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Synthesis and Molecular Structure of Tris[(trimethylsilyl)silyl](diisopropylamino)(diphenylphosphino)borane [1]

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Abstract. The 1:1 reaction of [$(Me_3Si)_3SiLi\cdot 3THF$] with ($iPr_2N)BCl_2$ in hexane provides [{$(Me_3Si)_3Si$}$\cdot$(iPr_2N)BCl] (**2**) in good yield as a colorless crystalline solid. This compound combined in a 1:1 ratio with $LiPPh_2$ in DME gives [{$(Me_3Si)_3Si$}$\cdot$(iPr_2N)B(PPh_2)] (**3**) as a yellow crystalline solid. The new compounds were characterized by IR, MS and ^1H, $^{13}C\{^1H\}$ and ^{11}B NMR spectroscopy and the molecular structure of **3** was determined by X-ray structure analysis.

Keywords: Phosphinoboranes; Aminoboranes; Silyl boranes; NMR spectra; Crystal structures

Introduction

Aminophosphino boranes display interesting reactivity and coordination chemistry properties and much of the work with these reagents has been summarized in a review [2].Since 1995, additional advances, mostly directed to the development of new low coordination number conditions, unusual ring and cage structures and new polymeric materials, have continued to appear in the literature [3−34]. In some of our studies, we have sought to construct sterically crowded N-B-P environments that might be introduced into more complex molecules. As part of that work, we have explored syntheses of tri-coordinate borane fragments with connectivities N-B(Si)-X. Pertinent to this, we described in 1981 the synthesis of several tris(trimethylsilyl)silyl boranes and borates including the amino derivatives [{$(Me_3Si)_3Si$}$B(NMe_2)_2$] and [{Me_3Si}$_3Si]_2B(NMe_2)$] [35]. Subsequently, *Haase* and *Klingebiel* reported the formation of [{Me_3Si}$_3Si$]B(F){N($SiMe_3)_2$}] (**1a**) that undergoes thermally promoted 1,2-Me_3SiF elimination with formation of the imino borane [{$(Me_3Si)_3Si$}B≡N($SiMe_3$)] [36]. The synthesis and characterization of additional examples of **1**, [{$(Me_3Si)_3M$}B(F){N(R)($SiMe)_3$}], M=C, Si; R=Me, Et, iPr, $SiMe_3$, CMe_3, and a molecular structure determination for the imino borane (Me_3C)B≡N($SiMe_3$) also have been described [37]. More recently, *Marschner* and coworkers [38] published the synthesis of [{$(Me_3Si)_3Si$}B(Cl)(tmp)] (tmp= 2,2,6,6-tetramethylpiperidinyl). For our synthesis applications, we are also interested in the B-B(Si)-P unit and we report here the synthesis and molecular structure determination for the molecule [{$(Me_3Si)_3Si$}B-($NiPr_2$)(PPh_2)](**3**), that is sufficiently congested that the phosphane lone pair becomes inactive toward simple metal carbonyl fragments.

Reactions

The 1:1 combination of [$(Me_3Si)_3SiLi\cdot 3THF$] [39, 40] with ($i$$Pr_2N$)$BCl_2$ [41] in hexane rapidly eliminates LiCl with formation of [{$(Me_3Si)_3Si$}B(Cl)(N^iPr_2)] (**2**) that is isolated in 94 % yield, following recrystallization, as an analytically pure, colorless, crystalline solid. The compound displays a single ^{11}B NMR resonance at δ = 43.0, and this shift is similar to that reported previously for [{$Me_3Si)_3Si$}B(Cl)(tmp)], δ = 48.5 [38]. As is typically found with other aminoboranes, the shift for the (tmpB) fragment is slightly deshielded compared to the ($^iPr_2NB$) fragment [2, 42]. The ^1H and ^{13}C NMR spectra show that the silyl methyl groups are equivalent; however, the isopropyl methyl and methine groups each display two inequivalent environments consistent with hindered rotation about the B-N bonds.

Compound **2** combined in a 1:1 ratio with Ph_2PLi in DME provides [{$(Me_3Si)_3Si$} B(N^iPr_2)(PPh_2)] (**3**) as an analytically pure yellow crystalline solid in 80 % yield following standard workup and recrystallization. It is worth noting that attempts to obtain **3** using hexane as the reaction solvent were unsuccessful. The FAB-MS analysis of **3** reveals a parent ion along with expected fragment ions. The ^{11}B NMR spectrum contains a single broad resonance at δ = 55 that is typical of three coordinate aminophosphino boranes [2]. The ^{31}P NMR spectrum also displays a single resonance at δ = −31.7, and this shift can be compared against the shift for [$(Et_2N)B(PPh_2)_2$], δ = −37.1 [43]. As found for **2**, the ^1H and ^{13}C NMR spectra show a single

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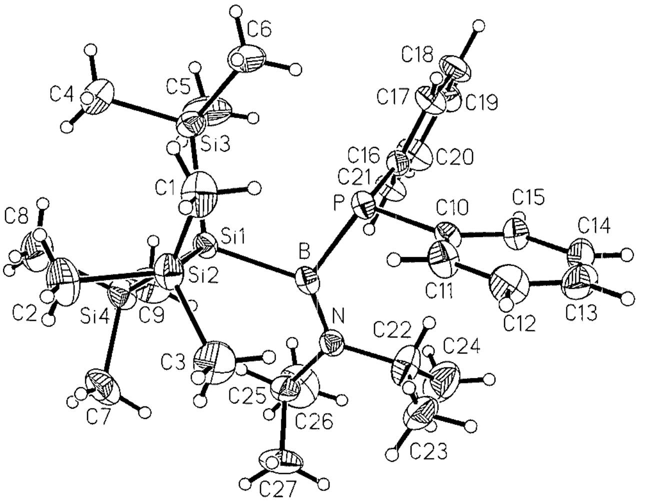

Figure 1 Plot of the molecular structure of compound **3**.Thermal ellipsoids are presented on a 25 % probability scale.

Selected bond lengths (in Å): B-P 1.982(5), B-N 1.391(7), B-Si1 2.063(5), P-Cl0 1.840(4), P-C16 1.834(4), N-C22 1.495(6), N-C25 1.491(6), Si1-Si2 2.365(2), Si1-Si3 2.378(2), Si1-Si4 2.386(2). − Selected bond angles (in degrees) − Si1-B-P 104.8(2), Si1-B-N 128.0(3), P-B-N 127.1(3), B-N-C22 121.7(4), B-N-C25 120.5(4), C22-N-C25 117.8(4), C10-P-C16 102.4(2), C10-P-B 115.1(2), C16-P-B 101.0(2), Si2-Si1-Si3 106.8(1), Si2-Si1-Si4 107.1(1), Si3-Si1-Si4 104.3(1), Si2-Si1-B 100.2(1), Si3-Si1-B 115.3(1), Si4-Si1-B 121.9(2).

methyl group resonance for the $(Me_3Si)_3Si$ group and inequivalent CH_3 and CH groups for the N^iPr_2 fragment.

Molecular Structure

The molecular structure of **3** was determined by X-ray diffraction techniques and a view of the molecule is shown in Figure 1. The compound contains planar coordinated N and B atoms and a pyramidal coordinated P atom (sum of angles 318.5°). The B-N bond length 1.391(7) Å is short, and together with the mutually planar coordination of the B and N atoms, indicate significant π-overlap between these atoms. The iPr$_2$N-B bond length compares favorably with values in $[Me_3SiPBN^iPr_2]_2$ 1.384(5) Å [44], $[^tBuPBN^iPr_2]_2$ 1.37(1) Å [45], $[HPBN^iPr_2]_2$ 1.377(3) Å [7] and in metal carbonyl complexes [{HPBN**i**Pr$_2$}$_2$·Cr(CO)$_5$] 1.36(1) Å (avg) [7], $[(^iPr_2N)_2BP(H)(SiPh_3)\cdot Cr(CO)_5]$ 1.41(1) Å (avg) [21] and $[(^iPr_2N)B(PH_2)_2\cdot[Cr(CO)_5]_2]$ 1.37(3) Å [7]. The B-P bond length, 1.982(5) Å, is at the long end of the range of B-P single bond lengths found in acyclic boron-phosphorus compounds 1.9−2.0 Å [2]. The B-Si bond length, 2.063(5) Å, are similar to values in the silylborazine $[\{(Me_3Si)Si\}(Me)_2B_3N_3(Me)_3]$, 2.097(4) Å [46], and in the iminoborane $^tBuN{\equiv}BSi(SiMe_3)_3$, 1.976(4) Å [37]. A series of transition metal complexes containing $(Me_3Si)_3SiB(X)$ fragments Å show B-Si bond lengths in the range 2.030(8)−2.052(11) [47].

Since aminophosphino boranes are generally good ligands toward transition metal carbonyl fragments [2], we examined the reactions of **3** with a set of standard metal carbonyl reagents including $Cr(CO)_6$, $[Cr(CO)_5\cdot THF]$, $[Cr(CO)_5\cdot NMe_3]$, $Mo(CO)_6$, $[Mo(CO)_4(CH_3CN)_2]$, $[Mo(CO)_4(NBD)]$, $W(CO)_6$, $[W(CO)_5\cdot THF]$, $Fe(CO)_5$, $Fe_2(CO)_9$ and $Ni(CO)_4$. None of these combinations led to the isolation of a complex. It appears, therefore, that **3** is a poor donor toward these metal carbonyl acceptor fragments and this is likely a result of steric crowding at the phosphorus atom.

Experimental Section

Standard inert-atmosphere techniques were used for the manipulation of reagents. Infrared spectra were recorded on a Mattson 2020 FT-IR spectrometer from KBr pellets. Mass spectra were obtained from the Midwest Center for Mass Spectrometry. NMR spectra were recorded on Bruker WP-250 and JEOL GSX-400 spectrometers from samples vacuum sealed in NMR tubes containing appropriate lock solvents. Spectra were referenced with Me_4Si (^1H, ^{13}C), 85 % H_3PO_4 (^{31}P) and $F_3B{\bullet}OEt_2$ (^{11}B) and downfield shifts relative to the reference were assigned positive δ values.

Tris[(trimethylsilyl)silyl](diisopropylamino)(chloro)borane **(2).** A solution of $[(Me_3Si)_3SiLi\cdot 3THF]$ (5.0 g, 10.6 mmol) [39, 40] in hexane (30 mL) was added to a stirred solution of iPr$_2$NBCl$_2$ (1.93 g, 10.6 mmol) [41] in hexane (20 mL) held at −78 °C. The mixture was stirred (30 min) and then warmed to 23 °C and stirred (1d). Solid LiCl formed and was removed by filtration. The filtrate was vacuum evaporated leaving a sticky oil (3.74 g) that was crystallized from hexane. Yield 3.5 g (84 %) colorless crystals: m.p. 142-144 °C.

$C_{15}H_{41}NBSi_4Cl$ (394.107):calc. C 45.72, H 10.49, N 3.55; found; C 45.50, H 10.33, N 3.62 %.

NMR (C_6D_6): **^{1}H-NMR**: δ = 0.36 (s, 27H, SiCH_3), 0.93 (d, J = 6.7 Hz, 6H, iPrCH_3), 1.38 (d, J = 7.1 Hz; 6H, iPrCH_3), 3.07 (sept, J = 7.1 Hz, 1H, iPrCH), 4.04 ppm (sept, J = 6.7 Hz, 1 H, iPrCH). − **^{13}C{^{1}H}-NMR**: δ = 3.08 (SiCH$_3$), 22.04 (iPrCH$_3$), 23.56 (iPrCH$_3$), 47.71 (iPrCH), 56.34 ppm (iPrCH). − **^{11}B{^{1}H}-NMR**: δ = 43 ($h_{1/2}$ = 190 Hz). **IR** /cm^{-1}: ν = 2969 (s), 2893 (m), 1472 (m), 1447 (m), 1395 (m), 1368 (m), 1310 (m), 1244 (s), 1184 (m), 1146 (m), 1117 (w), 1005 (m), 835 (vs), 748 (m), 685 (m), 623 (m), 583 (w).

Tris[(trimethylsilyl)silyl](diisopropylamino)(diphenylphosphino)-borane **(3).** N-Butyl lithium (Aldrich, 2 mL, 2.5 M in hexane) was added with stirring to Ph_2PH (Aldrich, 0.93 g, 5 mmol) in hexane (50 mL) at −78 °C. The mixture was stirred (10 min) and then warmed to 23 °C (3h). A yellow solid (Ph_2PLi) separated and was recovered by filtration. The solid was rinsed with fresh hexane (2 x 10 mL) and dried in vacuum. A sample of Ph_2PLi (0.551 g; 2.87 mmol) was dissolved in DME (15 mL) and added to a solution of **2** (1.13 g, 2.87 mmol) in DME at 23 °C. This mixture was stirred (12h) and the volatiles removed *in vacuo*. The yellow residue was treated with hexane (40 mL) and insoluble LiCl was removed by filtration. The filtrate was vacuum evaporated leaving a yellow solid (1.50 g) that was recrystallized from cold hexane leaving yellow crystals of **3**. Yield 1.24 g (80 %); m.p. 168-170 °C.

$C_{27}H_{51}NBSi_4P$ (543.841): calc. C 59.63, H 9.45, N 2.58; found; C 59.50, H 9.43, N 2.71 %.

Mass spectrum (30 eV):m/e 544 (M^+), 529 ($M\text{-}CH_3^+$), 471 ($M\text{-}TMS^+$). − **NMR** (C_6D_6) **^{1}H-NMR**: δ = 0.41 (s, 27H, SiCH_3), 0.76 (d, J=7.0 Hz, 6H, iPrCH_3), 1.27 (d, J=7.0 Hz, 6H, iPrCH_3), 4.47 (m, J ~ 7 Hz, 2H, ^{i}PrCH overlapped), 6.99 -7.11 (Ph), 7.41-7.67 ppm (Ph). − **^{13}-C{^{1}H}-NMR**: δ = 4.21 (SiCH$_3$), 25.00 (iPrCH$_3$), 26.16 (iPrCH$_3$), 55.41 (iPrCH), 59.39 (iPrCH),

Table 1 Crystal data for **3**.

Chem. formula	$C_{27}H_{51}BNPSi_4$
Form. wt.	543.8
Cryst. size /mm	0.28 x 0.35 x 0.46
Cryst. system	monoclinic
Space group	*P*2$_1$/*n*
a /Å	10.170(2)
b /Å	17.327(3)
c /Å	19.580(4)
β /°	96.58(3)
V /Å^3	3427.5(11)
Z	4
ρ(calcd.)/(Mg/m^3)	1.054
μ /mm^{-1}	0.236
F (000)	1184
Index range	$-10 \leq h \leq 10$
	$-18 \leq k \leq 18$
	$-21 \leq l \leq 21$
2θ /°	3 to 45
Refl. collected	9988
Refl. unique	4479
Refl. observed (1.5σ)	3214
R(int.)	1.92
No. variables	307
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0003F^2$
GOOF	0.93
Final R (1.5σ)	0.0576
Final wR2	0.0430
Larg. res. peak /(e/Å^3)	0.26/−0.25

127.24 127.61, 128.00, 128.38, 128.59, 128.68, 134.27, 134.53 ppm. − **^{11}B{^{1}H}-NMR**: δ = 55 ppm ($h_{1/2}$ = 380 Hz). − **^{31}P{^{1}H}-NMR**: δ = −31.7 ppm. **IR** /cm^{-1}: ν = 3050 (w), 2967 (m), 2947 (m), 2888 (m), 1582 (2), 1464 (w), 1429 (m), 1366 (w), 1319 (w), 1242 (m), 1182 (m), 1123 (w), 831 (vs), 743 (m), 696 (m), 623 (w).

X-Ray Structure

A single crystal of **3** was lodged inside a glass capillary, sealed under N_2 and mounted on the diffractometer (Siemens R3 m/V). Determinations of the crystal class, orientation matrix and unit cell dimensions were performed in a standard manner. Data were collected at 20 °C using the ω scan mode with monochromated MoKα radiation (λ = 0.71073 Å), a scintillation counter and pulse height analyzer. Crystal data are summarized in Table 1. A small semi-empirical absorption correction based upon psi-scans was applied.

All calculations were performed on a Siemens SHELXTL PLUS (VMS version) structure determination system [48]. Structure solution used direct methods and full-matrix refinements were employed [49].Neutral atom scattering factors and anomalous dispersion terms were used for all non-hydrogen atoms during the refinements.The function minimized was $\Sigma w(|F_o|-|F_c|)^2$. The refinement was well behaved.All non-hydrogen atoms were refined anisotropically and H-atoms on the carbon atoms were included in idealized positions (riding model) with $U_{iso} = 1.25\ U_{equiv}$ of the parent carbon atom.Additional data are deposited with the Cambridge Crystallographic Data Center as publication number CCDC-612617 and can be obtained free of charge from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK Fax +44-1223-336033; email: deposit@ccdc.com.as.uk.

References

[1] Contribution to the Chemistry of Boron, 262. For part 261: see K. Knabel, H. Nöth. R. T. Paine, *Z. Naturforsch.*, in print.

[2] R. T. Paine, H. Nöth, *Chem. Rev.* **1995**, *95*, 343.

[3] M. S. Lube, R. L. Wells, P. S. White, *Inorg. Chem.* **1996**, *35*, 5007.

[4] J. D. Watts, L. C. Van Zant, *Chem. Phys. Lett.* **1996**, *251*, 119.

[5] B. Riegel, H. D. Hausen, W. Schwarz, G. Heckmann, H. Binder, E. Fluck, A. Dransfeld, P. v. Schleyer, *Z. Anorg. Allg. Chem.* **1996**, *622*, 1472.

[6] S. Grundei, H. Nöth, R. T. Paine, *Chem. Ber.* **1996**, *129*, 1233.

[7] D. Dou, G. W. Linti, T. Q. Chen, E. N. Duesler, R. T. Paine, H. Nöth, *Inorg. Chem.* **1996**, *35*, 3626.

[8] M. Sigl, A. Schier, H. Schmidbaur, *Chem. Ber.* **1997**, *130*, 951.

[9] M. Sigl, A. Schier, H. Schmidbaur, *Chem. Ber.* **1997**, *130*, 1411.

[10] E. Herdtweck, F. Jäkle, M. Wagner, *Organometallics* **1997**, *16*, 4737.

[11] T. L. Breen, D. W. Stephan, *Organometallics* **1997**, *16*, 365.

[12] D. A. Hoic, M. DiMare, G. C. Fu, *J. Am. Chem. Soc.* **1997**, *119*, 7155.

[13] T. Q. Chen, E. N. Duesler, R. T. Paine, H. Nöth, *Inorg. Chem.* **1997**, *36*, 1070.

[14] T. Q. Chen, E. N. Duesler, R. T. Paine, H. Nöth, *Chem. Ber.* **1997**, *130*, 933.

[15] T. Q. Chen, R. T. Paine, E. N. Duesler, H. Nöth, *Phosphorus Sulfur and Silicon and the Related Elements* **1997**, *125*, 1.

[16] T. Q. Chen, E. N. Duesler, R. T. Paine, H. Nöth, *Inorg. Chem.* **1997**, *36*, 1534.

[17] M. Ohff, J. Holz, M. Quirmbach, A. Borner, *Synthesis* **1998**, 1391.

[18] T. Q. Chen, E. N. Duesler, R. T. Paine, H. Nöth, *Inorg. Chem.* **1998**, *37*, 490.

[19] H. Dorn, R. A. Singh, J. A. Massey, A. J. Lough, I. Manners, *Angew. Chem.* **1999**, *111*, 3540; *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 3321.

[20] T. Q. Chen, E. N. Duesler, R. T. Paine, H. Nöth, *Inorg. Chem.* **1999**, *38*, 4993.

[21] T. Q. Chen, J. Jackson, S. A. Jasper, E. N. Duesler, H. Nöth, R. T. Paine, *J. Organomet. Chem.* **1999**, *582*, 25.

[22] H. Dorn, R. A. Singh, J. A. Massey, J. M. Nelson, C. A. Jaska, A. J. Lough, I. Manners, *J. Am. Chem. Soc.* **2000**, *122*, 6669.

[23] L. Nyulaszi, *Tetrahedron* **2000**, *56*, 79.

[24] W. Keller, G. Sawitzki, W. Haubold, *Inorg. Chem.* **2000**, *39*, 1282.

[25] T. Q. Chen, E. N. Duesler, H. Nöth, R. T. Paine, *J. Organometal. Chem.* **2000**, *614*, 99.

[26] W. Köstler, G. Linti, *Eur. J. Inorg. Chem.* **2001**, 1841.

[27] K. Miquen, J. M. Sotiropoulos, G. Pfister-Guillouzo, A. C. Gaumont, J. M. Denis, *Organometallics* **2001**, *20*, 143.

[28] H. Dorn, J. M. Rudezno, B. Brunnhofer, E. Rivard, J. A. Massey, I. Manners, *Macromolecules* **2003**, *36*, 291.

[29] U. Vogel, P. Hoemensch, K. C. Schwan, A. Y. Timoshkin, M. Scheer, *Chem. Eur. J.* **2003**, *9*, 515.

[30] K. Kubo, I. Kanemitsu, E. Murakami, T. Mizuta, H. Nakazawa, K. Miyoshi, *J. Organomet. Chem.* **2004**, *689*, 2425.

[31] K. Knabel, T. M. Klapötke, H. Nöth, R. T. Paine, I. Schwab, *Eur. J. Inorg. Chem.* **2005**, 1099.

[32] U. Vogel, K. C. Schwan, P. Hoemensch, M. Scheer, *Eur. J. Inorg. Chem.* **2005**, 1453.

[33] K. Knabel, H. Nöth, R. T. Paine, *Z. Naturforsch.* **2006**, *61b*, 265.

[34] R. T. Paine, H. Nöth, T. Habereder, J. F. Janik, E. N. Duesler, D. Dressig, *ACS Symp. Ser.* **2006**, *917*, 152.

[35] W. Biffar, H. Nöth, *Z. Naturforsch.* **1981**, *36b*, 1509.

[36] M. Haase, U. Klingebiel, *Angew. Chem*. **1985**, *97*, 335; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 324.

[37] M. Haase, U. Klingebiel, R. Boese, M. Polk, *Chem. Ber.* **1986**, *119*, 1117.

[38] J. Markov, R. Fischer, H. Wagner, N. Noormofidi, J. Baumgartner, C. Marschner, *J. Chem. Soc. Dalton Trans.* **2004**, 2166.

[39] G. Gutekunst, A. G. Brook, *J. Organomet. Chem.* **1982**, *225*, 13.

[40] A. Heine, R. Herbst-Irmer, G. M. Sheldrick, D. Stalke, *Inorg. Chem.* **1993**, *32*, 2694.

[41] W. Gerrard, H. R. Hudson, E. R. Mooney, *J. Chem. Soc.* **1960**, 5168.

[42] H. Nöth, B. Wrackmeyer, *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*; Springer-Verlag: West Berlin, 1978.

[43] H. Nöth, S. Sze, *Z. Naturforsch.* **1978**, *33b*, 1313.

[44] P. Kölle, G. Linti, H. Nöth, G. L. Wood, C. K. Narula, R. T. Paine, *Chem. Ber.* **1988**, *121*, 871.

[45] G. Linti, H. Nöth, R. T. Paine, *Chem. Ber.* **1993**, *126*, 875.

[46] D. Srivastava, E. N. Duesler, R. T. Paine, *Eur. J. Inorg. Chem.* **1998**, 855.

[47] H. Braunschweig, M. Colling, C. Kollan, U. Englert, *J. Chem. Soc. Dalton Trans.* **2002**, 2289.

[48] G. M. Sheldrick, *Nicolet SHELXTL Operations Manual*: Nicolet XRD Corp:Cupertino, CA, 1981.

[49] *Crystallographic Computing*; F. R. Ahmed, S. R. Hall, C. P. Huber, Eds.; Munksgaard: Copenhagen, 1970.