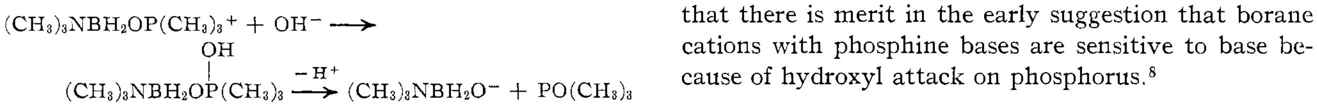
require an explanation invoking kinetic rather than thermodynamic parameters. One reasonable explanation for the base-catalyzed hydrolysis of $(CH_3)_3NBH_2OP(CH_3)_3^+$ is primary coordination of hydroxide to phosphorus and then abstraction of a proton



$$(CH_3)_3NBH_2OP(CH_3)_3^+ + OH^- \longrightarrow$$
$$(CH_3)_3NBH_2O\overset{OH}{\overset{|}{P}}(CH_3)_3 \xrightarrow{-H^+} (CH_3)_3NBH_2O^- + PO(CH_3)_3$$

Fast hydrogen-producing steps would follow. Because the analogous cation $(CH_3)_3NBH_2ON(CH_3)_3^+$ lacks low-lying empty orbitals, this base-catalyzed decomposition would not pertain. The observed second-order dependence on hydroxide could result from an equilibrium process in which there is produced a neutral intermediate, and the rate-controlling step would be the loss of proton. Much more quantitative work and other data are needed before detailed answers to the mechanistic questions can be given. It does appear, however, that there is merit in the early suggestion that borane cations with phosphine bases are sensitive to base because of hydroxyl attack on phosphorus.[8]

Acknowledgment.—Support of this work by a grant from the National Science Foundation is gratefully acknowledged.

---

[8] N. E. Miller and E. L. Muetterties, *J. Am. Chem Soc.*, **86**, 1033 (1964)

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ARIZONA, TUCSON, ARIZONA 85721

Tetraethylammonium Thiolotrihydroborate

BY PHILIP C. KELLER

Received January 6, 1969

Tetraethylammonium tetrahydroborate undergoes partial solvolysis in liquid hydrogen sulfide at −78° to produce hydrogen and tetraethylammonium thiolotrihydroborate, $[(C_2H_5)_4N][HSBH_3]$. No further reaction occurs under these conditions. Solid $[(C_2H_5)_4N][HSBH_3]$ suffers slight decomposition upon immediate warming from −78° to room temperature but thereafter only decomposes very slowly. A solution of $[(C_2H_5)_4N][HSBH_3]$ in liquid hydrogen sulfide at −78° reacts very slowly with excess hydrogen chloride to form tetraethylammonium trichlorothioloborate, $[(C_2H_5)_4N][Cl_3BSH]$. A hydrogen sulfide solution of $[(C_2H_5)_4N][HSBH_3]$ rapidly absorbs diborane to produce the unstable compound $[(C_2H_5)_4N][HS(BH_3)_2]$.

Introduction

The chemistry of boron–sulfur compounds has received relatively little attention up to the present time. A recent review of this area by Muetterties[1] reveals that, with the exception of a handful of compounds, most known materials with boron–sulfur bonds are boron sulfide derivatives, alkylthio-substituted organoboranes, or borane adducts of organic sulfides.

The insertion of sulfur into boron hydrides and boron hydride ions is a synthetic problem that should produce a family of new compounds with interesting properties. The presence of lone pairs of electrons on sulfur which are available for dative bonding should have a significant effect on the structure and reactivity of sulfur substituted boranes, while the presence of SH groups on neutral boranes might enable such compounds to behave as proton acids and form novel anions.

In this paper we describe a sulfur derivative of the tetrahydroborate ion, tetraethylammonium thiolotrihydroborate, $[(C_2H_5)_4N][HSBH_3]$, which is prepared by the solvolysis of $[(C_2H_5)_4N]BH_4$ in liquid hydrogen sulfide at −78°.

Experimental Section

General Data.—Volatile compounds were manipulated, separated, and purified with conventional high-vacuum apparatus. Noncondensable gases were collected and measured with an automatic Toepler pump and gas buret. Air-sensitive solids were handled in a polyethylene glove bag flushed with dry nitrogen.

Boron-11 nuclear magnetic resonance (nmr) spectra were obtained with a Varian HA-100 spectrometer equipped with a 32.1-MHz probe and standard accessories; ^{11}B chemical shifts were relative to $(C_2H_5)_2O\cdot BF_3$. Infrared and mass spectra were obtained with a Perkin-Elmer 337 spectrophotometer and a Hitachi Perkin-Elmer RMU-6E spectrometer, respectively.

Reagents.—CP grade hydrogen sulfide was purchased from the Matheson Gas Co., Inc., and was used without further purification. Tetraethylammonium tetrahydroborate was purchased from Alfa Inorganics, Inc., and was recrystallized from 2-propanol before use. Tetraethylammonium tetrahydroborate so prepared gave between 96 and 98% of the expected hydrogen upon acid hydrolysis. Other reagents were prepared and purified by standard methods.

Reaction of $[(C_2H_5)_4N]BH_4$ with Liquid H_2S.—In a typical experiment a Pyrex reaction tube equipped with a high-vacuum stopcock was charged with 0.290 g (2.00 mmol) of $[(C_2H_5)_4N]BH_4$. The vessel was evacuated and cooled to −196°, and sufficient hydrogen sulfide to form 2 ml of solution was condensed in. The vessel was sealed, warmed to −78°, and allowed to stand at this temperature for 24 hr. The tube was then recooled to −196° and opened to the vacuum line, and the evolved hydrogen was collected and found to be present in the amount of 1.92 mmol, corresponding to 96% of that expected for the reaction

$$[(C_2H_5)_4N]BH_4 + H_2S \longrightarrow [(C_2H_5)_4N][HSBH_3] + H_2 \quad (1)$$

The reaction vessel was sealed again and rewarmed to −78°. After 3 days it was recooled to −196° and opened to the vacuum line; less than 0.01 mmol of hydrogen was present.

---

[1] E. L. Muetterties in "The Chemistry of Boron and Its Compounds," E. L. Muetterties, Ed., John Wiley & Sons, Inc., New York, N. Y., 1967, Chapter 10.

The hydrogen sulfide was removed from the sample by continuous evacuation over a 48-hr period while the vessel was maintained at −78°. The sample was analyzed by hydrolyzing the residue in the vessel with 5 ml of 1 *N* sulfuric acid. Hydrogen and hydrogen sulfide were measured as gases in the vacuum line; boric acid was determined by titration of its D-mannitol complex with standard base.

Anal. Calcd for $[(C_2H_5)_4N][HSBH_3]$: B, 6.10; hydridic H, 1.69; S, 18.1. Found: B, 5.64; hydridic H, 1.60; S, 18.0. B:S:H = 1.00:1.07:3.06.

In an attempt to prepare the sodium salt of $HSBH_3^-$, $NaBH_4$ was substituted for $[(C_2H_5)_4N]BH_4$ in the above reaction, but even when the experiment was performed with liquid hydrogen sulfide at 25° in a heavy-wall tube no reaction occurred.

Characterization of $[(C_2H_5)_4N][HSBH_3]$.—A ^{11}B nmr spectrum of $[(C_2H_5)_4N][HSBH_3]$ was obtained using the apparatus shown in Figure 1. The vessel was charged with $[(C_2H_5)_4N]BH_4$ and hydrogen sulfide and was sealed at the constriction. The reaction was allowed to proceed in the wide end of the tube at −78° for 24 hr. The vessel was then totally immersed in a −78° bath, removed, inverted, and replaced in the cold bath. The sample was then quickly inserted into the nmr probe which had been precooled to −75°. The ^{11}B nmr spectrum consisted solely of a clean well-resolved quartet with δ +25.0 ppm and J = 97 Hz.

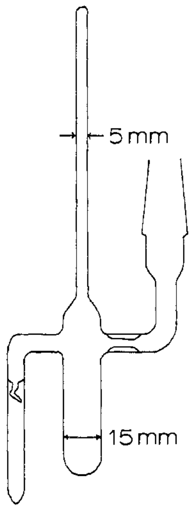


Figure 1.—Reaction vessel for nmr studies in liquid hydrogen sulfide.

In an experiment to determine the thermal stability of $[(C_2H_5)_4N][HSBH_3]$ a sample of this material was allowed to stand at room temperature in an evacuated vessel for 48 hr. The physical appearance of the solid did not change within this period. Hydrogen and hydrogen sulfide were produced in a quantity indicating 10–15% decomposition, most of which took place during the first 60 min at room temperature. The solid redissolved cleanly in liquid hydrogen sulfide and showed an ^{11}B nmr spectrum identical with that previously described.

The infrared spectrum of a fresh sample of $[(C_2H_5)_4N][HSBH_3]$ in a potassium bromide matrix exhibited peaks at the following frequencies (in cm^{-1}) in addition to those assigned to the cation: 2570 (w), 2340 (s), 2290 (s), 2220 (m, sh), and 1105 (s). Samples of $[(C_2H_5)_4N][HSBH_3]$ exposed to moist air began to turn yellow within a few minutes. An infrared spectrum of a sample exposed to air for 1 hr showed that bands assigned to the anion had greatly diminished in intensity, and characteristic -OH absorptions had appeared.

Reaction of $[(C_2H_5)_4N][HSBH_3]$ with HCl.—A hydrogen sulfide solution of $[(C_2H_5)_4N][HSBH_3]$ was prepared as described above, a 20-fold excess of hydrogen chloride was condensed into the reaction tube, and the mixture was allowed to stand at −78°. The reaction progressed very slowly, and after 20 days a quantity of hydrogen corresponding to only 75% of that expected for reaction 2 had been evolved. The infrared spectrum of the colorless solid product was identical with that of an authentic sample of $[(C_2H_5)_4N][Cl_3BSH]$ prepared as described by Cotton and Waddington.[2] The reaction of solid $[(C_2H_5)_4N][HSBH_3]$ with pure liquid hydrogen chloride also occurred very slowly, in part owing to low solubility, and gave the same product.

$$[(C_2H_5)_4N][HSBH_3] + 3HCl \longrightarrow [(C_2H_5)_4N][Cl_3BSH] + 3H_2 \qquad (2)$$

Reaction of $[(C_2H_5)_4N][HSBH_3]$ with B_2H_6.—A solution of $[(C_2H_5)_4N][HSBH_3]$ in 1 ml of liquid hydrogen sulfide was generated from 0.646 mmol of $[(C_2H_5)_4N]BH_4$ in an nmr tube reaction vessel like that shown in Figure 1. The vessel was inverted as previously described and cooled with liquid nitrogen, and a 0.74-mmol sample of diborane was condensed in. The tube was sealed and warmed to −78° whereupon reaction occurred as evidenced by effervescence in the solution. The ^{11}B nmr spectrum of the solution at −75°, shown in Figure 2, exhibited, in addition to a triplet of triplets signal characteristic of diborane, a strong quartet with δ +23.9 ppm and J = 102 Hz. From the appearance of this signal it was apparent that a third, weaker resonance of nearly the same chemical shift was also present. The spectrum did not change over a period of 3 hr at −78°.

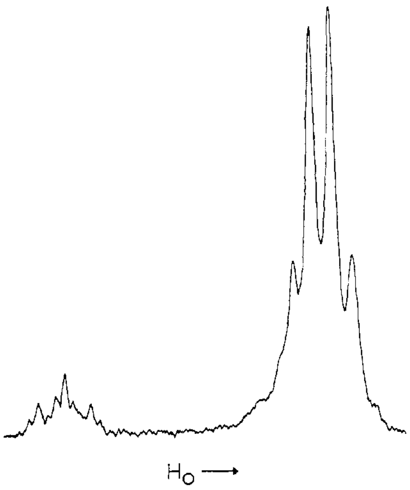


Figure 2.—Boron-11 nmr spectrum of $[(C_2H_5)_4N][HSBH_3]$ with excess B_2H_6 in liquid hydrogen sulfide.

Tensimetric Titration of $[(C_2H_5)_4N][HSBH_3]$ with B_2H_6.—A hydrogen sulfide solution of $[(C_2H_5)_4N][HSBH_3]$ was generated from 1.67 mmol of $[(C_2H_5)_4N]BH_4$ and 3 ml of liquid hydrogen sulfide at −78° in a reaction vessel equipped with a mercury manometer and a side tube connected to the vacuum line for admitting diborane and removing noncondensable gas. The titration was carried out in steps by cooling the apparatus to −196°, condensing an increment of about 0.1 mmol of diborane into the vessel, and warming to −78°. After each addition a small amount of hydrogen was produced and this was removed by cooling the solution to −196° and evacuating the apparatus. The solution was rewarmed to −78° and the pressure in the system was measured. The titration curve, shown in Figure 3, exhibits a clear break at $B_2H_6:HSBH_3^-$ = 0.5. This ratio and the ^{11}B nmr spectrum strongly suggest the formation of $HS(BH_3)_2^-$.

Stability of $[(C_2H_5)_4N][HS(BH_3)_2]$.—A 1.84-mmol sample of $[(C_2H_5)_4N]BH_4$ was used to prepare a solution of $[(C_2H_5)_4N][HSBH_3]$ in liquid hydrogen sulfide. A 0.875-mmol sample of diborane was added and the resulting solution was allowed to stand at −78° for 40 hr. At the end of this period the hydrogen in the tube was collected and was found to be 0.775 mmol.

---

[2] J. D. Cotton and T. C. Waddington, *J. Chem. Soc., A*, 789 (1966).

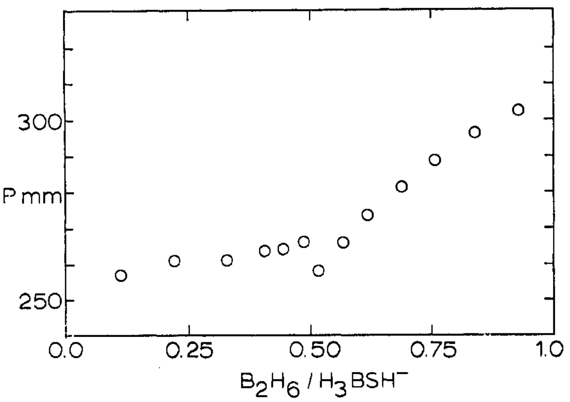


Figure 3.—Tensimetric titration of $[(C_2H_5)_4N][HSBH_3]$ with B_2H_6 in liquid hydrogen sulfide.

After an additional 48-hr period under the same conditions only 0.05 mmol of hydrogen was generated. The hydrogen sulfide was then removed while keeping the nonvolatile residue at −78°. The tube was warmed to room temperature, and during this time the white solid remaining in the tube partially liquefied and frothed vigorously. Within the first 2 hr at room temperature 2.09 mmol of hydrogen was evolved. The glassy colorless residue continued to produce hydrogen slowly, and after 4 days another 0.93 mmol had appeared.

Results and Discussion

$[(C_2H_5)_4N][HSBH_3]$.—The solvolysis of the tetrahydroborate ion has been the subject of a considerable amount of detailed study.[3] Using ^{11}B nmr, Gardener and Collat[4] succeeded in detecting a hydrolysis intermediate which they postulated to be the hydroxotrihydroborate ion, $HOBH_3^-$. The intermediate species in the hydrolysis of the tetrahydroborate ion, however, have so far escaped actual isolation and characterization.

Tetraethylammonium tetrahydroborate dissolves easily in liquid hydrogen sulfide at −78° and reproducibly undergoes slow solvolysis to yield 1 mol of hydrogen and $[(C_2H_5)_4N][HSBH_3]$. The use of the quaternary ammonium salt is necessary to ensure solution of the tetrahydroborate; $NaBH_4$ is inert to liquid hydrogen sulfide. In contrast to the behavior of the aqueous solvolysis intermediates, solutions of $[(C_2H_5)_4N][HSBH_3]$ in liquid hydrogen sulfide at −78° are stable with respect to further reaction with the solvent over a period of several days, and the solid product may be isolated by removal of the solvent at −78°. Solid $[(C_2H_5)_4N][HSBH_3]$ undergoes slight decomposition upon immediate warming to room temperature but thereafter decomposes only very slowly.

The ^{11}B nmr and infrared spectra of $[(C_2H_5)_4N][HSBH_3]$ are consistent with the assigned structure. The ^{11}B nmr spectrum consists of a well-resolved quartet, demonstrating the presence of a BH_3 group.[5] The infrared spectrum shows a weak band at 2570 cm^{-1}, which may be assigned to S–H stretching,[6] and B–H stretching bands at 2340, 2290, and 2220 (sh) cm^{-1}. The frequencies of the latter absorptions are in good agreement with the values observed for other substituted hydroborates.[7,8]

The resistance of the $HSBH_3^-$ ion to further solvolysis in liquid hydrogen sulfide at −78° is consistent with the very slow reaction of the ion with hydrogen chloride, both in hydrogen sulfide solution and with liquid hydrogen chloride. Although hydrogen chloride does not ionize in liquid hydrogen sulfide,[9] it should still be a much better proton donor than the solvent, and it is somewhat surprising that the reaction does not occur at a faster rate. The fact that the reaction does not yield diborane and hydrogen sulfide is probably due to the greater strength of the B–Cl bond compared to that of the B–H bond and the high energy of the S–B linkage.[10]

Reaction of $[(C_2H_5)_4N][HSBH_3]$ with B_2H_6.—Owing to the very low thermal stability of the product of the reaction of $[(C_2H_5)_4N]]HSBH_3]$ with diborane, reliable analytical data on the compound could not be obtained. However, the combined results of the tensimetric titration (Figure 3) and the ^{11}B nmr spectrum (Figure 2) provide considerable support for the formation of $HS(BH_3)_2^-$ by

$$HSBH_3^- + 0.5B_2H_6 \longrightarrow HS(BH_3)_2^- \qquad (3)$$

Cotton and Waddington[2] examined the reaction of diborane with hydrogen sulfide ion in liquid hydrogen sulfide by following the change in conductivity of the solution with the addition of diborane. The authors found a break in the conductometric titration curve at $HS^-:B_2H_6 = 1.0$ and postulated the formation of $HS(BH_3)_2^-$. They also observed that hydrogen was evolved after each addition of diborane and that the tetraalkylammonium salt of the product, isolated by removal of the solvent at −78°, decomposed rapidly upon warming to ambient temperature. There can be little doubt that the product described by Cotton and Waddington is the same as that formed by the reaction of diborane with $[(C_2H_5)_4N][HSBH_3]$, since the ^{11}B nmr spectrum of a hydrogen sulfide solution of the former[11] is identical with that shown in Figure 2.

The fact that hydrogen is evolved when diborane is added to a hydrogen sulfide solution of $[(C_2H_5)_4N][HSBH_3]$ suggests that the reaction of diborane with hydrogen sulfide ion under the conditions employed by Cotton and Waddington may proceed through the intermediate formation of the $HSBH_3^-$ ion. Since diborane was added in small quantities to the solution of hydrogen sulfide ion, it is not unreasonable to assume formation of $HSBH_3^-$ by reaction 4, followed by addi-

$$HS^- + 0.5B_2H_6 \longrightarrow HSBH_3^- \qquad (4)$$

---

[3] J. A. Gardener and J. W. Collat, *J. Am. Chem. Soc.*, **87**, 1692 (1965), and earlier references cited therein.

[4] J. A. Gardener and J. W. Collat, *ibid.*, **86**, 3165 (1964).

[5] In studying the reaction of $LiBH_4$ with H_2S in tetrahydrofuran at −22° B. F. Spielvogel and E. F. Rothgery, *Chem. Commun.*, 765 (1966), observed the ^{11}B nmr spectrum of an unstable intermediate which they assigned to be $LiHSBH_3$. The nmr parameters of this product agree very well with those reported in this paper, and it is likely that the anion of this unstable species is identical with that described here.

[6] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1958, p 350.

[7] D. S. Rustad and W. L. Jolly, *Inorg. Chem.*, **7**, 213 (1968).

[8] V. D. Aftandilian, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **83**, 2471 (1961).

[9] J. D. Cotton and T. C. Waddington, *J. Chem. Soc., A*, 785 (1966).

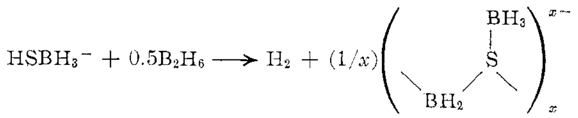
[10] Reference 1, p 13.

[11] P. C. Keller, *Chem. Commun.*, 209 (1969).

tion of more diborane (reaction 3) to yield $HS(BH_3)_2^-$ as the principal product.

The nature of the side reaction producing hydrogen when diborane reacts with $HSBH_3^-$ is uncertain. The products of the reaction remain in solution, but their ^{11}B nmr spectrum is obscured by the signal assigned to $HS(BH_3)_2^-$. The $HS(BH_3)_2^-$ ion is isoelectronic with $CH_3SH \cdot BH_3$, and in speculation one may draw analogy to the chemistry of the latter complex. Burg and Wagner[12] found that $CH_3SH \cdot BH_3$ decomposes slowly at −78° by loss of hydrogen to form a methylthioborane polymer (reaction 5). It is possible that this sort of reaction occurs as a secondary process when diborane reacts with $HSBH_3^-$ to produce a material isoelectronic with the methylthioborane polymer (reaction 6). This product does not arise from decomposition of $HS(BH_3)_2^-$, however, since, once formed, solutions of $HS(BH_3)_2^-$ subsequently evolve very little hydrogen at −78°.

$$CH_3SH \cdot BH_3 \longrightarrow H_2 + (1/x)(CH_3SBH_2)_x \qquad (5)$$



$$HSBH_3^- + 0.5B_2H_6 \longrightarrow H_2 + (1/x)\left(\diagdown BH_2 \diagup \overset{\overset{BH_3}{|}}{S} \diagdown\right)_x^{x-} \qquad (6)$$

Acknowledgment.—This work was supported by a grant from the National Science Foundation.

---

[12] A. B. Burg and R. I. Wagner, *J. Am. Chem. Soc.*, **76**, 3307 (1954).

CONTRIBUTION NO. 1686 FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY, BLOOMINGTON, INDIANA 47401, AND THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS

Monocarbon Carboranes. III.[1] Polyhedral Phosphacarbadodecaborane(11) Derivatives and Related 11-Atom Cage Fragments[2]

BY LEE J. TODD,[3] JOHN L. LITTLE, AND HOWARD T. SILVERSTEIN

Received February 6, 1969

Treatment of $Na_3B_{10}H_{10}CH$ with phosphorus trichloride leads to 1,2-$B_{10}H_{10}CHP$. This compound has chemical and physical properties quite similar to those of the isoelectronic molecule 1,2-$B_{10}H_{10}C_2H_2$. Thermal rearrangement of 1,2-$B_{10}H_{10}CHP$ gives both 1,7- and 1,12-$B_{10}H_{10}CHP$. Aluminum chloride catalyzed bromination of 1,2- and 1,7-$B_{10}H_{10}CHP$ occurs at boron producing tribromo and dibromo derivatives, respectively, as the ultimate products. Piperidine abstracts a boron atom from 1,2- and 1,7-$B_{10}H_{10}CHP$ to give the 7,8- and 7,9-$B_9H_{10}CHP^-$ ions, respectively. These phosphacarborane ions react with methyl iodide at the phosphorus atom to give the neutral derivatives 7,8- and 7,9-$B_9H_{10}CHPCH_3$.

In the past few years several molecules isoelectronic with $B_{12}H_{12}^{2-}$ but containing one or two heteroatoms in the icosahedral cage have been prepared. The first member of this class of compounds to be reported was 1,2-dicarba-*closo*-dodecaborane(12) which was prepared from decaborane(14) and acetylene in the presence of a Lewis base.[4] Thermal rearrangement of the 1,2 isomer at 500° produced a new isomer of $B_{10}C_2H_{12}$ with carbon atoms at the 1,7 positions of the icosahedron.[5] Papetti and Heying isolated the 1,12 isomer in low yield from the pyrolyzate of a thermal reaction at 600°.[6] The one-carbon analog, $B_{11}H_{11}CH^-$, was prepared by a thermal disproportionation reaction (eq 1)[7] and by reaction of the carbollide ion $B_{10}H_{10}CH^{3-}$ with phenyldichloroborane (eq 2).[8] More recently the corresponding sulfur derivative, $B_{10}H_{10}SBC_6H_5$, was obtained by a similar reaction between $B_{10}H_{10}S^{2-}$ and phenyldichloroborane.[9]

$$2CsB_{10}H_{12}CH \xrightarrow{320°} CsB_9H_9CH + CsB_{11}H_{11}CH + 2H_2 \qquad (1)$$

$$Na_3B_{10}H_{10}CH + C_6H_5BCl_2 \longrightarrow NaB_{10}H_{10}CHBC_6H_5 + 2NaCl \qquad (2)$$

In this paper are described the preparation and characterization of the 1,2, 1,7, and 1,12 isomers of $B_{10}H_{10}CHP$, certain substituted derivatives of the icosahedral molecules, and 11-atom phosphacarboranes obtained by boron atom abstraction from the closed-cage species.

Results and Discussion

The Parent *closo*-Phosphacarboranes.—The fact that $Na_3B_{10}H_{10}CH(THF)_2$ could be used to prepare sandwich-bonded complexes[10] in which the metal atom simultaneously completes two icosahedra led to attempts to insert other elements into the carbollide ion to obtain *closo* structures. The fragments PH^+ and P are isoelectronic with CH and BH^-. Insertion of a P atom into $B_{10}H_{10}CH$ should therefore give a molecule

---

[1] For the previous paper in this series, see F. R. Scholer and L. J. Todd, *J. Organometal. Chem.* (Amsterdam), **14**, 261 (1968).

[2] Presented in preliminary form at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967.

[3] Correspondence should be addressed to this author at the Department of Chemistry, Indiana University, Bloomington, Indiana 47401.

[4] T. L. Heying, J. W. Ager, Jr., S. L. Clark, D. J. Mangold, H. L. Goldstein, M. Hillman, R. J. Polak, and J. W. Szymanski, *Inorg. Chem.*, **2**, 1089 (1963).

[5] D. Grafstein and J. Dvork, *ibid.*, **2**, 1128 (1963).

[6] S. Papetti and T. L. Heying, *J. Am. Chem. Soc.*, **86**, 2295 (1964).

[7] W. H. Knoth, *ibid.*, **89**, 1274 (1967).

[8] J. R. Lawrence and L. J. Todd, unpublished results.

[9] W. R. Hertler, F. Klanberg, and E. L. Muetterties, *Inorg. Chem.*, **6**, 1696 (1967).

[10] D. E. Hyatt, J. L. Little, J. T. Moran, F. R. Scholer, and L. J. Todd, *J. Am. Chem. Soc.*, **89**, 3342 (1967).