mol. wt., 228. Found: C, 32.8, 32.9; H, 9.4, 9.3; B, 46.8, 46.9; mol. wt., 232.

**Acknowledgment.**—This work was supported in large part by the U. S. Air Force under Contract AF 33(616)-5934 monitored by the Propulsion Laboratory, Rocket and Flight Test Center, Edwards Air Force Base, California, and in part by the Office of Naval Research. The authors are also grateful to many associates for helpful suggestions regarding many phases of this work and especially to Dr. J. R. Norman, who interpreted the mass spectra, and Messrs. E. A. Cox, F. S. Natoli, and J. W. Szymanski, who prepared some of the compounds in quantity.

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CONTRIBUTION FROM THE RESEARCH LABORATORIES, ORGANICS DIVISION,
OLIN MATHIESON CHEMICAL CORPORATION, NEW HAVEN, CONNECTICUT

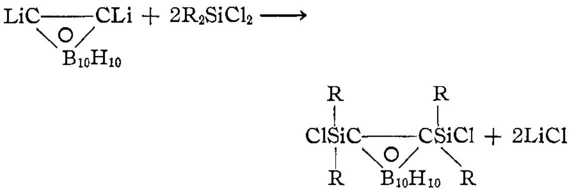
# A New Series of Organoboranes. IV. The Participation of the 1,2-Dicarbaclovododecaborane(12) Nucleus in Some Novel Heteratomic Ring Systems

BY STELVIO PAPETTI AND T. L. HEYING

*Received June 14, 1963*

Various chlorosilylcarborane derivatives were prepared. In subsequent reactions with amines or water a marked propensity for the formation of five-membered disilaazane and disilaoxane rings was exhibited. In reactions with dilithiocarborane, novel disilacyclohexane analogs were formed.

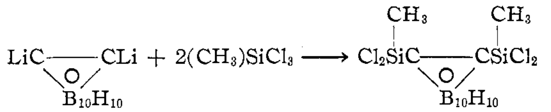
In the preceding paper[1] several examples of the synthesis of mono- and disilylcarboranes were given. Utilization of the same general preparative procedures has proven quite satisfactory for the preparation of 1,2-bis-(chlorosilyl)-carboranes in good yield as indicated in reaction 1.



(1)

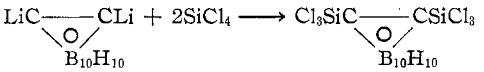
I, $R = CH_3$
II, $R = C_6H_5$

By applying the proper stoichiometry we were able to prepare the corresponding tetrachloro and hexachloro derivatives in surprisingly good yield.



(2)

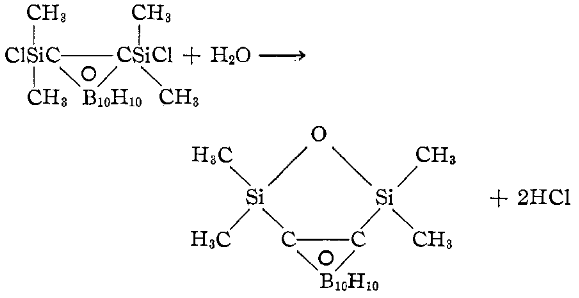
III



(3)

IV

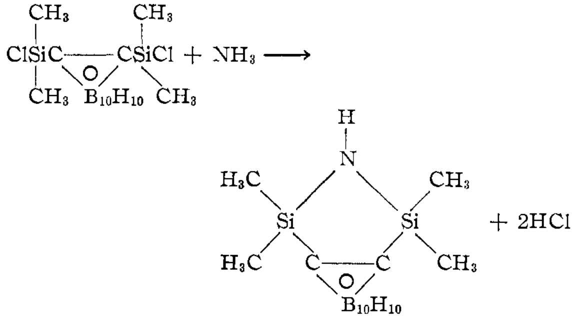
To determine whether 1,2-bis-(chlorodimethylsilyl)-carborane (I) would behave chemically as do the conventional organic derivatives, it was subjected to hydrolysis, expecting to form a macrocyclic siloxane, a linear silicone, or possibly the corresponding dihydroxy compound. To the contrary, under all of the many sets of conditions attempted to date, I was converted to the cyclic tetramethyldisilaoxane, V. In most instances it is achieved in high purity in essentially quantitative yield



(4)

V

The cyclic structure was first assigned on the basis of its elemental analysis, molecular weight, and infrared spectrum. This assignment was borne out subsequently by examination of its mass spectrum, which is in agreement in every detail. The same evidence has been gained for those novel cyclic structures discussed below. Compound V above has also been prepared by the reaction of dilithiocarborane with excess tetramethyldichlorodisiloxane.



(5)

VI

When 1,2-bis-(chlorodimethylsilyl)-carborane was treated with ammonia, a similar reaction occurred to

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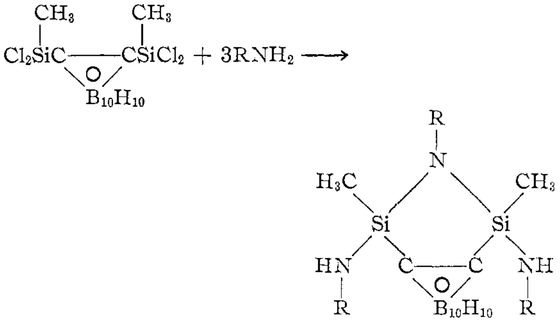
(1) T. L. Heying, J. W. Ager, Jr., S. L. Clark, R. P. Alexander, S. Papetti, J. A. Reid, and S. I. Trotz, *Inorg. Chem.*, **2**, 1097 (1963).

give in this instance the cyclic tetramethyldisilaazane, VI. Unlike the numerous organic silicon–nitrogen-bonded compounds which have been noted to readily react with moisture, we have been unable to hydrolyze this and related compounds. Also this compound and its disilaoxane analog V were recovered quantitatively unchanged after heating at 500°. Above this temperature some methane was evolved.

Amminolysis of 1,2-bis-(dichloromethylsilyl)-carborane (III) with ammonia and methylamine was next studied and here high yields of the substituted cyclic disilaazanes VI and VII formed. Hydrolysis of these compounds also left the disilaazane ring intact but the pendant –NHR groups were attacked.

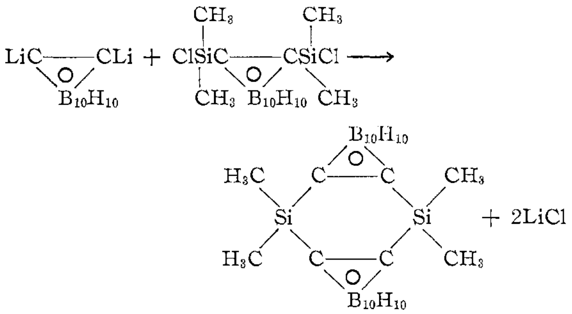


(6)

VII, R = H
VIII, R = $CH_3$

The ease with which these reactions occur to form five-membered rings bears notice. We have observed a similar situation in other carborane derivatives wherein the three ring atoms other than the carboranyl carbon pair are –C–C–C–, –C–O–C–, and –C–Si–C–.[1] Other workers in these laboratories[2] have encountered a similar situation wherein the noncarboranyl ring atoms are –P–N–P–. This suggests that the exonuclear bond angles and the bond distance of the two carborane carbon atoms are of a magnitude particularly suited for participation in five-membered rings. Also, to our knowledge, there is no instance of the participation of one carboranyl nucleus in a larger ring, and this further suggests that this bond angle is quite invariant. Further support of this concept comes from the fact that the infrared carbon–hydrogen stretching absorption occurs at 3.25 $\mu$, which is essentially the same as that of the rigidly oriented acetylenic ≡C–H.

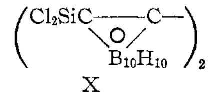
When 1,2-bis-(chlorodimethylsilyl)-carborane was treated with dilithiocarborane a reaction occurred which gave a product having a six-membered ring composed of four carbon atoms of two carborane nuclei and two silicon atoms.



(7)

IX

All chemical and instrumental analyses are in complete agreement again. This too seems to be a favored type of ring system since an analogous system wherein the silicon atoms are replaced by phosphorus(III) has recently been discovered.[2] When bis-(trichlorosilyl)-carborane was similarly treated with an equimolar quantity of dilithiocarborane the analogous reaction occurred to give the cyclic tetrachloro derivative



X

It is of interest that no change in X occurred when it was treated with water at room temperature, thereby not showing the normal tendency of the silicon–chlorine for hydrolysis. This phenomenon is being investigated in more detail as is the general preparative and polymer chemistry of all of the novel heterocyclic compounds herein reported.

## Experimental

**1,2-Bis-(chlorodimethylsilyl)-carborane (I).**—A dilithiocarborane slurry[1] was prepared from 50.0 g. (0.347 mole) of carborane[3] and 2.05 moles of butyllithium in ether and slowly added to a stirred, ethereal solution of 98.33 g. (0.762 mole) of dichlorodimethylsilane cooled in an ice bath. When addition was complete the mixture was refluxed overnight and then filtered. The filtrate was evaporated to dryness, the residue was sublimed under vacuum at a bath temperature of 125–130°, and the sublimate was recrystallized from heptane. Bis-(chlorodimethylsilyl)-carborane (m.p. 112.5–113.5°)[4] was recovered in 88% yield.

*Anal.*[5] Calcd. for $C_6H_{22}B_{10}Cl_2Si_2$: C, 21.84; H, 6.86; B, 32.79; Cl, 21.49; Si, 17.02. Found: C, 22.05; H, 6.67; B, 32.57; Cl, 21.15; Si, 16.79.

**1,2-Bis-(chlorodiphenylsilyl)-carborane (II).**—The reaction was identical with that for I using 15.35 g. (0.106 mole) of carborane and 59.3 g. (0.234 mole) of dichlorodiphenylsilane. The sublimation was omitted and the 22.7% yield of bis-(chlorodiphenylsilyl)-carborane (m.p. 244–245°) was obtained directly by recrystallization from heptane.

*Anal.* Calcd. for $C_{26}H_{30}B_{10}Cl_2Si_2$: C, 54.05; H, 5.23; B, 18.12; Cl, 12.26; Si, 9.73. Found: C, 53.80; H, 5.13; B, 18.80; Cl, 12.15; Si, 9.27.

**1,2-Bis-(dichloromethylsilyl)-carborane (III).**—This compound was prepared as was II but from 21.6 g. (0.150 mole) of carborane and 49.7 g. (0.333 mole) of methyltrichlorosilane. The 69.5% yield of bis-(chloromethylsilyl)-carborane (m.p. 119–120°) was recovered by recrystallization from 30–60° petroleum ether.

*Anal.* Calcd. for $C_4H_{16}B_{10}Cl_4Si_2$: C, 12.97; H, 4.35; B, 29.22; Cl, 38.29; Si, 15.17. Found: C, 13.10; H, 4.34; B, 29.30; Cl, 38.35; Si, 14.75.

**1,2-Bis-(trichlorosilyl)-carborane (IV).**—The procedure of II was followed using 15.87 g. (0.11 mole) of carborane and 41.15 g. (0.242 mole) of tetrachlorosilane. The crude product was recrystallized from heptane to give a 60% yield of bis-(trichlorosilyl)-carborane (m.p. 121–122°).

*Anal.* Calcd. for $C_2H_{10}B_{10}Cl_6Si_2$: C, 5.85; H, 2.43; B, 26.31; Cl, 51.74; Si, 13.67. Found: C, 5.74; H, 2.51; B, 26.61; Cl, 51.35; Si, 13.17.

**1,2-(1′,1′,3′,3′-Tetramethyldisilaoxanyl-1′,3′)-carborane**

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[2] R. P. Alexander and H. Schroeder, *Inorg. Chem.*, **2**, 1107 (1963).

[3] We thank Mr. R. W. Blundon for preparing a continuing supply of carborane for this work.

[4] All melting points were taken with a Mel-Temp apparatus and are uncorrected.

[5] Analyses were by the Olin Microanalytical Section.

(V).—This compound is readily prepared by adding excess water to a benzene–acetone solution of bis-(chlorodimethylsilyl)-carborane (I) at room temperature. The resulting solution is concentrated under reduced pressure until most of the benzene and acetone is removed, the remaining mixture is filtered, and the residue is either recrystallized from heptane or sublimed. A practically quantitative yield of V (m.p. 160–161°) is obtained.

*Anal.* Calcd. for $C_6H_{22}B_{10}OSi_2$: C, 26.20; H, 8.07; B, 39.33; Si, 20.42. Found: C, 26.55; H, 8.06; B, 39.30; Si, 19.7.

This compound (V) was prepared in 74.8% yield when dilithiocarborane was treated with excess tetramethyldichlorodisiloxane.

**1,2-(1′,1′,3′,3′-Tetramethyldisilaazanyl-1′,3′)-carborane (VI).**—Bis-(chlorodimethylsilyl)-carborane (I) (2.69 g., 0.0081 mole) was dissolved in 50 ml. of ethyl ether and cooled in an ice bath. Ammonia was passed through at a rapid rate for 15 min., during which time a precipitate formed. The mixture was filtered and the filtrate was evaporated to dryness. The residue so formed was recrystallized from high boiling petroleum ether to give an essentially quantitative yield of VI (m.p. 190–192°).

*Anal.* Calcd. for $C_6H_{23}B_{10}NSi_2$: C, 26.29; H, 8.46; B, 39.49; N, 5.11; Si, 20.49; mol. wt., 274. Found: C, 26.58; H, 8.21; B, 39.70; N, 5.05; Si, 19.6; mol. wt., 270 (osmometric).

**1,2-(1′,3′-Diamino-1′,3′-dimethyldisilaazanyl-1′,3′)-carborane (VII).**—The procedure for VI was followed exactly using 2.0 g. (0.006 mole) of bis-(dichloromethylsilyl)-carborane (III) to give a quantitative yield of VII (m.p. 189–191.5°).

*Anal.* Calcd. for $C_4H_{21}B_{10}NSi_2$: C, 17.42; H, 7.68; B, 39.26; N, 15.25; Si, 20.38; mol. wt., 276. Found: C, 17.41; H, 7.83; B, 38.48; N, 14.64; Si, 20.08; mol. wt., 278 (cryoscopic).

**1,2-(1′,2′,3′-Trimethyl-1′,3′-dimethylaminodisilaazanyl-1′,3′)-carborane (VIII).**—Methylamine was bubbled through a cooled solution of 4.7 g. (0.014 mole) of bis-(dichloromethylsilyl)-carborane (III) in 60 ml. of ether for 30 min. The mixture was filtered, the filtrate was concentrated, and the resulting solid was recrystallized from 30–60° petroleum ether to give an essentially quantitative yield of VIII (m.p. 128–129.5°).

*Anal.* Calcd. for $C_7H_{27}B_{10}N_3Si_2$: N, 13.23; Si, 17.68; mol. wt., 318. Found: N, 13.31; Si, 17.68; mol. wt., 325 (cryoscopic).

**Compound IX.**—A dilithiocarborane slurry in ether prepared from 7.5 g. (0.052 mole) of carborane was added to a cooled solution of 0.11 mole of 1,2-bis-(chlorodimethylsilyl)-carborane (I) in ether. The mixture was refluxed overnight, filtered, and the filtrate evaporated to dryness. This residue was heated at 130–140° *in vacuo* to remove unreacted I. The residue was recrystallized from acetone to give a 23% (based on the original amount of I) yield of IX (m.p. 309–310°).

*Anal.* Calcd. for $C_8H_{32}B_{20}Si_2$: C, 23.97; H, 8.05; B, 53.97; Si, 14.01; mol. wt., 400. Found: C, 22.95; H, 7.78; B, 53.84; Si, 14.42; mol. wt., 379 (osmometric).

**Compound X.**—1,2-Bis-(trichlorosilyl)-carborane (0.484 g., 0.0118 mole) in 50 ml. of ether was allowed to react with dilithiocarborane prepared from 1.550 g. (0.0107 mole) of carborane in the usual manner. The reaction was refluxed overnight and then filtered. The residue was extracted several times with ether and the combined extracts were evaporated to dryness. This solid was recrystallized from benzene (2.0 g.). The filtrate from the original reaction was concentrated and the solid which formed was removed and recrystallized from benzene (0.5 g.). All mother liquors were combined and evaporated to dryness, and this solid was also recrystallized from benzene (0.2 g.). All three materials were shown to be identical, which gave a 52.2% yield of X (m.p. 271–272°).

*Anal.* Calcd. for $C_4H_{20}B_{10}Cl_4Si_2$: C, 9.95; H, 4.18; Cl, 29.39. Found: C, 9.74; H, 4.11; Cl, 29.7. Mass spectral analysis also identified the product as X in greater than 98% purity.

**Acknowledgment.**—The authors thank Mr. Herman Hoberecht, for obtaining and interpreting the mass spectra of these compounds which conclusively allowed the assignment of the ring structures, and also Dr. H. Schroeder and Mr. H. C. Kaufman, for their suggestions. This work was sponsored by the Office of Naval Research.

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CONTRIBUTION FROM THE ORGANICS DIVISION,
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# Chemistry of Decaborane–Phosphorus Compounds. IV. Monomeric, Oligomeric, and Cyclic Phosphinocarboranes[1,2]

BY ROY P. ALEXANDER AND HANSJUERGEN SCHROEDER

*Received June 12, 1963*

Dilithiocarborane, $B_{10}H_{10}C_2Li_2$, was allowed to react with chlorophosphines containing one, two, and three chlorine atoms. $(C_6H_5)_2PCl$ and $C_6H_5PCl_2$ gave the expected disubstituted compounds, $B_{10}H_{10}C_2[P(C_6H_5)_2]_2$ and $B_{10}H_{10}C_2(C_6H_5P\cdot Cl)_2$, respectively. $B_{10}H_{10}C_2Li_2$ and $PCl_3$, however, formed a compound having two phosphorus atoms and two carborane nuclei in a six-membered ring. This unique ring system also arose from the reaction of $B_{10}H_{10}C_2Li_2$ with $B_{10}H_{10}C_2(C_6H_5P\cdot Cl)_2$. Subsequent reactions of such molecules with ammonia and $NaN_3$ are described. The cyclic bis-azide, $(B_{10}H_{10}C_2P\cdot N_3)_2$, and $p$-$[(C_6H_5)_2P]_2C_6H_4$ reacted to form a PNP bonded oligomer.

In previous papers of this series we reported the synthesis of bifunctional decaborane–phosphine monomers[3] and their conversion into linear polymers.[1] The high-thermal and hydrolytic stability of PNP bonded decaborane–phosphine polymers,[1] especially of compound I, made them an obvious object for further investigation.

Since it was established[1] that compound I lost hydrogen from the decaborane nuclei under cross linking at 340°, a logical extension of this work with regard to improving heat stability was the replacement of those

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(1) Preceding communication: H. Schroeder, J. R. Reiner, and T. A. Knowles, *Inorg. Chem.*, **2**, 393 (1963).

(2) Presented before the Inorganic Division of the American Chemical Society at the 145th National Meeting, New York, N. Y., Sept. 10, 1963.

(3) H. Schroeder, J. R. Reiner, and T. L. Heying, *Inorg. Chem.*, **1**, 618 (1962).