F–N–O–S–F bond and space system. A somewhat related system, F–C–O–S–F, in $C_2F_5OSF_5$ has been studied by Merrill and co-workers,[22] who found coupling constants to be 3 and 10 c.p.s. between the $-CF_2-$ group fluorines and the A and B fluorines, respectively, of the pentafluorosulfur group.

Acknowledgment.—This work was performed in part under contract with the Office of Naval Research.

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[22] C. Merrill, S. Williamson, G. H. Cady, and D. Eggers, Jr., *Inorg. Chem.*, **1**, 215 (1962).

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

Chemistry of Decaborane–Phosphorus Compounds. II. Synthesis and Reactions of Diphenylphosphinodecaborane-14[1]

BY HANSJUERGEN SCHROEDER

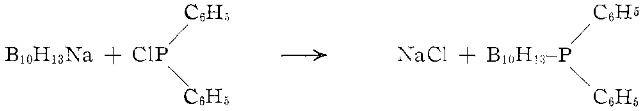
Received August 2, 1962

Decaboranyl sodium and diphenylchlorophosphine reacted in ether solution to form diphenylphosphinodecaborane-14 ($(C_6H_5)_2P{-}B_{10}H_{13}$), the first phosphine substituted decaborane-14 with trivalent phosphorus. B^{11} n.m.r. spectral investigation proved the substituent to be at the 6-position. Unlike monomeric phosphinoboranes ($R_2P{-}BR_2$), it is unreactive toward Lewis acids, oxidation, and quaternization, but undergoes partial degradation with alcohols to form $B_9H_{13}{-}((C_6H_5)_2PH)$. Its reactions with amines and phosphines resulting in salts containing the $(C_6H_5)_2PB_{10}H_{12}$ anion are described.

The original instance of the formation of a decaborane–phosphine compound occurred when decaborane-14 was found to react with triphenylphosphine to form bis-(triphenylphosphine)-decaborane,[2] a compound of the $B_{10}H_{12}$(ligand)$_2$ type in which the ligands donate electrons to the $B_{10}H_{12}$ units. Recently two other such compounds with pentavalent phosphorus, bis-(tri-*n*-butylphosphine)-decaborane and bis-(diethylphosphine)-decaborane, have been reported.[3] The present investigation was undertaken with the objective of synthesizing phosphinodecaboranes ($R_2P{-}B_{10}H_{13}$) with trivalent phosphorus, to study their properties, and thus to gain additional insight into the character of phosphorus–borane bonding. No examples of higher phosphinoboranes had been reported, and only a few monomeric phosphinoboranes ($R_2P{-}BR_2$) have been described.[4]

To this end, decaborane-14 was treated with diphenylphosphine, diphenylchlorophosphine, and ethyl diphenylphosphinite. Substitution involving the elimination of hydrogen, hydrogen chloride, or ethanol, respectively, did not occur; rather the corresponding $B_{10}H_{12}((C_6H_5)_2P\cdot R)_2$ compounds were obtained: bis-(diphenylphosphine)-decaborane (I), bis-(chlorodiphenylphosphine)-decaborane (II), and bis-(ethoxydiphenylphosphine)-decaborane (III). $B_{10}H_{12}((C_6H_5)_2P\cdot Cl)_2$ was the subject of a comprehensive study of nucleophilic chlorine substitution, also the ligands of II and III were proved to be attached at the 6,9 positions of the decaborane nucleus.[1]

More promising for the desired purpose appeared to be the application of an established reaction for the preparation of substituted decaboranes, namely, the interaction of a metallodecaborane and a halogenide as exemplified by the synthesis of benzyldecaborane from decaboranyl sodium[5] or decaboranyl magnesium chloride[6] and benzyl bromide (or chloride). Treatment of $B_{10}H_{13}Na$ with diphenylchlorophosphine in ether solution resulted in the desired substitution; diphenylphosphinodecaborane (IV, m.p. 147°) was recovered



$$B_{10}H_{13}Na + ClP(C_6H_5)_2 \longrightarrow NaCl + B_{10}H_{13}{-}P(C_6H_5)_2$$

IV

in 56.5% yield.[6a] Compound IV is readily soluble in organic solvents except petroleum ether. It was of particular interest to determine whether the lone pair of electrons would be available for additional reaction. Appropriate reactions were attempted, but $B_{10}H_{13}{-}P(C_6H_5)_2$ was found not to form adducts with Lewis acids such as borine (from diborane), trimethylborane, boron trifluoride, or boron trichloride, it could not be oxidized (*e.g.*, with sulfur in hot benzene), and quaternization attempted with methyl (and ethyl) iodide in ether as well as in benzene solution did not occur. This markedly contrasts the behavior of tertiary phosphines or monomeric phosphinoboranes, and clearly indicates that the unshared electron pair at the phosphorus atom has been absorbed into the electron-deficient decaborane nucleus.

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[1] Preceding communication: H. Schroeder, J. R. Reiner, and T. L. Heying, *Inorg. Chem.*, **1**, 618 (1962).

[2] M. F. Hawthorne and A. R. Pitochelli, *J. Am. Chem. Soc.*, **80**, 6685 (1958).

[3] G. W. Parshall, U. S. Patent 3,035,949 (1962).

[4] (a) A. B. Burg and R. I. Wagner, *J. Am. Chem. Soc.*, **75**, 3872 (1953); (b) G. E. Coates and J. G. Livingstone, *J. Chem. Soc.*, 1000 (1961); (c) H. Noeth and W. Schraegle, *Z. Naturforsch.*, **16b**, 473 (1961).

[5] R. J. F. Palchak, J. H. Norman, and R. E. Williams, *J. Am. Chem. Soc.*, **83**, 3380 (1961).

[6] B. Siegel, J. L. Mack, J. U. Lowe, Jr., and J. Gallaghan, *ibid.*, **80**, 4523 (1958).

[6a] NOTE ADDED IN PROOF.—After this paper was accepted for publication, E. L. Muetterties and V. D. Aftandilian reported the reaction between $B_{10}H_{13}MgI$ and $(C_6H_5)PCl$ to give $B_{10}H_{13}P(C_6H_5)_2$, m.p. 136–137° (*Inorg. Chem.*, **1**, 731 (1961)).

Evaluation of the B^{11} magnetic resonance spectrum of $B_{10}H_{13}$–$P(C_6H_5)_2$ led to the conclusion that the diphenylphosphino group is attached to the boron 6 atom of the decaborane nucleus.[7] The high field part of the spectrum exhibited two doublets which were decoupled by exciting the protons at 60.0 Mc. These doublets were due to the coupling interaction of the apex borons 2 and 4 with their terminal proton and prove the absence of the diphenylphosphino group at the apex borons. Substitution on boron 1 would affect the chemical shifts of the apex borons 2 and 4 equally because of the relative position to these atoms, therefore the shift observed between those doublets rules out such substitution. Since a substitution on boron 5 does not affect the apex borons, as shown by the example of 5-ethyldecaborane,[8,9] 6-substitution is established by exclusion of the other possibilities.[10]

Of special interest appeared to be a study of IV regarding its behavior toward solvolysis. $B_{10}H_{12}$(ligand)$_2$ compounds recently have been converted into ligand derivatives ($B_9H_{13}X$) of nonaborane (B_9H_{15}) by solvolytic (alcohol) degradation with removal of either the 6 or 9 boron atom,[11,12] but there is no reported instance where decaborane or a simple substituted derivative has been partially solvolyzed. Additional interest engendered when the conversion of $(CH_3)_2B$–PH_2 into methoxydimethylborane with methanol was considered.[4a]

$$(CH_3)_2B\text{–}PH_2 + CH_3OH \longrightarrow (CH_3)_2BOCH_3 + PH_3$$

An analogous course of reaction of $B_{10}H_{13}$–$P(C_6H_5)_2$ would provide a new method of alkoxylation in the decaborane field.

When IV was treated for a few minutes with hot ethanol or methanol, a compound (V, m.p. 169°) was isolated, the analysis of which was in good agreement with the formula of a diphenylphosphinononaborane, believed to be either a B_9H_{15} (6330 topology) or a B_9H_{13} (2702 topology)[13] derivative. However, the infrared spectrum of V showed a weak absorption at 4.25 μ which indicated the presence of a P–H bond, and its B^{11} n.m.r. spectrum was remarkably similar to the ligand compound $B_9H_{13}(S(C_2H_5)_2)$ (VI) which was recently reported by Hawthorne, *et al.*[11,12] Since they further reported that the ethyl sulfide could be replaced by other electron-donor compounds, *e.g.*, CH_3CN, $B_9H_{13}(S(C_2H_5)_2)$ was treated with diphenylphosphine and $B_9H_{13}((C_6H_5)_2PH)$ (m.p. 168–169°) resulted. Elemental and instrumental analyses, especially the chemical shifts of its B^{11} n.m.r. spectrum, as well as the physical properties of this compound, were identical with those of compound V, which, therefore, must also be $B_9H_{13}((C_6H_5)_2PH)$. The course of the conversion of the diphenylphosphino group to the diphenylphosphine ligand has not been explained as yet but it could be possible that there is an equilibrium between two tautomeric forms of $B_{10}H_{13}$–$P(C_6H_5)_2$, where in one form one proton appears in the normal bridge position of the decaborane nucleus while in the other it acts as phosphine hydrogen.

$$\begin{tikzcd}
\underset{\text{IV}}{B_{10}H_{13}\text{–}P(C_6H_5)_2} \arrow[dr, "ROH"] & \\
& B_9H_{13}((C_6H_5)_2PH) \\
\underset{\text{VI}}{B_9H_{13}(S(C_2H_5)_2)} \arrow[ur, "(C_6H_5)_2PH"'] &
\end{tikzcd}$$

The apparent inclusion of the lone-pair of phosphorus electrons in the electronic system of the, normally, electron-deficient decaborane nucleus suggested the possibility that IV might not react further with electron-donor compounds, and thus prompted a study of the reaction of IV with amines and phosphines. Treatment of IV with an equimolar amount or with an excess of triethylamine in ether converted it quantitatively into the triethylammonium salt (VII), which is analogous to the conversion of decaborane into its triethylammonium derivative.[14] The presence of a $(C_2H_5)_3NH$ cation was clearly shown by the presence of the characteristic NH infrared absorption at 3.15 μ. The formation of a $B_{10}H_{12}P(C_6H_5)_2^-$ anion was proved by treating VII with triphenylethylphosphonium iodide in acetone to give the respective triphenylethylphosphonium salt VIII in 90% yield. As expected, no reaction was observed upon treatment of VII with triphenylphosphine, which should have resulted in a typical ligand replacement reaction if VII was simply an addition compound of IV and triethylamine.

$$\begin{tikzcd}
B_{10}H_{13}P(C_6H_5)_2 + N(C_2H_5)_3 \arrow[r] & ((C_2H_5)_3NH)^+B_{10}H_{12}P(C_6H_5)_2^- \quad (\text{VII}) \arrow[d, "(C_6H_5)_3PC_2H_5I"] \\
& ((C_6H_5)_3PC_2H_5)^+B_{10}H_{12}P(C_6H_5)_2^- \quad (\text{VIII})
\end{tikzcd}$$

In a comparison of the ultraviolet spectra, it is of interest to note that the characteristic absorptions of the $B_{10}H_{13}^-$ anion at 267 and 335 mμ[14] are not exhibited by compounds VII and VIII or by $((CH_3)_4N)B_{10}H_{12}CN$,[15] which is believed to be of the same general structure ($B_{10}H_{12}X^-$), although the points of attachment of the anion substituents might be different. The recently described $CsB_{10}H_{13}$–$(CH_3)_2S$, however, is reported to have ultraviolet maxima at 265 and 335 mμ.[16] To demonstrate that $RB_{10}H_{13}$ compounds in general can be converted into their respective anions, benzyldecaborane[5] also was treated with triethylamine to give $(C_2H_5)_3NH^+B_{10}H_{12}CH_2C_6H_5^-$ (IX).

Since triphenylphosphine,[2] and in our studies di-

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[7] For structure and B^{11} assignments of decaborane and derivatives refer to R. L. Williams, J. Dunstan, and N. J. Blay, *J. Chem. Soc.*, 5009 (1960), and the references cited therein.

[8] N. J. Blay, J. Williams, and R. L. Williams, *ibid.*, 424 (1960).

[9] J. Dunstan, R. L. Williams, and N. J. Blay, *ibid.*, 5012 (1960).

[10] A detailed treatment of B^{11} n.m.r. spectra of $B_{10}H_{14}$ derivatives will be published by Dr. C. Naar-Colin.

[11] B. M. Graybill, A. R. Pitochelli, and M. F. Hawthorne, *Inorg. Chem.*, **1**, 626 (1962).

[12] B. M. Graybill, J. K. Ruff, and M. F. Hawthorne, *J. Am. Chem., Soc.*, **83**, 2669 (1961).

[13] W. N. Lipscomb, *Proc. Natl. Acad. Sci. U.S.*, **47**, 1791 (1961).

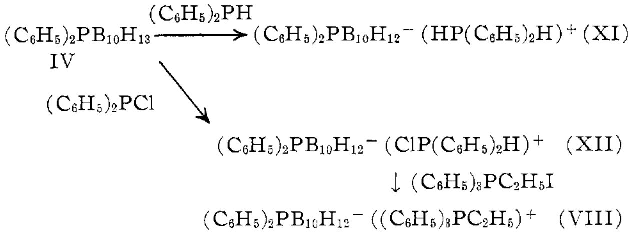
[14] M. F. Hawthorne, A. R. Pitochelli, R. D. Strahm, and J. J. Miller, *J. Am. Chem. Soc.*, **82**, 1825 (1960).

[15] V. D. Aftandilian, H. C. Miller, and E. L. Muetterties, *ibid.*, **83**, 2471 (1961).

[16] W. H. Knoth and E. L. Muetterties, *J. Inorg. Nucl. Chem.*, **20**, 66 (1961).

phenylphosphine and diphenylchlorophosphine, had been found to react with decaborane with bis-ligand formation and elimination of hydrogen, excess quantities of these phosphines therefore were allowed to react with $B_{10}H_{13}$–$P(C_6H_5)_2$ in ether or benzene solution. Whereas in the reaction with triphenylphosphine a diadduct X ($(C_5H_5)_2PB_{10}H_{13}\cdot 2(C_6H_5)_3P$) was formed, the other phosphines gave adducts having the molecular ratio 1:1, $(C_6H_5)_2PB_{10}H_{13}\cdot(C_6H_5)_2PH$ (XI) and $(C_6H_5)_2P$–$B_{10}H_{13}\cdot(C_6H_5)_2PCl$ (XII). In no case was hydrogen evolution observed.

Since Knoth and Muetterties[16] recently had prepared decaborane–monobase complexes of the type $B_{10}H_{12}$(ligand), and since no report of the formation of a phosphonium ion from the reaction of decaborane or a decaborane derivative and phosphines had been made, it originally was suspected that XI and XII were of a structure such as $B_{10}H_{13}R$(ligand). However, when the B^{11} n.m.r. spectra of the salts VII and VIII were compared with that of compound XII, they were found to be identical. This indicated the presence of a $(C_6H_5)_2P$–$B_{10}H_{12}$ anion in compound XII which was confirmed by the reaction of XII with $(C_6H_5)_3PC_2H_5I$ to give a product which was identical, in all respects, with the salt VIII. This unprecedented displacement of one phosphonium ion ($(C_6H_5)_2P^+ClH$) by a second ($(C_6H_5)_3P^+C_2H_5$) proves that XI and XII are salts of the structures as indicated below.



$$(C_6H_5)_2PB_{10}H_{13} \xrightarrow{(C_6H_5)_2PH} (C_6H_5)_2PB_{10}H_{12}^-\ (HP(C_6H_5)_2H)^+\ \text{(XI)}$$

IV

$$(C_6H_5)_2PB_{10}H_{13} \xrightarrow{(C_6H_5)_2PCl} (C_6H_5)_2PB_{10}H_{12}^-\ (ClP(C_6H_5)_2H)^+\quad \text{(XII)}$$

$$\downarrow (C_6H_5)_3PC_2H_5I$$

$$(C_6H_5)_2PB_{10}H_{12}^-\ ((C_6H_5)_3PC_2H_5)^+\quad \text{(VIII)}$$

Due to the poor solubility of X in suitable solvents, clarification of its structure by B^{11} n.m.r. treatment has not been established as yet, but based on the preceding results it is suspected to be of the form $(C_6H_5)_3 \rightarrow B_{10}H_{12}P(C_6H_5)_2^-\ ((C_6H_5)_3PH)^+$. Although here formulated as a substituted $B_{10}H_{14}$ dianion, it should be noted that its infrared spectrum shows, besides a PH band at 4.21 μ, three terminal BH peaks at 3.98, 4.12, and 4.32 μ which are almost identical with those reported by DuPont and Hawthorne[17] for a $B_{10}H_{15}$ anion.

Experimental[18]

Starting Materials.—Decaborane was sublimed prior to use. Diphenylchlorophosphine was obtained from Victor Chemical Company and used as received; it also served for the preparation of diphenylphosphine.[19]

B^{11} N.m.r. Spectra.—A Varian high-resolution n.m.r. spectrometer was used at 19.3 Mc.p.s. The spectra were obtained in acetone solution; the line positions were determined with an accuracy of ±5 c.p.s. using trimethylborate as an external standard.

Decaboranyl Sodium.—A solution of decaborane (6.1 g., 0.05 mole) in ether (80 ml.) was added, with stirring, through a dropping funnel within 5 min. to a suspension of sodium hydride (4.5 g.) in ether (70 ml.). After stirring for another 45 min., the mixture was filtered by suction (glass-fritted funnel, medium porosity) to give a clear yellow filtrate.

Diphenylphosphinodecaborane (IV).—To a solution of decaboranyl sodium (0.05 mole) in ether (150 ml.) was added a solution of diphenylchlorophosphine (11 g., 0.05 mole) in ether (50 ml.) at 30°. After stirring for 2 hr., the reaction mixture was filtered by suction, and the filtrate was evaporated to dryness. The residue was recrystallized from petroleum ether (b.p. 60–110°) to give 8.65 g. (56.5%) of IV, m.p. 147° dec.

Anal. Calcd. for $C_{12}H_{23}B_{10}P$ (306.5): C, 47.02; H, 7.56; B, 35.30; P, 10.11. Found: C, 46.96; H, 7.59; B, 35.32; P, 9.90; mol. wt. (cryoscopic in benzene), 298.

Reactions of IV with Lewis Acids.—Boron trichloride was condensed onto IV at −196°. While stirring, it was permitted to warm to 0° over 3 hr. Then the BCl_3 was evaporated, leaving pure IV. Boron trifluoride was passed into a solution of IV in benzene at 10° for 2 hr. No reaction was observed and IV was recovered. Trimethylborane was bubbled through a solution of IV in ether at 0°. Compound IV was recovered unchanged. Diborane was passed into solutions of IV in ether (at 0°) and in benzene (at 10°) for 2 hr. Again no reaction occurred.

Diphenylphosphine Nonaborane (V). (a) From Diphenylphosphinodecaborane (IV).—Addition of anhydrous ethanol (16 ml.) to diphenylphosphinodecaborane (IV, 1 g.) caused a slightly exothermic reaction. Upon refluxing the mixture for 2 min. (oil bath heating) almost complete solution was effected. After hot filtration 470 mg. (48.8%) of V, m.p. 166–168° dec., was obtained from the ice-cooled filtrate. For analysis a specimen (100 mg.) was recrystallized from ethanol (10 ml.), m.p. 168–169° dec.

Anal. Calcd. for $C_{12}H_{24}B_9P$ (296.7): C, 48.75; H, 8.08; B, 32.94; P, 10.48. Found: C, 48.95; H, 8.13; B, 32.70; P, 10.40.

Refluxing for 2 min. of 20 ml. of methanol with 1 g. of IV followed by filtration yielded 150 mg. of V from the filtrate and 310 mg. of V as filter residue, m.p. 166–167° dec. A mixture melting point of this product with the product obtained from the ethanol reaction did not show a depression.

(b) From Diethylsulfide Nonaborane (VI).—A mixture of diphenylphosphine (2.24 g., 0.0012 mole), diethylsulfide nonaborane (VI, 2.4 g., 0.0012 mole), and benzene (30 ml.) was refluxed for 1 hr. under nitrogen. After evaporating the benzene a quantitative yield of diphenylphosphine nonaborane (V, m.p. 166–168°) was obtained. A specimen was recrystallized from ethanol (m.p. 168–169°) and was identical with the material prepared by the two preceding procedures.

Triethylammoniumdiphenylphosphinodecaborane (VII).—A solution of triethylamine (1.4 g., 0.014 mole) in ether (30 ml.) was added dropwise, with stirring, to a solution of diphenylphosphinodecaborane (IV, 2.14 g., 0.007 mole) in ether (100 ml.) at ambient temperature. A heavy precipitate formed immediately. After the addition was complete, efficient stirring was maintained for 0.5 hr., then the reaction mixture was filtered by suction. The filter residue was washed with ether and dried *in vacuo*, m.p. 205° (2.8 g., 98%). Recrystallization from ethanol gave pure VII, m.p. 209°, which was soluble in acetone and ethyl acetate.

Anal. Calcd. for $C_{18}H_{35}B_{10}NP$ (407.7): C, 53.03; H, 9.40; B, 26.54; N, 3.44; P, 7.60. Found: C, 53.21; H, 9.99; B, 25.86; N, 3.44; P, 7.20.

For exact measurement of hydrogen possibly evolved in the reaction, the experiment was repeated by maintaining the temperature at 25° (external bath) and connecting the outlet to a gas trap. The reaction again gave a quantitative yield of VII, but *no* hydrogen was collected.

Triphenylethylphosphoniumdiphenylphosphinodecaborane (VIII). (a) From Triethylammoniumdiphenylphosphinodecaborane (VII).—Solutions of VII (1.02 g., 0.0025 mole) in acetone

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[17] J. A. DuPont and M. F. Hawthorne, *Chem. Ind.* (London), 405 (1962).

[18] Melting points are uncorrected; micro analyses were by R. Rittner and R. Culmo of the Olin Mathieson Microchemical Section.

[19] L. Horner, P. Beck, and H. Hoffmann, *Chem. Ber.*, **92**, 2098 (1959).

(15 ml.) and triphenylethylphosphonium iodide (1.05 g., 0.0025 mole) in acetone (35 ml.) were mixed and refluxed for 0.5 hr., then evaporated to dryness *in vacuo*. The solid residue was thoroughly washed with water and, after drying, recrystallized from a mixture (3:1) of acetone and ethyl acetate to give pure VIII (1.28 g., 86%), m.p. 242°. It was soluble in acetone and acetonitrile.

Anal. Calcd. for $C_{32}H_{43}B_{10}P_2$ (596.8): C, 64.40; H, 7.09; B, 18.13; P, 10.38. Found: C, 64.28; H, 7.51; B, 18.20; P, 10.10.

(b) **From Diphenylchlorophosphoniumdiphenylphosphinodecaborane (XII).**—A solution of XII (1.32 g., 0.0025 mole) and triphenylethylphosphonium iodide (1.05 g., 0.0025 mole) in anhydrous acetone (90 ml.) was refluxed for 0.5 hr., then evaporated to dryness *in vacuo*. The solid residue was extracted with 45 ml. of hot chloroform; the undissolved product (0.91 g., 61%) was pure VIII, m.p. 242°. *Anal.* Found: P, 10.18. The infrared spectrum was identical with that of the above product.

Triethylammoniumbenzyldecaborane (IX).—A solution of ethylamine (0.5 g., 0.005 mole) in ether (10 ml.) was added slowly to a stirred solution of benzyldecaborane[5] (0.53 g., 0.0025 mole) in ether (20 ml.). The reaction product separated as a viscous liquid. Solidification was achieved by replacing the ether with petroleum ether (b.p. 30–40°) and rapid stirring of this mixture; yield of crude IX: 0.71 g. (91%); m.p. 94–95°. A sample was recrystallized from CCl_4, m.p. 95°.

Anal. Calcd. for $C_{13}H_{35}B_{10}N$ (313.6): C, 49.78; H, 11.25; B, 34.50; N, 4.47. Found: C, 49.48; H, 11.94; B, 34.20; N, 4.18.

Triphenylphosphoniumtriphenylphosphine Diphenylphosphinodecaborane (X).—A solution of triphenylphosphine (1.73 g., 0.006 mole) in ether (10 ml.) was added with stirring to a solution of diphenylphosphinodecaborane (IV, 1 g., 0.0033 mole) in ether (40 ml.). The reaction product started precipitating immediately, but the mixture was refluxed for 3 hr. Filtration gave 2.3 g. (92%) of product, m.p. 130–146°. Upon washing with a small amount of acetone, the m.p. was raised to 149–151°.

Anal. Calcd. for $C_{48}H_{53}B_{10}P_3$ (831.0): C, 69.37; H, 6.43; B, 13.02; P, 11.18. Found (washed product): C, 70.46; H, 6.75; B, 13.40; P, 11.10.

Diphenylphosphoniumdiphenylphosphinodecaborane (XI).—A solution of diphenylphosphine (1.23 g., 0.0066 mole) in benzene (10 ml.) was added with stirring to a solution of diphenylphosphinodecaborane (IV, 1 g., 0.0033 mole) in benzene (20 ml.); the system was kept under nitrogen. After 10 min., a precipitate started to form which dissolved upon heating. After refluxing for 3 hr. and standing for 12 hr. at room temperature, some insoluble product (m.p. < 300°) was removed by filtration and the filtrate was evaporated to dryness. The residue was recrystallized from CCl_4 to give 1 g. (61%) of XI, m.p. 114–117°.

Anal. Calcd. for $C_{24}H_{34}B_{10}P_2$ (492.7): C, 58.51; H, 6.96; P, 12.58. Found: C, 60.18; H, 6.99; P, 12.60.

Diphenylchlorophosphoniumdiphenylphosphinodecaborane (XII).—To a solution of diphenylphosphinodecaborane (IV, 1.22 g., 0.004 mole) in ether (45 ml.) was added at 20° a solution of diphenylchlorophosphine (1.76 g., 0.008 mole) in ether (25 ml.). Upon refluxing for 1 hr., a viscous oil separated which solidified after standing for 20 hr. at room temperature; yield of crude XII: 2 g. (95%), m.p. 173–177°; after washing with a small amount of acetone, m.p. 182–184°.

Anal. Calcd. for $C_{24}H_{33}B_{10}ClP_2$ (527.1): C, 54.67; H, 6.31; B, 20.53; Cl, 6.73; P, 11.75. Found: C, 54.54; H, 6.81; B, 19.60; Cl, 6.85; P, 11.60.

Acknowledgment.—This work was supported by the Office of Naval Research. The author is indebted to Dr. C. Naar-Colin for performing the B^{11} n.m.r. spectra and to Drs. T. L. Heying and S. I. Trotz for stimulating discussions.

CONTRIBUTION FROM THE ORGANICS DIVISION,
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Chemistry of Decaborane–Phosphorus Compounds. III. Decaborane-14–Phosphine Polymers[1]

BY HANSJUERGEN SCHROEDER, JOSEPH R. REINER, AND THOMAS A. KNOWLES

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Under basic conditions $B_{10}H_{12}((C_6H_5)_2P{\cdot}Cl)_2$ and $B_{10}H_{12}((C_6H_5)_2P{\cdot}OH)_2$ were found to enter into a condensation polymerization with elimination of hydrogen chloride to form a P–O–P linked polymer, $(\text{-}OP(C_6H_5)_2B_{10}H_{12}P(C_6H_5)_2\text{-})_x$. A study of the pyrolysis of this polymer and monomeric compounds of the type $B_{10}H_{12}((C_6H_5)_2P{\cdot}R)_2$ was conducted. $B_{10}H_{12}((C_6H_5)_2P{\cdot}N_3)_2$ and diphosphines reacted in refluxing benzene with evolution of nitrogen to give P=N—P linked polymers of high thermal stability, *e.g.*, $(=P(C_6H_5)_2—C_6H_4—P(C_6H_5)_2=N—P(C_6H_5)_2B_{10}H_{12}P(C_6H_5)_2N=)_x$, dec. >340°.

In the first paper of this series, the syntheses of bis-(chlorodiphenylphosphine)decaborane-14 (I) and various derivatives were described.[2] Interest in this class of compounds had been stimulated by the possibility that some members of this series might serve as starting materials for the preparation of unusual boron based polymers. The original impetus for the present work arose from an observation made during an attempt to prepare bis-(diethylaminodiphenylphosphine)-decaborane (II) by treating $B_{10}H_{12}((C_6H_5)_2P{\cdot}Cl)_2$ with triethylamine hoping to split out ethyl chloride and thus obtain $B_{10}H_{12}((C_6H_5)_2PN(C_2H_5)_2)_2$. Several experiments of this type using commercial benzene and technical grade triethylamine gave no indication of proceeding as desired.

$$B_{10}H_{12}((C_6H_5)_2PCl)_2 + 2(C_2H_5)_3N \longrightarrow B_{10}H_{12}((C_6H_5)_2PN(C_2H_5)_2)_2 + 2C_2H_5Cl$$

Instead, the bistriethylammonium salt of bis-(hydroxydiphenylphosphine)-decaborane, $B_{10}H_{12}((C_6H_5)_2P{\cdot}OH)_2{\cdot}2(C_2H_5)_3N$ (III), and a very insoluble and high melting

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[1] Preceding communication: H. Schroeder, *Inorg. Chem.*, **2**, 390 (1963).

[2] H. Schroeder, J. R. Reiner, and T. L. Heying, *ibid.*, **1**, 618 (1962).