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1,2-Dimethyl-1,2-disila-*closo*-dodecaborane(12), the First Silicon Analog of an ortho-Carborane* *

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The icosahedral carboranes, especially those in which the two cluster carbon atoms are vicinal (*o*-carboranes), have received much attention since the first reports of their existence in 1963.(1) Notably absent in the many publications on this class of boron cluster compounds over the intervening 25 odd years have been examples of icosahedral clusters in which the two mono-substituted carbon atoms of an *o*-carborane have been replaced by two mono-substituted silicon, germanium, tin or lead atoms. We report here the synthesis and structural characterization of **1**, the first such Group IVA analog of an *o*-carborane: 1,2-dimethyl-1,2-disila-*closo*-dodecaborane(12) (or 1,2-dimethyl-*o*-silaborane). This compound is notable also in that it is the first example of a formal derivative of a disilyne, $CH_3Si{\equiv}SiCH_3$ in the present case,

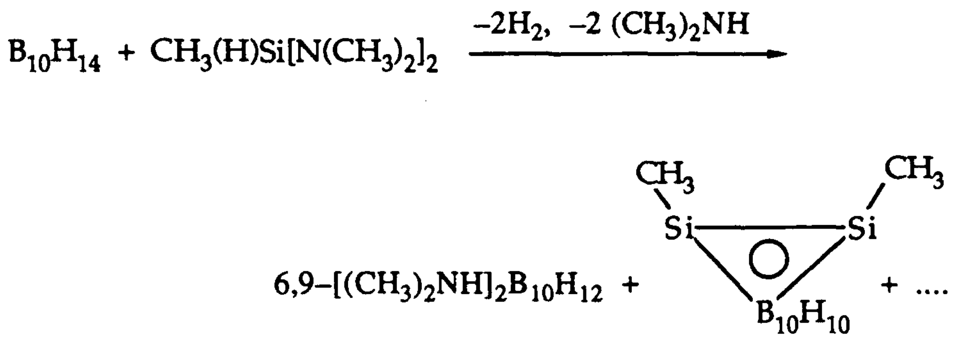
(Triple bonds)

Cont in the next page

a class of unsaturated organosilicon compounds of which there are to date no known examples.

Keywords: Carboranes, Silaboranes, Organosilicon Compounds, organic chemistry, Silicon, Boron

The synthesis of 1,2-dimethyl-o-silaborane, 1, was the result of a deviation from the expected reaction course when a benzene solution of decaborane(14) and methylbis(dimethylamino)silane, $CH_3(H)Si[N(CH_3)_2]_2$, 2, was heated at reflux under nitrogen. In prior work[2], such a reaction of $B_{10}H_{14}$ with $(CH_3)_2Si[N(CH_3)_2]_2$ in refluxing benzene had resulted in formation of a linear polymer, $[6,9\text{-}(CH_3)_2NSi(CH_3)_2N(CH_3)_2 \bullet B_{10}H_{12}]_x$, a pale yellow, resinous material from whose melt fibers could be drawn and whose pyrolysis in a stream of ammonia to 1000°C gave boron nitride that contained 2-4% Si in high yield. However, the reaction of $B_{10}H_{14}$ with 2 in refluxing benzene or toluene resulted in formation of a mixture of two white solids, 1 in 15% yield, based on $B_{10}H_{14}$, and $6,9\text{-}[(CH_3)_2NH]_2B_{10}H_{12}$, 3, in 58% yield (eq. 1). The former could be purified by sublimation at 90°C (0.01 Torr). Its yield has not been optimized. Compound 1 may be handled without exclusion of the laboratory atmosphere since it is stable to air and moisture.



(1)

3 1

Very slow crystallization of 1 from dilute benzene solution at 3°C gave the 1:1 solvate, $1,2\text{-}(CH_3)_2Si_2B_{10}H_{10}\bullet C_6H_6$, as rods whose structure was determined by single crystal X-ray diffraction.[3] The o-silaborane, like the o-carboranes, has a slightly distorted icosahedral structure (Fig. 1). The Si-Si bond distance of 2.308(2) Å is slightly less than that of "normal" Si-Si single bonds (~ 2.33 - 2.34 Å)[4], but significantly longer than known Si-Si double bonds.[5] In comparison, the C-C bond distances in o-carboranes (1.655 Å, the mean value found in X-ray and gas phase electron diffraction studies[6]) are longer than the normal C(sp^3)-C(sp^3) distance of 1.54 Å. This is understandable in terms of the larger size of a silicon atom (covalent radius 1.18 Å), compared with a carbon atom (covalent radius 0.77 Å). The Si-B bond distances in 1 [2.017(3), 2.018(3), 2.113(4) and 2.116(3) Å] are very close to the sum of the covalent radii of Si and B, 2.07Å (using 0.89 Å as the average boron covalent radius in o-carboranes[6]). These distances may be compared to those of the Si-B bonds in *commo*-3,3'-Si(3,1,2-$SiC_2B_9H_{11})_2$, which contains a single silicon atom bonded within a 12-atom boron-containing cluster: 2.05(1) and 2.14(1) Å.[7]

The ^1H, ^{13}C, ^{29}Si and ^{11}B NMR spectra of 1 were recorded.[8] The ^{11}B NMR spectrum (160.367 MHz, acetone-d_6, 25°C, external $BF_3 \bullet OEt_2$) was in agreement with the 1,2-disila-closo-dodecaborane(12) cage structure, showing four doublets in 2:2:2:4 intensity ration at δ_B –11.2 (d, J = 147 Hz, B9, 12), –12.6 (d, J = 144 Hz, B8, 10), –13.5 (d, J = 152 Hz, B3, 6) and –14.5 (d, J = 147 Hz, B4, 5, 7, 11). The assignments are based on a 2D proton-decoupled ^{11}B–^{11}B FT NMR spectrum. The CH_3 resonance was observed at -0.07 ppm in the ^1H NMR spectrum of 1 in C_6D_6 solution. The proton-decoupled ^{29}Si NMR spectrum of 1 in C_6D_6 solution at 50°C showed a singlet at -37.77 ppm, the proton-decoupled ^{13}C NMR spectrum, also in C_6D_6 at 40°C, a singlet at -12.80 ppm. The upfield shifts observed in the ^{13}C and ^{29}Si spectra of 1 taken in C_6D_6 solution, as compared with TMS, are consistent with the well-documented electron-deficient nature of boron cages.

Compound 1 is less stable than the o-carboranes. It melts at 201-203°C (sealed capillary) and decomposes with gas evolution above 230°C. It remains undecomposed when heated at reflux in wet tetrahydrofuran solution for several days. It was unaffected when treated with an excess of CF_3CO_2H in THF at room temperature and remained largely undecomposed when this solution was heated at reflux for 14 hr. It was found to be stable toward $AlCl_3$ in refluxing benzene. It reacts with and is degraded by alcoholic KOH in THF at room temperature within minutes and it decolorizes a solution of bromine in carbon tetrachloride after several hours at reflux.

Now that the first member of this new class of boron cluster compounds has been isolated, it may be expected that other $1,2\text{-}R_2Si_2B_{10}H_{10}$ compounds can be prepared. The development of their chemical reactivity at silicon and at boron will be of some interest as will a comparison of their chemistry with that of the o-carboranes. Our further research will deal with these questions.

Experimental Procedure

A 250 ml three-necked flask equipped with a reflux condenser, an addition funnel and a magnetic stir-bar was flushed with argon and charged with 6.6 g (54.0 mmol) of $B_{10}H_{14}$ and 120 ml of dry toluene. To the resulting solution was added dropwise at room temperature 7.1 g (53.7 mmol) of 2[9]. The reaction mixture was stirred and heated at reflux under argon for 24 hr. During this time a white solid precipitated. The reaction mixture was filtered and the filtrate evaporated at reduced pressure. The residue was extracted with two 100 ml portions of hot benzene. Filtration of the extracts and cooling to 3°C resulted in deposition of 1.45 g of 1 as an amorphous white powder that contained a small amount of white needles. Evaporation of the remaining benzene solution gave 0.6 g of 3, identified on the basis of its ^1H and ^{11}B NMR and mass spectra. The solid which had precipitated during the reaction was sublimed at 90°C (0.01 Torr) to give additional 0.15 g of 1. The sublimation residue was 6.0 g of 3. The total yield of the latter was 6.6 g, (58%). The total yield of 1 was 1.60g, a yield of 15% based on $B_{10}H_{14}$. Anal. Calcd. for $C_2H_{16}Si_2B_{10}$: C, 11.75; H, 7.89; Si, 27.48. Found: C, 11.64; H, 7.75; Si, 27.62. The high resolution MS showed molecular ion peaks at m/z 206.1720

($^{12}C_2H_{16}$ $^{11}B_{10}$ $^{28}Si_2$ calcd. 206.17211), 207.1715 ($^{12}C_2H_{16}$ $^{11}B_{10}$ ^{28}Si ^{29}Si calcd. 207.17168), 208.1688 ($^{12}C_2H_{16}$ $^{11}B_{10}$ ^{28}Si ^{30}Si calcd. 208.16898), and 209.1685 ($^{12}C_2H_{16}$ $^{11}B_{10}$ ^{29}Si ^{30}Si calcd 209.16855).

1. Gmelin Handbook of Inorganic Chemistry, 8th Edition, "Borverbindungen", 2 (1974), 6 (1975), 11 (1977), and 12 (1977), and chapters in the first and second supplements (1980-1983), Springer-Verlag, Berlin. See also: R.N. Grimes, "Carboranes", Academic Press, New York, 1970, Chapter 6 and literature cited therein.
2. D. Seyferth and W.S. Rees, Jr., unpublished work.
3. The 1,2-$(CH_3)_2Si_2B_{10}H_{10}\bullet C_6H_6$ molecule crystallizes with crystallographic two-fold symmetry. One molecule of benzene was found for every molecule of 1 in two sites of equal occupancy; each site has the same crystallographic two-fold symmetry. Crystal data for $1\bullet C_6H_6$: orthorhombic, space group Pccn (#56); a = 10.081(1), b = 10.666(8), c = 16.130(5) Å, V = 1734 Å, Z = 4; $\rho_{calcd} = 1.052$ g cm^{-3}, F(000) = 592, $\mu(MoK_\alpha) = 1.78$ cm^{-1}, 2291 reflections measured, 2291 unique reflections, 1050 observed $(I>3\sigma(I))$, 89 variables, R = 0.044, $R_w = 0.058$, Rigaku AFC6R diffractometer, MoK_α ($\lambda = 0.71069$ Å). Further details of the crystal structure determination may be obtained from the Fachinformationszentrum Karlsruhe Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2 (FRG)

on quoting the deposition number *******, the names of the authors and the journal citation.

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5. Si-Si double bond distances: 2.143(1) and 2.160(1) Å: M.J. Fink, M.J. Michalczyk, K.J. Haller, J. Michl, R. West, Organometallics 3 (1984) 793; 2.140(9) Å: S. Masamune, S. Murakami, J.T. Snow, H. Tobita, D.J. Williams, Organometallics 3 (1984) 3330.

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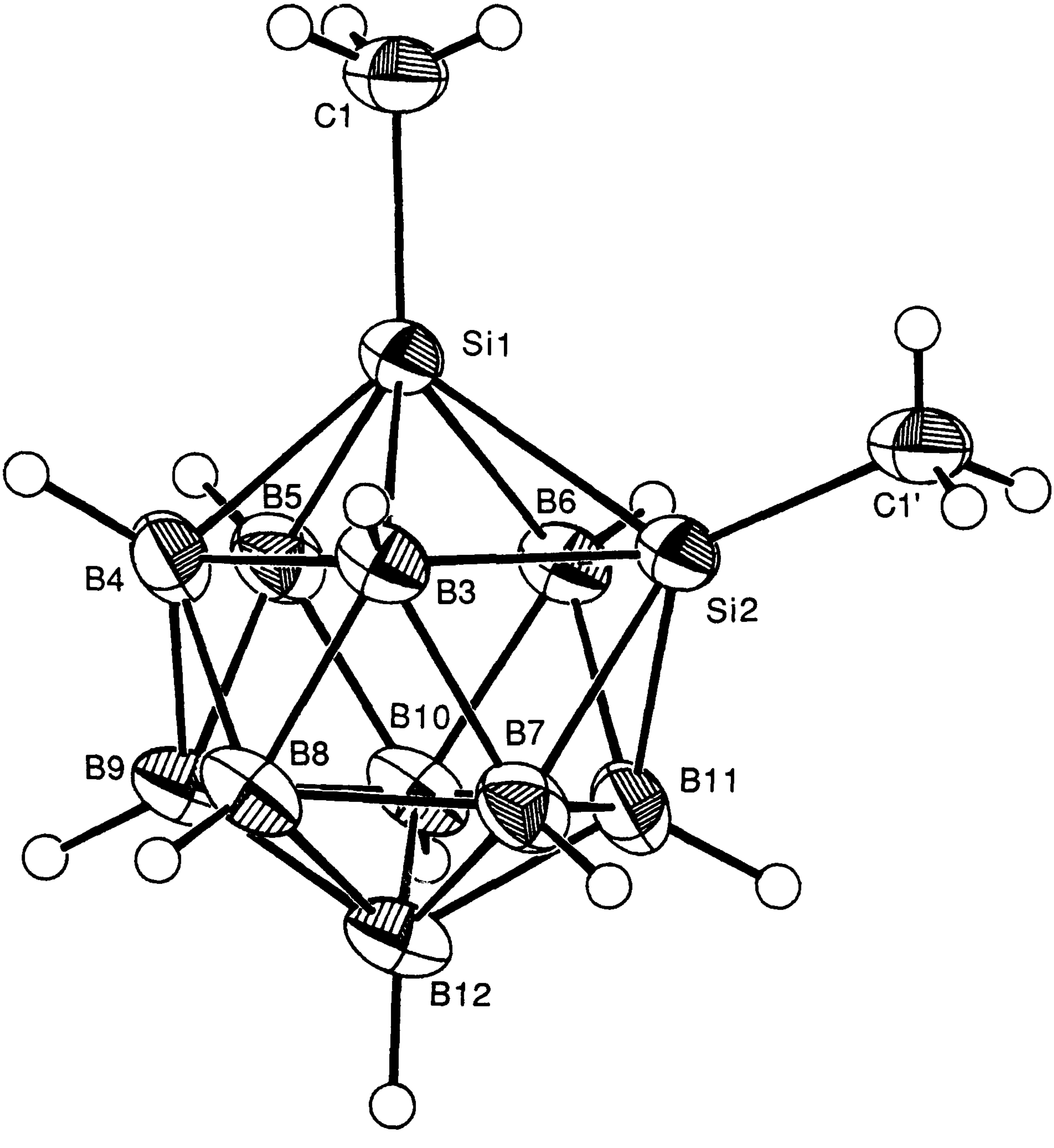
8. NMR spectra, conditions: All measurements at 25°C unless otherwise specified. ^{11}B, 160.37 and 96.235 MHz, $BF_3 \bullet OEt_2$; ^{1}H, 300 MHz, TMS; ^{29}Si, 99.34 MHz, TMS; ^{13}C, 75.43 MHz, TMS.

9. S.S. Washburne, W.R. Peterson, Jr., J. Organomet. Chem. 21 (1970) 59.

CAPTION FOR FIGURE 1

ORTEP representation of 1,2-dimethyl-1,2-disila-*closo*-dodecaborane(12), drawn with 35% probability ellipsoids. Hydrogen atoms have been given arbitrary thermal parameters for clarity. Due to molecular symmetry, distances involving Si 2 are equivalent to those involving Si 1. Other symmetry related atoms are: C 1 and C 2; B 3 and B 6; B 4 and B 11; B 5 and B 7; B 8 and B 10; B 9 and B 12. Selected interatomic distances (in Å, with standard deviations of the last digit given in parentheses) are:

Si 1 - C 1	1.827(3)	B 3 - B 4	1.848(5)
Si 1 - Si 2	2.308(2)	B 4 - B 5	1.859(5)
Si 1 - B 3	2.116(3)	B 4 - B 8	1.774(5)
Si 1 - B 4	2.018(3)	B 4 - B 9	1.765(5)
Si 1 - B 5	2.017(3)	B 5 - B 6	1.849(5)
Si 1 - B 6	2.113(4)	B 5 - B 9	1.769(5)
B 6 - B 10	1.771(4)	B 5 - B 10	1.765(5)
B 8 - B 12	1.782(5)	B 9 - B 12	1.775(8)
B 10 - B 12	1.784(5)		


C1
Si1
B4
B5
B3
B6
Si2
C1'
B10
B7
B9
B8
B11
B12

ABSTRACT

The reaction of $CH_3(H)Si[N(CH_3)_2]_2$ with $B_{10}H_{14}$ in refluxing benzene gives 6,9-$[(CH_3)_2NH]_2B_{10}H_{12}$ and 1,2-$(CH_3)_2Si_2B_{10}H_{10}$, $\underline{\underline{1}}$, in 15% yield. An X-ray diffraction study of the latter showed it has the ortho-carborborane structure in which the two carbon atoms have been replaced by two silicon atoms. NMR spectroscopic (^{11}B, ^{1}H, ^{13}C, ^{29}Si) and high resolution MS data are reported for $\underline{\underline{1}}$.