(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.

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

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.

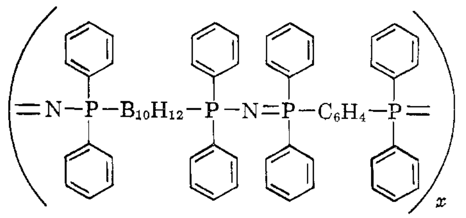
Since it was established[1] that compound I lost hydrogen from the decaborane nuclei under cross linking at 340°, a logical extension of this work with regard to improving heat stability was the replacement of those

---

(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).

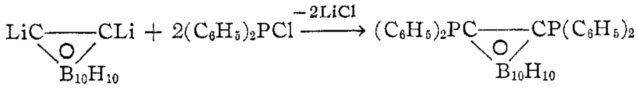

($x = \sim 20$)

I

or all hydrogens by atoms more firmly bonded to boron such as chlorine and fluorine. Initial attempts to chlorinate the starting monomer $B_{10}H_{12}[(C_6H_5)_2P\cdot Cl]_2$ met with failure. However, before a more thorough halogenation study of compounds containing the $B_{10}H_{12}$ unit was conducted, attention was turned to the easily chlorinated carborane[4] moiety instead.

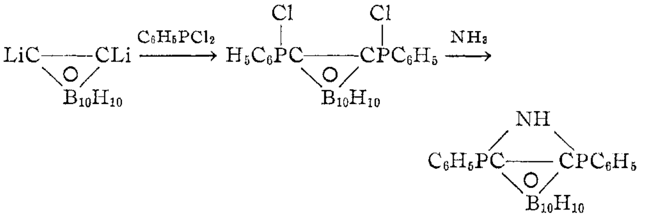
Interest in this laboratory has been focused recently on the chlorination of carborane resulting in polychlorocarboranes such as $B_{10}Cl_{10}C_2H_2$.[5] The potential utility of the chlorinated carborane nucleus for the formation of PNP bonded carborane polymers led us to initiate an investigation aimed at the preparation of difunctional phosphorus-containing carborane and polychlorocarborane derivatives. The present study describes the first part of our research dealing with the synthesis of chlorophosphinocarboranes followed by the application of the PNP polymer scheme to those compounds obtained containing the unchlorinated carborane nucleus.

The ability of carborane to undergo direct lithiation upon treatment with *n*-butyllithium[6] provided dilithiocarborane, an appropriate starting compound for reactions with various chlorophosphines. In a prototype experiment, metathesis was found to occur between dilithiocarborane and diphenylchlorophosphine to give bis-(diphenylphosphino)-carborane.



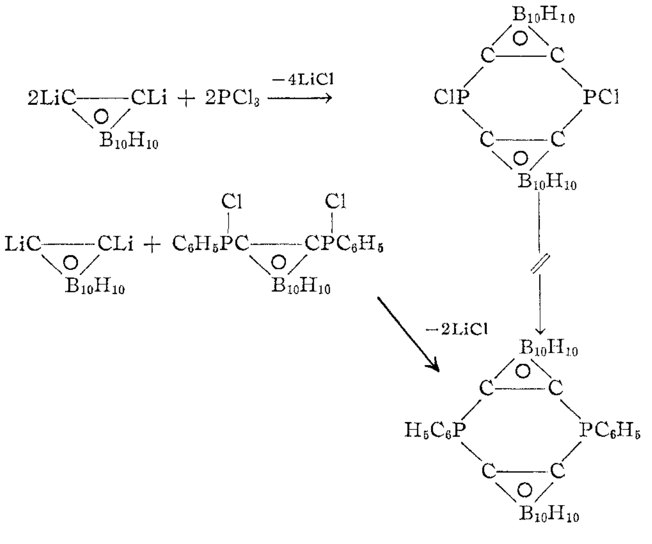
Having demonstrated the fundamental reaction, the dilithio salt was treated with phenyldichlorophosphine. As expected, two molar equivalents of $C_6H_5PCl_2$ reacted with one equivalent of $B_{10}H_{10}C_2Li_2$ to form the desired bis-chloro compound $B_{10}H_{10}C_2(C_6H_5P\cdot Cl)_2$.

To determine the reactivity of the phosphorus-bound chlorine atoms, ammonia was passed, at room temperature, into a solution of $B_{10}H_{10}C_2(C_6H_5P\cdot Cl)_2$ in benzene. Ammonolysis occurred, but instead of the expected bis-amino compound $B_{10}H_{10}C_2[P(C_6H_5)NH_2]_2$, a cyclic diphospha(III)azane, $B_{10}H_{10}C_2[(PC_6H_5)_2NH]$, was recovered in 70% yield. The infrared spectrum was consistent with this formulation in showing only a single N–H stretching absorption at 3 μ, and the parent mass spectral peak corresponded to the expected molecular weight.



On the other hand, treatment of $B_{10}H_{10}C_2(C_6H_5P\cdot Cl)_2$ with sodium azide in ethanol at 0° gave the desired bis-azide, $B_{10}H_{10}C_2(C_6H_5P\cdot N_3)_2$, m.p. 126–128° dec. In benzene solution the compound undergoes decomposition at approximately 40° with evolution of nitrogen, yielding a product, the analysis of which is in general agreement with the formula $(=NP(C_6H_5)CB_{10}H_{10}C(C_6H_5)PN=)_x$. The decomposition is promoted by the addition of a phosphine such as $(C_6H_5)_3P$, since in their presence nitrogen evolution begins at 10 to 20°. The phosphines do not interact with this phosphorus(III) bis-azide, a finding in sharp contrast to the easy formation of phosphorus–nitrogen double bonds[1] observed in the reaction of $B_{10}H_{12}[(C_6H_5)_2P\cdot N_3]_2$, a compound having tetracoordinate phosphorus, with phosphines.

In view of these results it appeared of interest to investigate next the reaction of $B_{10}H_{10}C_2Li_2$ with PCl_3. It was found that equimolar amounts of these reactants form a product which analyzes as $(B_{10}H_{10}C_2PCl)_x$. On the evidence of an accurate cryoscopic molecular weight determination corroborated by mass spectral analysis, a cyclic structure containing two carborane moieties and two phosphorus atoms in the ring was assigned for this reaction product. Another example of this diphosphacyclohexane system was obtained by reaction of $B_{10}H_{10}C_2(C_6H_5P{\cdot}Cl)_2$ with $B_{10}H_{10}C_2Li_2$ to give the diphenyl-substituted derivative. However, the dichloro compound has resisted attempts to convert it to the diphenyl compound by either Friedel–Crafts, Grignard, or aryllithium procedures.



---

(4) For brevity, the term carborane is used for 1,2-dicarbaclovododecaborane; for structure of carborane see ref. 5.

(5) H. Schroeder, T. L. Heying, and J. R. Reiner, *Inorg. Chem.*, **2**, 1092 (1963).

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

In a comparison of the carborane infrared spectrum with those of $B_{10}H_{10}C_2(C_6H_5P \cdot Cl)_2$ and $(B_{10}H_{10}C_2P \cdot Cl)_2$ (see Fig. 1), several significant differences can be observed. The characteristic carborane absorptions[5] are at 3.25 (carbon–hydrogen stretching) and 3.9 μ (boron–hydrogen stretching); there are two strong bands between 8 and 9 μ which we ascribe to carbon–hydrogen deformation, three strong absorptions around 10 μ which we believe to be boron–hydrogen deformation modes, and finally the very strong vibration at 14 μ believed to be due to the cage structure. In the $B_{10}H_{10}C_2(C_6H_5P \cdot Cl)_2$ spectrum, the carbon–hydrogen stretching and deformation absorptions are not present; boron–hyrogen stretching is unchanged whereas boron–hydrogen deformation has changed into a doublet. In addition, there are the typical phosphorus–phenyl absorption at 7 μ and several phenyl absorptions between 13 and 15 μ. The simplicity of the spectrum of $(B_{10}H_{10}C_2P \cdot Cl)_2$ indicates high symmetry for this molecule. Boron–hydrogen stretching is unchanged, boron-hydrogen deformation has changed to a single very strong band (9.3 μ), and the absorption resulting from the cage is found at 13.8 μ.

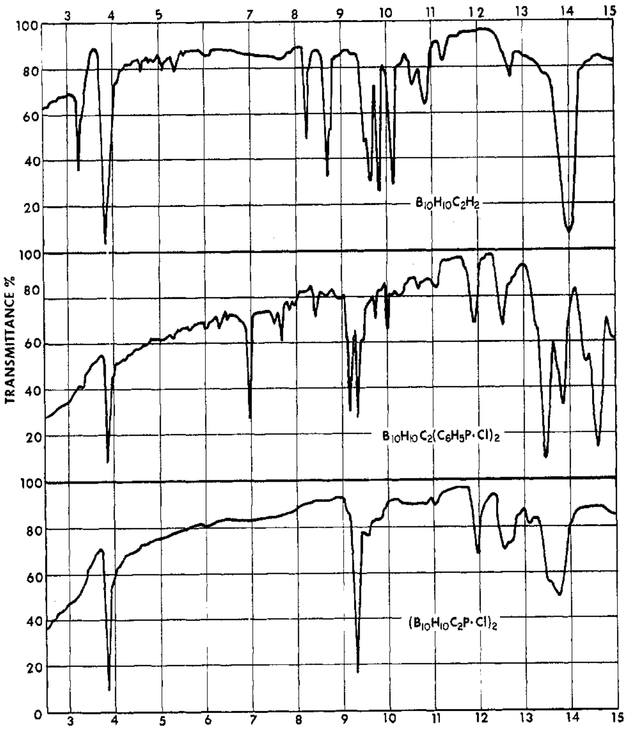
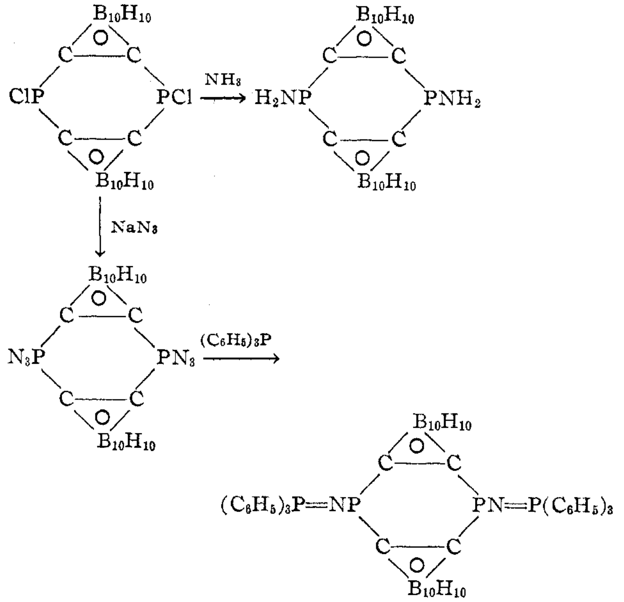


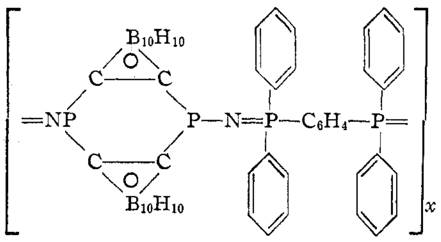
Fig. 1.—Infrared spectra of carborane, bis-(chlorophenylphosphino)-carborane, and dimeric chlorophospha(III)carborane (Kel-F and Nujol mulls).

Treatment of the cyclic bis-chloro compound with ammonia and with sodium azide, respectively, afforded in good yields the cyclic bis-amino compound, $(B_{10}H_{10}C_2P \cdot NH_2)_2$, and the cyclic bis-azide, $(B_{10}H_{10}C_2P \cdot N_3)_2$. Unlike the preceding bis-azide, $B_{10}H_{10}C_2(C_6H_5P \cdot N_3)_2$, it proved to be stable in refluxing benzene and reacted with triphenylphosphine according to the equation



This is the first example of a phosphorus(III) azide reacting with a phosphine to form a phosphineimino compound.

Upon extension of this reaction to the use of a diphosphine following the PNP polymer pattern, equimolar amounts of $(B_{10}H_{10}C_2P \cdot N_3)_2$ and p-$[(C_6H_5)_2P]_2$-C_6H_4 reacted with evolution of nitrogen to form compound II.



II

This reaction was repeated several times and in each instance the elemental analysis was precise for the structure shown, and molecular weight determination gave x a value of 3 (±5%). A rigorous structural determination of this apparently trimeric substance is in progress.

Experimental[7]

Starting Materials.—$B_{10}H_{10}C_2H_2$ was prepared as described in ref. 6 in n-propyl ether (Eastman Kodak) from resublimed $B_{10}H_{14}$, diethyl sulfide (Matheson Coleman and Bell), and acetylene which was purified by standard procedures.[8] Diphenylchlorophosphine was obtained from Victor Chemical Company.

Molecular Weights.—These were obtained in benzene either using a Mechrolab osmometer, Model 301, or by cryoscopic determination.

Dilithiocarborane.[6]—A 100-ml. three-neck flask fitted with a magnetic stirrer, a nitrogen inlet and outlet, and an addition funnel is purged with nitrogen and then charged with a solution of butyllithium (0.066 mole) in ethyl ether (approximately 60 ml.). With ice-cooling a solution of carborane (4.33 g., 0.03 mole) in ethyl ether (20 ml.) is added over a period of 10 min., and the

---

[7] Melting points are uncorrected; elemental analyses were by R. Culmo, A. C. Mayer, and J. D. Giunta of the Olin Mathieson Microchemical Section.

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

resulting white slurry is stirred under nitrogen and ice-cooling for another 30 min. Ether and excess butyllithium are then filtered from the precipitate through a coarse sintered-glass filter stick. The remaining $B_{10}H_{10}C_2Li_2$ is washed with ethyl ether (50 ml.) in two portions, dried under vacuum, and then stored in an inert atmosphere.

1,2-Bis-(diphenylphosphino)-carborane.—A solution of diphenylchlorophosphine (14.6 g., 0.066 mole) in ether (15 ml.) was added, with ice-cooling, within 25 min. to a dilithiocarborane slurry in ether prepared from 4.33 g. (0.03 mole) of carborane as described in the preceding example. The slightly yellow mixture was stirred for 20 min. at 20°, then refluxed for 30 min., and, after cooling to 10°, hydrolyzed with 20 ml. of water. The insoluble reaction product was recovered by filtration, dried *in vacuo*, and recrystallized from petroleum ether (b.p. 60–110°) to give 9.0 g. (58.5%) of $B_{10}H_{10}C_2[P(C_6H_5)_2]_2$, m.p. 219°.

Anal. Calcd. for $C_{26}H_{30}B_{10}P_2$ (512.7): C, 60.91; H, 5.90; B, 21.11; P, 12.09. Found: C, 61.15; H, 6.23; B, 20.63; P, 11.68.

1,2-Bis-(chlorophenylphosphino)-carborane.—A dilithiocarborane (0.173 mole) slurry in ether, prepared from 25 g. of carborane, was slowly added to a cooled solution of phenyldichlorophosphine (77.5 g., 0.43 mole) in ether (600 ml.). The mixture was stirred at room temperature for 90 min., then refluxed for 1 hr. Upon evaporation of the ether a yellow solid remained which was extracted with hot petroleum ether (800 ml., b.p. 60–110°). After concentration and cooling, 43.7 g. (58%) of $B_{10}H_{10}C_2(C_6H_5P{\cdot}Cl)_2$, m.p. 172–174°, precipitated from the solution.

Anal. Calcd. for $C_{14}H_{20}B_{10}Cl_2P_2$ (429.4): C, 39.16; H, 4.70; B, 25.20; Cl, 16.51; P, 14.43. Found: C, 38.87; H, 4.67; B, 24.95; Cl, 16.81; P, 14.18; mol. wt., 420.1.

1,2-Bis-[phenylphospha(III)-]-azanyl-(P,P′)-carborane.—Gaseous ammonia was bubbled into a solution of $B_{10}H_{10}C_2(C_6H_5P{\cdot}Cl)_2$ (4.3 g., 0.01 mole) in anhydrous benzene (100 ml.) for 30 min. The temperature was maintained at 20° by external cooling. The reaction mixture was then evaporated to dryness, and the solid residue was refluxed with 150 ml. of hot petroleum ether (b.p. 60–110°). After filtration, concentration, and cooling, the imino compound precipitated and was recrystallized from petroleum ether; yield of $B_{10}H_{10}C_2[(PC_6H_5)_2NH]$ 2.6 g. (70%); m.p. 222–224°.

Anal. Calcd. for $C_{14}H_{21}B_{10}NP_2$ (373.5): C, 45.02; H, 5.67; B, 28.97; N, 3.75; P, 16.59. Found: C, 45.00; H, 5.82; B, 28.46; N, 3.72; P, 16.65.

1,2-Bis-(azidophenylphosphino)-carborane.—A mixture of $B_{10}H_{10}C_2(C_6H_5P{\cdot}Cl)_2$ (10.7 g., 0.025 mole), sodium azide (6.5 g., 0.1 mole), and ethanol (150 ml.) was stirred with ice-cooling for 1 hr. The solid reaction products were recovered by filtration and thoroughly washed with water. The remaining bis-azide was dried *in vacuo* over diphosphorus pentoxide; m.p. 126–128° dec.; yield 9.1 g. (82%).

Anal. Calcd. for $C_{14}H_{20}B_{10}N_6P_2$ (442.5): C, 38.00; H, 4.56; B, 24.45; N, 18.99; P, 14.00. Found: C, 38.29; H, 4.60; B, 24.55; N, 17.80; P, 13.85.

Pyrolysis.—A solution of 6 g. of $B_{10}H_{10}C_2(C_6H_5P{\cdot}N_3)_2$ in 125 ml. of dry benzene was slowly warmed. At a bath temperature of approximately 50° gas evolution started. After keeping the mixture for 90 min. at 55°, it was cooled to 20° and the precipitate formed (2.5 g.) was recovered by filtration. It did not show the characteristic azide absorption at 4.8 μ; m.p. 170–180°.

Anal. Calcd. for $(C_{14}H_{20}B_{10}N_2P_2)_x$ (386.4): C, 43.51; H, 5.22; B, 28.00; N, 7.23; P, 16.03. Found: C, 41.93; H, 4.82; B, 28.44; N, 6.22; P, 14.89.

Dimeric Chlorophospha(III)carborane.—A dilithiocarborane (0.139 mole) slurry in ether (500 ml.) prepared from 20 g. of carborane was added in small portions, with ice-cooling, to a stirred solution of phosphorus trichloride (41.1 g., 0.3 mole) in ether (1000 ml.). The mixture immediately became purple and a colorless precipitate began to form. After stirring for 20 hr. at 20°, the mixture had turned blue and was evaporated to dryness. The green solid residue was extracted with 300 ml. of petroleum ether (b.p. 60–110°) from which, at 0°, 12.7 g. (44%) of colorless $(B_{10}H_{10}C_2P{\cdot}Cl)_2$ separated, m.p. 240–241°.

Anal. Calcd. for $C_4H_{20}B_{20}Cl_2P_2$ (417.5): C, 11.51; H, 4.83; B, 51.84; Cl, 17.00; P, 14.84. Found: C, 11.17; H, 4.96; B, 51.69; Cl, 17.50; P, 14.86; mol. wt., 407.5.

Dimeric Aminophospha(III)carborane.—Anhydrous ammonia was passed into a solution of 2 g. of $(B_{10}H_{10}C_2P{\cdot}Cl)_2$ in 50 ml. of benzene at 15 to 20° for 1 hr. The reaction mixture was filtered and the filtrate was evaporated to dryness. The residue was recrystallized from carbon tetrachloride to give 1.1 g. (60.5%) of $(B_{10}H_{10}C_2P{\cdot}NH_2)_2$, m.p. 280°.

Anal. Calcd. for $C_4H_{24}B_{20}N_2P_2$ (378.6): C, 12.69; H, 6.39; B, 57.16; N, 7.40; P, 16.36. Found: C, 11.95; H, 6.18; B, 56.81; N, 7.28; P, 15.82; mol. wt., 389. The infrared spectrum showed a doublet at 2.9 and 3.0 μ consistent with the asymmetric and the symmetric stretching modes of the primary amino group, as well as the NH_2 deformation at 6.5 μ.

Dimeric Azidophospha(III)carborane.—A mixture of $(B_{10}H_{10}C_2P{\cdot}Cl)_2$ (4.17 g., 0.01 mole), sodium azide (2.6 g., 0.04 mole), and ethanol (100 ml.) was stirred with ice-cooling for 2 hr. After filtration, the filter cake was thoroughly washed with water, then dried *in vacuo* over diphosphorus pentoxide, to give 3.5 g. (81%) of $(B_{10}H_{10}C_2P{\cdot}N_3)_2$, m.p. 150° dec.

Anal. Calcd. for $C_4H_{20}B_{20}N_6P_2$ (430.6): C, 11.16; H, 4.68; B, 50.25; N, 19.52; P, 14.39. Found: C, 10.95; H, 4.50; B, 50.45; N, 18.88; P, 14.34; mol. wt., 445.5.

Dimeric Triphenylphosphineiminophospha(III)carborane.—To a mixture of $(B_{10}H_{10}C_2P{\cdot}N_3)_2$ (2.15 g., 0.005 mole) and triphenylphosphine (2.62 g., 0.01 mole) was added, in one portion, cold benzene (50 ml.). Solution was effected, accompanied by vigorous foaming. After 25 min., gas evolution subsided and the solution was gradually heated to reflux temperature over a 30-min. period. The hot reaction mixture was filtered and cooled to 10 °. The colorless reaction product precipitated and was washed with petroleum ether; yield of $[(C_6H_5)_3P{=}NPC_2B_{10}H_{10}]_2$ 2.4 g. (53.5%); m.p. 311–312°.

Anal. Calcd. for $C_{40}H_{50}B_{20}N_2P_4$ (899.2): C, 53.43; H, 5.61; B, 24.07; N, 3.12; P, 13.78. Found: C, 53.89; H, 5.92; B, 24.08; N, 3.54; P, 13.73.

Reaction of Dimeric Azidophospha(III)carborane with 1,4-Bis-(diphenylphosphino)-benzene.—Addition of cold benzene (75 ml.) to a mixture of $(B_{10}H_{10}C_2P{\cdot}N_3)_2$ (3.45 g., 0.008 mole) and p-$[(C_6H_5)_2P]_2C_6H_4$ (3.55 g., 0.008 mole) produced, with evolution of nitrogen, a clear, purple solution. Stirring at 20° for 1 hr. followed by refluxing for 2 hr. changed the color to pale blue. After filtration from a small amount of solid, the filtrate was poured into 500 ml. of petroleum ether. A solid separated which was recovered by filtration and purified by washing with hot petroleum ether; yield of product 4.6 g. (70%); m.p. 225–250°.

Anal. Calcd. for $C_{34}H_{44}B_{20}N_2P_4$ (821.0): C, 49.74; H, 5.40; B, 26.36; N, 3.41; P, 15.09. Found: C, 50.20; H, 5.65; B, 26.06; N, 3.05; P, 14.59; mol. wt., 2367 (expt. 1), 2585 (expt. 2), 2498 (expt. 3).

Dimeric Phenylphospha(III)carborane.—A solution of $B_{10}H_{10}C_2(C_6H_5P{\cdot}Cl)_2$ (6.9 g., 0.016 mole) in ether (200 ml.) was added, with stirring, to an ice-cooled dilithiocarborane (0.016) slurry in ether (100 ml.) prepared from 2.32 g. of carborane. After stirring the mixture for 12 hr. at room temperature, it was filtered to give 3.6 g. of insoluble residue. Extraction with hot benzene afforded 2.0 g. of product which was recrystallized from benzene to give 1.6 g. (20%) of $(B_{10}H_{10}C_2P{\cdot}C_6H_5)_2$, m.p. 356–358°.

Anal. Calcd. for $C_{16}H_{30}B_{20}P_2$ (500.8): C, 38.38; H, 6.04; B, 43.21; P, 12.37. Found: C, 38.28; H, 5.79; B, 42.36; P, 11.93.

Acknowledgment.—We are grateful to Dr. T. L. Heying for stimulating discussions and to Mr. Herman Hoberecht for obtaining and interpreting mass spectral analyses. This work was supported by the Office of Naval Research.