The yields from this procedure varied considerably, and in most cases were very low (20%) if a very pure crystalline product was required. Compound **2** is obtained as colourless crystals, of m.p. 164–166°C, which are insensitive to oxidation and hydrolysis, even when in solution or finely powdered.



Compound **2** was identified and fully characterized from its analytical and spectroscopic data (Experimental section).

Compound **2** crystallizes from diethyl ether in orthorhombic needles, space group *Pca*2₁ (No. 29, International Tables) with cell dimensions *a* = 11.335(1), *b* = 11.888(1), *c* = 17.590(1) Å, *V* = 2370.3 Å³, *Z* = 4, *D*_{calc} = 1.027 g cm⁻³. The molecular structure is shown in Fig. 1.

The two large atoms, phosphorus and silicon, have a quasi-tetrahedral configuration. The angles at P or Si reflect the steric congestion, but none of the deviations from the tetrahedral standard is really very large. The angle P–B–Si = 122.1(2)° is also indicative of repulsive steric interactions. The conformations at P, B and Si can be described as all-staggered, with dihedral angles C2–Si–B–P and C31–P–B–Si close to 156 and 180°, respectively. During solution of the structure the hydrogen atoms H1 and H2 on boron were located by difference Fourier syntheses and included in the refinement. Their coordinates confirm the tetrahedral coordination of the boron atom. The cyclohexyl rings are all in a strain-free chair conformation as judged from the normal C–C bond lengths and C–C–C bond angles.

The distance Si–B, 2.007(4) Å, in **2** provides an important benchmark reference, since it appears to be the first data on such a bond involving tetracoordinate (sp³-hybridized) boron. This distance is significantly longer than that in the borazine Me₃CNBSi(SiMe₃)₃

which contains two-coordinate (sp-hybridized) boron [1.976(4) Å] [3]. For trigonally tricoordinate (sp²-hybridized) boron, the Si–B distance is also expected to be shorter, but no data are at present available.

The distance P–B = 1.913(4) Å in **2** is not unusual, and well within the range established for other phosphine-borane molecules [11–13]. The shortening relative to the Si–B bond is due not only to the smaller covalent radius of phosphorus compared with that of silicon but also to the dipolar nature of the P–B bond with its full +1/–1 formal charges, which require significant corrections of the reference values for electroneutral compounds.

3. Experimental section

All experiments were carried out under pure dry nitrogen or argon. Glassware was oven-dried and filled with inert gas. Solvents were dried and distilled prior to use. Tri(cyclo-hexyl)phosphine, trimethyl-chlorosilane, and the tetrahydrofuran-borane complex (THF · BH₃) were commercially available (Aldrich). NMR: Jeol GX 400 spectrometer; IR: Perkin-Elmer FT spectrometer; melting points: IA 9200, Electrothermal Eng. Ltd.; MS: MAT 311A (EI, 70 eV).

3.1. Tri(cyclo-hexyl)phosphine-borane (**1**)

A solution of Cy₃P (5.3 g, 18.9 mmol) in THF (50 ml) was treated with THF · BH₃ (18.9 ml of a 1 M solution in THF) and the mixture stirred for 4 h. The mixture was then concentrated to 5 ml and pentane was added (80 ml) to precipitate the product. Yield 4.61 g (83%), m.p. 177°C. ¹H NMR (C₆D₆): δ = 1.01–1.88 ppm (m, Cy and BH₃). {¹H}¹³C NMR (C₆D₆): δ = 26.39 [s, C4]; 27.44 [d, *J*(P, C) = 10.7 Hz, C2]; 28.19 [d, *J*(P, C) = 1.5 Hz, C3]; 31.31 [d, *J*(P, C) = 29.0 Hz, C1]. ³¹P NMR (C₆D₆): δ = 29.86 [broad s]. ¹¹B NMR (C₆D₆): δ = –42.74 [d · q, *J*(B, H) = 92.4, *J*(P, B) = 66.6 Hz]. MS (EI): *m/z* = 293 [M⁺]. IR (KBr): 2925s, 2853s ν(CH); 2376s, 2340s, 2245sh ν(BH); 1445s, ν(PB). C₁₈H₃₆BP (293.8) Calc. C 73.52, H 12.25. Found C 72.64, H 11.85%.

3.2. Tri(cyclo-hexyl)phosphine-iodoborane (**1a**)

To a solution of compound **1** (2.78 g, 9.46 mmol) in benzene (80 ml) was added a solution of iodine (1.60 g, 6.30 mmol) in benzene (40 ml). The mixture was stirred at 45°C for 6 h and then at the reflux temperature for a further 8 h. The volume of the solution, which was never completely colourless, was then reduced to 5 ml under vacuum, and pentane was added (80 ml) to precipitate the product as a light brown powder. Yield 3.17 g (80%), m.p. 153°C. The small amount of residual iodine was not removed by attempts to further purify

the material. ^1H NMR (C_6D_6): $\delta = 0.93\text{--}2.02$ [m, Cy and BH_3]. $\{^1\text{H}\}^{13}\text{C}$ NMR (C_6D_6): $\delta = 26.12$ [s, C4]; 27.28 [d, $J(\text{P}, \text{C}) = 11.4$ Hz, C2]; 28.28 [d, $J(\text{P}, \text{C}) = 28.3$ Hz, C3]; 31.25 [d, $J(\text{P}, \text{C}) = 32.8$ Hz, C4]. ^{31}P NMR (C_6D_6): $\delta = 6.10$ [broad s]. ^{11}B NMR (C_6D_6): $\delta = -37.11$ [broad s]. MS (EI): $m/z = 420$ [M^+]. IR (KBr): 2928s , 2853s $\nu(\text{CH})$; 2455s , 2413s $\nu(\text{BH})$; 1447s $\nu(\text{PB})$. $\text{C}_{18}\text{H}_{35}\text{BIP}$ (419.7) Calc. C 51.46, H 8.34, P 7.39, I 30.23. Found C 50.41, H 7.97, P 6.21, I 31.56%.

3.3. Tri(cyclo-hexyl)phosphine-trimethylsilylborane (2)

Compound **1a** (0.44 g, 1.05 mmol) and Me_3SiCl (2.0 ml, 15.8 mmol) were dissolved in THF (15 ml) and the solution was cooled to -78°C and treated with a solution of LiDBB, prepared from lithium-powder (0.10 g, 14.2 mmol), di-*t*-butyl-biphenyl (1.0 g, 3.76 mmol) and N,N,N',N' -tetramethyl-ethylenediamine (0.50 ml, 3.3 mmol) in THF (12 ml) at 0°C under argon. After 1 h water (20 ml) was added and the product extracted with diethyl ether (two portions of 30 ml). The ether extract was washed with saturated aqueous sodium bicarbonate and dried over sodium sulphate, and the volume was reduced to 5 ml under vacuum. The product crystallized from this solution when it was cooled to -25°C as colourless crystals, yield 85 mg (20%), m.p. $164\text{--}166^\circ\text{C}$. Single crystals could be grown from diethyl ether. ^1H NMR (C_6D_6): $\delta = 0.53$ [s, 9H, Me]; $1.08\text{--}1.90$ [m, 33H, Cy]. $\{^1\text{H}\}^{13}\text{C}$ NMR (C_6D_6): $\delta = 4.51$ [d, $J(\text{P}, \text{C}) = 4.6$ Hz, Me], 26.39 [s, C4], 27.50 [d, $J(\text{P}, \text{C}) = 9.9$ Hz, C2], 28.42 [d, $J(\text{P}, \text{C}) = 1.5$ Hz, C3], 32.44 [d, $J(\text{P}, \text{C}) = 31.3$ Hz, C1]. ^{31}P NMR (C_6D_6): $\delta = 32.8$ [broad s]. ^{11}B NMR (C_6D_6): $\delta = -47.29$ [broad d, $J(\text{P}, \text{B}) = 67.1$ Hz]. IR (KBr): 2932s , 2830s $\nu(\text{CH})$; 2357s $\nu(\text{BH})$; 1440s $\nu(\text{PB})$.

3.4. Crystal data and structure solution for compound 2

Crystals of **2** (grown from diethyl ether) were mounted in a sealed glass capillary under argon and data were collected on an Enraf Nonius CAD4 diffractometer. Crystal data for $\text{C}_{21}\text{H}_{44}\text{BPSi}$ (366.46), $a = 11.335(1)$, $b = 11.888(1)$, $c = 17.590(1)$ Å, orthorhombic, space group $Pca2_1$, $V = 2370.3$ Å³, $Z = 4$, $D_{\text{calc}} = 1.027$ g cm⁻³. Graphite-monochromated Mo K α radiation, $\lambda = 0.71069$ Å, ω -scan, $(\sin \theta/\lambda)_{\text{max}} = 0.639$ Å⁻¹, hkl range $+14, +15, \mp 22$; $T = 23^\circ\text{C}$. 5144 measured reflections (5144 unique), 4248 observed [$F_0 \geq 4\sigma(F_0)$], no absorption correction was applied. The structure was solved by direct methods (SHELXS-86). All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms on boron were located in a difference Fourier syntheses and included in the refinement (SHELX-76). 24 of the Cy hydrogen atoms were also located, but the remaining 18 hydrogen atoms of the Cy and Me groups were placed in calculated

TABLE 1. Fractional atomic coordinates and equivalent isotropic displacement parameters for **2**. ($U_{\text{eq}} = (U_1 * U_2 * U_3)^{1/3}$, where U_1, U_2, U_3 are the eigenvalues of the U_{ij} matrix. E.s.d.'s in parentheses).

Atom	x	y	z	U_{eq}
P	0.20813(7)	0.69974(6)	0.55840	0.037
B	0.0679(4)	0.6731(4)	0.6162(3)	0.047
Si	0.01055(8)	0.78145(8)	0.69548(8)	0.048
C1	-0.0898(4)	0.8950(4)	0.6582(3)	0.075
C2	-0.0817(4)	0.7000(4)	0.7633(3)	0.076
C3	0.1234(4)	0.8570(4)	0.7543(2)	0.067
C11	0.3376(3)	0.7215(3)	0.6200(2)	0.041
C12	0.4559(3)	0.7350(3)	0.5814(2)	0.057
C13	0.5496(4)	0.7697(4)	0.6388(3)	0.082
C14	0.5590(3)	0.6894(4)	0.7057(2)	0.065
C15	0.4378(4)	0.6723(4)	0.7418(2)	0.065
C16	0.3467(3)	0.6364(3)	0.6849(2)	0.055
C21	0.2012(3)	0.8226(3)	0.4959(2)	0.043
C22	0.2094(4)	0.9348(3)	0.5376(2)	0.057
C23	0.2048(5)	1.0312(3)	0.4820(3)	0.075
C24	0.0961(5)	1.0290(3)	0.4330(3)	0.076
C25	0.0813(5)	0.9188(4)	0.3924(2)	0.072
C26	0.0892(3)	0.8199(3)	0.4468(2)	0.054
C31	0.2294(4)	0.5805(3)	0.4915(2)	0.049
C32	0.3178(4)	0.5979(4)	0.4261(2)	0.063
C33	0.3186(6)	0.4949(5)	0.3736(3)	0.083
C34	0.3226(4)	0.3887(4)	0.4081(3)	0.066
C35	0.2408(5)	0.3720(3)	0.4723(3)	0.071
C36	0.2427(5)	0.4708(4)	0.5271(3)	0.080

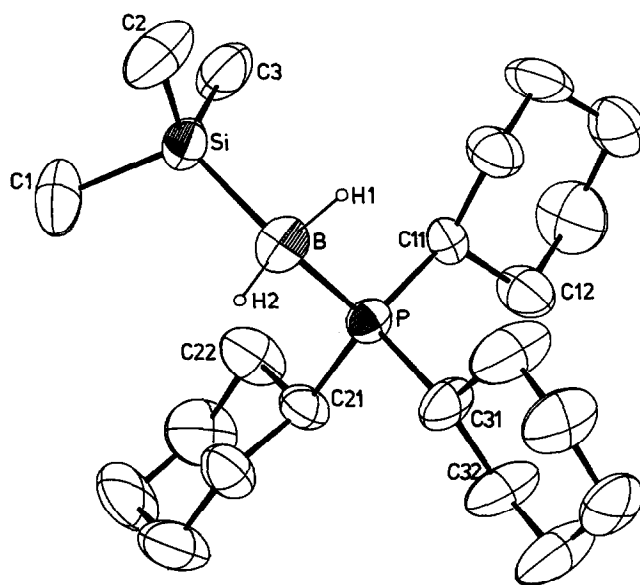


Fig. 1. Molecular structure of compound **2** with atomic numbering scheme (ORTEP, 50% probability ellipsoids; hydrogen atoms at carbon atoms omitted for clarity). Selected bond distances [Å] and angles [°] (with standard deviations): P-B 1.913(4), P-C11 1.842(3), P-C21 1.829(3), P-C31 1.858(3), B-Si 2.007(4), Si-C1 1.883(4), Si-C2 1.859(4), Si-C3 1.874(4); B-P-C11 111.9(2), B-P-C21 114.6(2), B-P-C31 108.5(2), P-B-Si 122.1(2), B-Si-C1 114.4(2), B-Si-C2 107.1(2), B-Si-C3 118.0(2).

positions and included with $U_{\text{iso}} = 0.05 \text{ \AA}^2$. With 224 parameters the refinement converged to R (R_w) = 0.0567(0.0467). For the second enantiomorph the R -factors were 0.0570(0.0470). $(\text{shift/error})_{\text{max}} = 0.001$, $\Delta\rho_{\text{fin}}(\text{max/min}) = +0.73/-0.66 \text{ e\AA}^{-3}$. Fractional atomic coordinates and isotropic thermal parameters are given in Table 1. Interatomic distances and angles are included in the caption to Fig. 1. Supplementary data have been deposited with Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Zusammenarbeit, D-76344 Eggenstein-Leopoldshafen. Information may be obtained by quoting the depository number CSD-57709, the names of the authors, and the full journal citation.

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References

- 1 D. Seyferth and H.P. Kögler, *J. Inorg. Nucl. Chem.*, **15** (1960) 99.
- 2 W. Biffar, H. Nöth and R. Schwerthöffer, *Liebigs Ann. Chem.*, (1981) 2067, and references therein.
- 3 M. Haase, U. Klingebiel, R. Boese and M. Polk, *Chem. Ber.*, **119** (1986) 1117.
- 4 A. Blumenthal, H. Beruda and H. Schmidbaur, *J. Chem. Soc., Chem. Commun.*, (1993) 1005.
- 5 T. Imamoto, T. Hikosaka, International Symposium on Heteroatom Chemistry, Riccione, June 1992, and personal communication.
- 6 T. Imamoto, *Pure Appl. Chem.*, **65** (1993) 655.
- 7 H. Schmidbaur, *J. Organomet. Chem.*, **200** (1980) 287 (review).
- 8 H. Schmidbaur, T. Wimmer and G. Reber, *Angew. Chem.*, **100** (1988) 1135; *Angew. Chem. Int., Ed. Engl.*, **27** (1988) 1071. H. Schmidbaur, T. Wimmer, A. Grohmann, O. Steigelmann and G. Müller, *Chem. Ber.*, **122** (1989) 1607; T. Wimmer, O. Steigelmann, G. Müller and H. Schmidbaur, *Chem. Ber.*, **122** (1989) 2109.
- 9 H. Schmidbaur, A. Stützer and E. Herdtweck, *Chem. Ber.*, **124** (1991) 1095; H. Schmidbaur, T. Wimmer, J. Lachmann and G. Müller, *Chem. Ber.*, **124** (1991) 275.
- 10 H. Schmidbaur, *Acc. Chem. Res.*, **8** (1975) 62.
- 11 H. Schmidbaur and W. Tronich, *Chem. Ber.*, **100** (1967) 1032.
- 12 H. Schmidbaur and W. Malisch, *Chem. Ber.*, **103** (1970) 3007.
- 13 H. Schmidbaur and W. Malisch, *Chem. Ber.*, **104** (1971) 3448.
- 14 R.C. Moose, S.S. White and H.C. Kelly, *Inorg. Synth.*, **12** (1979) 109.
- 15 K. Das and S. Roy, *Synth. React. Inorg. Met.-Org. Chem.*, **16** (1986) 67.
- 16 H.H. Sisler and M.A. Mathur, *J. Inorg. Nucl. Chem.*, **39** (1977) 1745.