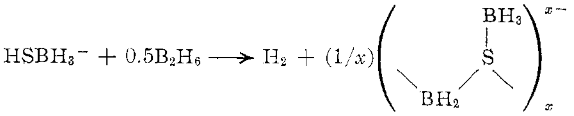
tion of more diborane (reaction 3) to yield $HS(BH_3)_2^-$ as the principal product.

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°.

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



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

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

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

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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]

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

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

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

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[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).

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[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).

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TABLE I

ANALYTICAL DATA FOR PHOSPHACARBORANE DERIVATIVES

	% Calcd						% Found					
Compound	C	H	N	P	B	Br	C	H	N	P	B	Br
1,2-$B_{10}H_{10}CHP$	7.41	6.84	...	19.09	66.66	...	7.50	6.84	...	20.0		...
1,7-$B_{10}H_{10}CHP$	7.41	6.84	...	19.09	66.66	...	7.93	6.98	...			...
1,12-$B_{10}H_{10}CHP$	7.41	6.84	...	19.09	66.66	...	6.85	6.78	...			...
$C_5H_{10}NH_2[7,8\text{-}B_9H_{10}CHP]$	30.34	9.76	5.90	13.04	40.96	...	30.46	9.50	5.91			...
$C_5H_{10}NH_2[7,9\text{-}B_9H_{10}CHP]$	30.34	9.76	5.90	13.04	40.96	...	30.93	9.78	5.97			...
$(CH_3)_4N[7,9\text{-}B_9H_{10}CHP]$	26.63	10.28	6.21	13.73	43.14	...	26.95	10.42	6.15		43.21	...
7,8-$B_9H_{10}CHPCH_3$	14.44	8.48	...	18.6	58.47	...	14.15	8.22	...		58.22	...
7,9-$B_9H_{10}CHPCH_3$	14.44	8.48	...	18.6	58.47	...	14.69	7.94	...	18.7		...
7,9-$B_9H_{10}CHPH$	7.88	7.94	...	20.33	63.84	...	8.21	8.11	...			...
1,2-$B_{10}H_9BrCHP$	4.98	4.18	...	12.85	44.85	33.15	5.30	4.18	...			33.32
1,2-$B_{10}H_8Br_2CHP$	3.75	2.83	...	9.68	33.79	49.95	3.75	2.83	...			50.52
1,2-$B_{10}H_7Br_3CHP$	3.04	2.02	...	7.76	27.12	60.10	3.14	2.19	...			60.58
1,7-$B_{10}H_9BrCHP$	4.98	4.18	...	12.85	44.85	33.15	5.66	4.22	...			33.19
1,7-$B_{10}H_8Br_2CHP$	3.75	2.83	...	9.68	33.79	49.95	3.90	2.70	...			49.54

isoelectronic with carborane ($B_{10}C_2H_{12}$). Heterogeneous reaction of $Na_3B_{10}H_{10}CH(THF)_2$ with a phosphorus trihalide in solvents such as petroleum ether (bp 90–110°), benzene, or toluene produced 1,2-$B_{10}H_{10}CHP$ (I)[11] in moderate yield (40–50%). This compound is a sublimable, air-stable, colorless solid with an odor reminiscent of carborane. The molecular composition of I was confirmed by its elemental analysis (Table I) and its parent ion peak at *m/e* 164.1530 (calcd for $^{11}B_{10}{}^1H_{11}{}^{12}C^{31}P$, 164.1529). The boron ($^{11}B$) nmr spectrum of I (Figure 1) is consistent with a 1:1:2:2:2:2 pattern expected for either 1,2- or 1,7-$B_{10}H_{10}CHP$. The doublets at lowest field (one centered at −9.6 ppm) must represent the two unique boron atoms located on the mirror plane which also contains the carbon and phosphorus atoms. In the boron nmr spectrum of 1,2-$B_{10}C_2H_{12}$ the analogous 9 and 10 boron atoms are also found at lowest field.[12] Additional evidence that the carbon and phosphorus atoms in I are nearest neighbors is obtained from the proton nmr spectrum. The resonance attributed to the hydrogen on carbon is a broad doublet at τ 7.85 with a J_{P-C-H} of 14 cps.

Thermal isomerization of I in a sealed tube at 500° for 10 hr produced a new isomeric product (II) in moderate yield. The mass spectrum of this compound contained a parent peak at *m/e* 164.1531 (calcd, 164.1529). The ^{11}B nmr spectrum of isomer II (Figure 2) although difficult to interpret is too complex to be assigned to the 1,12-$B_{10}H_{10}CHP$ isomer. The proton nmr spectrum of II contains a broad singlet at τ 7.52 assigned to the hydrogen on carbon. Since there is no observable ^{31}P–^1H coupling, it is suggested that II has the 1,7-$B_{10}H_{10}CHP$ configuration (Figure 3). A recent X-ray study supports this postulate.[13]

Pyrolysis of I at higher temperatures (650°) produces a mixture of II and a third very volatile species (III). The new compound was purified by column chromatography. Elemental analysis and measurement of its mass spectral parent ion peak at *m/e* 164.1531 (calcd, 164.1529) confirm that III is the remaining $B_{10}H_{10}CHP$ isomer. The 32-MHz ^{11}B nmr spectrum of III is a doublet (J_{BH} = 167 cps) centered at +9.8 ppm relative to $BF_3 \cdot (C_2H_5)_2O$. Ideally for 1,12-$B_{10}H_{10}CHP$ this spectrum should be two doublets of equal area, but in this case the doublets are accidentally equivalent. The proton nmr spectrum of III contains a singlet at τ 7.3 attributed to the hydrogen on carbon.

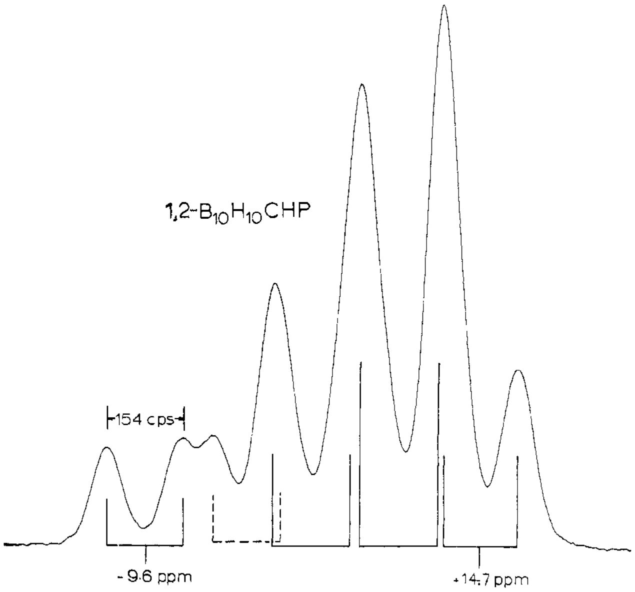

Figure 1.—A 32.1-MHz ^{11}B nmr spectrum of 1,2-$B_{10}H_{10}CHP$ (I) in benzene solution referenced to $BF_3 \cdot (C_2H_5)_2O$.

The relative gas chromatographic retention times of the phosphacarboranes (I, II, and III) and the carboranes (1,2-, 1,7- and 1,12-$B_{10}C_2H_{12}$) are quite similar. The retention times increase in the order 1,12, 1,7, and 1,2 isomer paralleling the increase in polarity of these isomers.

The ^{31}P nmr spectra of I and II at 24.3 MHz give very broad singlets centered at +57 and +71 ppm, respectively, relative to 85% orthophosphoric acid. Trivalent phosphorus derivatives such as $R_2PC_6H_5$ and R_2PH have similar ^{31}P chemical shift values. However, relative to trialkylphosphines, I and II appear to be weak Lewis bases since neither is attacked at the phosphorus by methyl iodide or bromine.

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[11] J. L. Little, J. T. Moran, and L. J. Todd, *J. Am. Chem. Soc.*, **89**, 5495 (1967).

[12] G. D. Vickers, H. Schroeder, W. N. Lipscomb, and J. A. Potenza, *ibid.*, **88**, 628 (1966).

[13] L. J. Todd, I. C. Paul, J. L. Little, P. S. Welcker, and C. R. Peterson, *ibid.*, **90**, 4489 (1968).

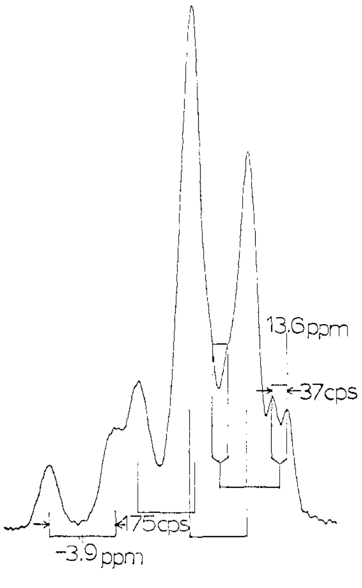

Figure 2.—A 32.1-MHz ^{11}B nmr spectrum of 1,7-$B_{10}H_{10}CHP$ (II) in benzene solution referenced to $BF_3 \cdot (C_2H_5)_2O$.

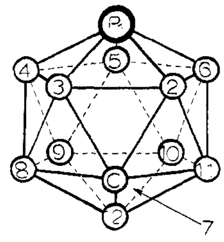

Figure 3.—The proposed structure of 1,7-$B_{10}H_{10}CHP$ (II) with its numbering system.

Bromination of 1,2- and 1,7-Phosphacarbadodecaborane(11).—Aluminum chloride catalyzed bromination of 1,2-$B_{10}H_{10}CHP$ gives a mono-, di-, and, with excess bromine, ultimately a tribromo derivative. The evolution of hydrogen bromide in this reacton and the appearance of a broad doublet attributable to the hydrogen on carbon in the proton nmr spectra of these products indicate that halogen substitution occurs on the boron atoms. Bromination of 1,7-$B_{10}H_{10}CHP$ under similar conditions gives only mono- and dibromo derivatives. Reactions of 1,2- and 1,7-$B_{10}H_{10}C_2H_2$ with bromine and aluminum chloride are reported to give the same amount of halogen substitution.[14] That exhaustive bromination produces disubstitution with II suggests that this isomer is less polar than the 1,2 isomer and gives further support for the proposed structure of II.

The doublet of unit area at lowest field in the ^{11}B nmr spectrum of I (Figure 1) has transformed to a singlet in the boron spectrum of 1,2-$B_{10}H_8Br_2CHP$ (Figure 4). This indicates that one of the substituted boron atoms lies on the mirror plane of the molecule (B_9 or B_{12}). Thus at least one of the positions of substitution appears to be at a boron atom *para* to a heteroatom. Bromine substitution in 9,12-dibromo-*o*-carborane is also found to be *para* to the carbon atoms.[15]

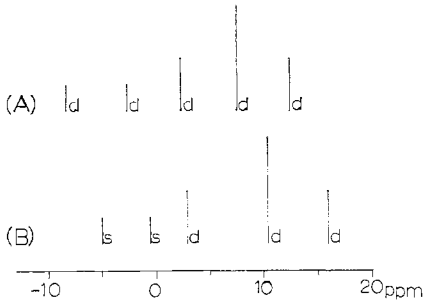

Figure 4.—Relative positions of the ^{11}B nmr resonance lines (32 MHz) of (A) 1,2-$B_{10}H_{10}CHP$ (I) and (B) 1,2-$B_{10}H_8Br_2CHP$ (X) externally referenced to $BF_3 \cdot (C_2H_5)_2O$: s, singlet; d, doublet.

11-Atom Polyhedral Fragments.—Reaction of 1,2-$B_{10}H_{10}CHP$ with sodium ethoxide in ethanol at reflux produces a low yield of the $B_{10}H_{12}CH^-$ ion as indicated by elemental analysis and infrared and ^{11}B nmr spectra of its tetramethylammonium salt. In this case base attack removes the phosphorus atom of the cage. In contrast, treatment of 1,7-$B_{10}H_{10}CHP$ with sodium ethoxide in ethanol produces in moderate yield an ion with the composition $B_9H_{10}CHP^-$. Zakharkin and Kalinin have reported that a boron atom could be easily abstracted from 1,2-$B_{10}C_2H_{12}$ with piperidine to form 1,2-$B_9C_2H_{12}^-$.[16] Using this amine we have been able to obtain good yields of two isomeric $B_9H_{10}CHP^-$ ions (IV and V) from I and II, respectively. The degradation of 1,2-$B_{10}H_{10}CHP$ is faster than that of the 1,7 isomer. Attempts to degrade 1,12-$B_{10}H_{10}CHP$ with methoxide ion or piperidine at 150° for 7 days were not successful. Analytical data for the piperidinium salts of IV and V and the tetramethylammonium salt of V are given in Table I. It is plausible that both IV and V have the gross geometry of 11-particle icosahedral fragments with the phosphorus in the open face. This, together with the negative charge, suggests that the new ions might have stronger Lewis-base properties than I and II. Treatment of the tetramethylammonium salts of IV and V with methyl iodide in tetrahydrofuran solution gives a nearly quantitative yield of $(CH_3)_4NI$ and the colorless, sublimable solids VI and VII, respectively, having the molecular composition $B_9H_{10}CHPCH_3$. Solid samples of these neutral species show detectable borate formation after 3-month storage in the air. The proton nmr spectra of VI and VII contain sharp doublets at τ 7.57 (J = 11 cps) and τ 8.03 (J = 12 cps), respectively, which are assigned to a methyl group attached to a phosphorus atom.

The structures of V and VII are based primarily upon the single-crystal X-ray study of $(B_9H_9CHPCH_3)_2Fe$.[13] Assuming that the heteroatoms did not rearrange under the relatively mild conditions needed to form the metal complex, then V and VII are most likely 7,9-$B_9H_{10}CHP^-$ and 7,9-$B_9H_{10}CHPCH_3$, respectively, having the 11-atom structure shown in Figure 5.[17] Formation of

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[14] H. D. Smith, T. A. Knowles, and H. Schroeder, *Inorg. Chem.*, **4**, 107 (1965).

[15] J. A. Potenza and W. N. Lipscomb, *ibid.*, **5**, 1471 (1966).

[16] (a) L. I. Zakharkin and V. N. Kalinin, *Tetrahedron Letters*, 407 (1965); (b) M. F. Hawthorne, P. A. Wegner, and R. C. Stafford, *Inorg. Chem.*, **4**, 1675 (1965).

[17] The numbering systems employed in this article follow the new nomenclature rules which recently appeared: *ibid.*, **7**, 1945 (1968).

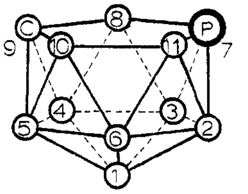

Figure 5.—Proposed structure and numbering system of the 7,9-$B_9H_{10}CHP^-$ ion (V). The position of the 11th hydrogen is not known.

V is accomplished by base removal of either B_2 or B_3 from 1,7-$B_{10}H_{10}CHP$ (Figure 3). These two boron atoms are adjacent to both carbon and phosphorus and would be expected to be most susceptible to base attack. This should give enantiomeric $B_9H_{10}CHP^-$ ions. This point has been demonstrated indirectly by partial resolution of the *dd*- and *ll*-$(B_9H_9CHPCH_3)_2Fe$ isomers.[13] The proton nmr spectrum of IV contains a broad doublet at τ 8.86 ($J_{PCH} = 26$ cps) assigned to the hydrogen bonded to carbon. The CH resonance of 7,9-$B_9H_{10}CHP^-$ is a broad singlet. This suggests that carbon and phosphorus are nearest neighbors in IV and VI and these are assigned the 7,8-$B_9H_{10}CHP^-$ and 7,8-$B_9H_{10}CHPCH_3$ configurations on this basis.

When the 7,9-$B_9H_{10}CHP^-$ ion is passed through an acid ion-exchange column, a sublimable hygroscopic solid (VIII) is obtained in good yield. The low-voltage mass spectrum cuts off at *m/e* 154, corresponding to the $^{11}B_9{}^1H_{12}{}^{12}C^{31}P^+$ ion. The elemental analyses are consistent with this formulation (Table I). VIII dissolves in water and can be titrated with sodium hydroxide to give an equivalent weight of 159 (calcd, 152). The infrared spectrum of this compound (CS_2 solution) contains a weak but sharp peak at 2400 cm^{-1} attributable to a PH stretching frequency. The proton nmr spectrum of VIII ($CDCl_3$ solution) contains a sharp singlet at τ 5.95 and a broad singlet at τ 7.35, both of equal area assigned to the PH and CH protons, respectively. The lack of ^{31}P–^1H coupling in the low-field peak may be due to rapid exchange of the acidic phosphine proton. The ^{11}B nmr spectrum of VIII is similar to that of 7,9-$B_9H_{10}CHPCH_3$. Attempted protonation of 7,8-$B_9H_{10}CHP^-$ by the ion-exchange method gives a nonvolatile, hygroscopic solid (protonic salt) which has been difficult to characterize.

Although the ^{11}B nmr spectra of IV–VII are too complex for complete interpretation, the 32.1-MHz boron spectrum of 7,9-$B_9H_{10}CHPCH_3$ (Figure 6) contains two unusually sharp doublets ($J = 52$ cps) which may be due to either spin coupling with the 11th hydrogen attached to the cage or to ^{11}B–^{31}P spin coupling. In support of the latter suggestion, it is observed that irradiation of ^{31}P at 24,282,960 Hz while observing the 19.3-MHz ^{11}B nmr spectrum of VII causes collapse and sharpening of two peaks in the low-field region (Figure 7). Similar coupling is observed in the ^{11}B nmr spectra of II (Figure 2) and VIII but not in the boron spectra of I and IV. This type of coupling has been observed to date only in molecules believed to have the phosphorus and carbon atoms 1,7 (*meta*) to one another in the icosahedral cage or 11-atom fragment. No coupling is detectable in the 24.3-MHz ^{31}P nmr spectrum of VII which is a very broad singlet centered at +95 ppm relative to 85% orthophosphoric acid.

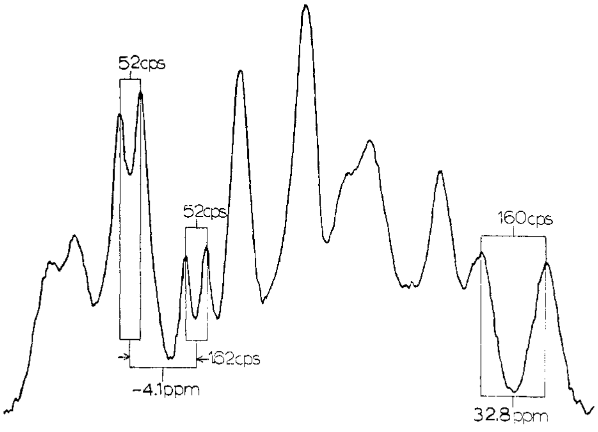

Figure 6.—A 32.1-MHz ^{11}B nmr spectrum of 7,9-$B_9H_{10}CHPCH_3$ (VII) in acetone solution referenced to $BF_3 \cdot (C_2H_5)_2O$.

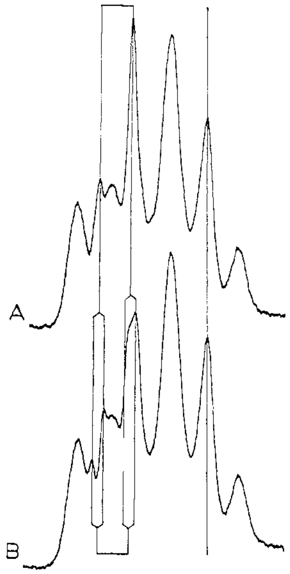

Figure 7.—Boron (^{11}B) nmr spectra at 19.3 MHz of 7,9-$B_9H_{10}CHPCH_3$ (VII): A, with ^{31}P decoupled; B, normal spectrum.

Other aspects of the chemistry of these phosphacarboranes are presently being studied and will be presented in subsequent papers.

Experimental Section

Apparatus and Materials.—The infrared spectra for which a solvent is not indicated have been recorded as KBr disks. All infrared spectra were measured on a Perkin-Elmer 521 or 621 instrument. Intensities of absorptions are reported as strong (s), medium (m), or weak (w). Low-resolution mass spectra were obtained with an Atlas CH-4 instrument. High-resolution mass spectra were obtained with either an AEI MS-9 instrument (Indiana University) or a CEC Type 21-103B instrument (Union Oil Co.). Boron (^{11}B) nmr spectra at 32.1 MHz were obtained with a Varian HA-100 spectrometer. Spectral integrals were measured with a planimeter. Boron chemical shift data were measured relative to external trimethyl borate. All data presented in this paper are referenced to the $BF_3 \cdot (C_2H_5)_2O$ standard by addition of −18.15 ppm to the trimethyl borate chemical shift value. Proton nmr spectra were obtained with a Varian A-60, A-60A, or HA-100 spectrometer. Boron nmr at 19.3 MHz and ^{31}P nmr at 24.3 MHz were obtained with a Varian DP-60 spectrometer. Melting points were obtained in evacuated sealed capillaries and are uncorrected. Gas chromatographic analyses were carried out with an F & M Model 700 instrument employing a 0.25-in. diameter column 4 ft long. The column was packed with 10% General Electric Co. SE-30 silicone rubber on 60–80 mesh Chromosorb P. Elemental analyses (C, H, N, P, Br) were obtained from the University of Illinois Microanalytical Laboratory. Boron analyses were obtained from Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. All reactions were carried out under an atmosphere of prepurified nitrogen or argon.

1,2-$B_{10}H_{10}CHP$ (I).—To a 1-l. three-necked flask fitted with an overhead stirrer, nitrogen inlet, and reflux condenser were added 40.0 g of $(CH_3)_3NCB_{10}H_{12}$ prepared by the method of Knoth,[7] 300 ml of tetrahydrofuran (THF), and then 14.9 g of freshly cut sodium metal. The solution was stirred at reflux while maintaining a positive pressure of inert gas until a pyrophoric white solid precipitated[18] which had been shown to have the composition $Na_3B_{10}H_{10}CH(THF)_2$.[19] After cooling, the solvent and trimethylamine were removed under vacuum. The flask was then charged with dry high-boiling petroleum ether and fitted with a pressure-compensating addition funnel containing a solution of 14.5 ml of PCl_3 in 200 ml of high-boiling petroleum ether. With refluxing and vigorous stirring the PCl_3 was added dropwise over 3–4 hr. The solvent was removed *in vacuo* without heating until dry powdery solids were obtained. These solids were transferred to a large sublimer with a water-cooled probe and sublimation at 100° (0.01 mm) for 24–36 hr yielded 13.5–16.8 g (40–50%) of I (mp 353.5–354.5). The infrared spectrum of I (CCl_4 solution) included absorptions at λ_{max} 3056 (w), 2592 (vs), 1118 (m), 1040 (m), 995 (m), 717 (m), and 670 (w) cm^{-1}. The molecular weight of I was determined cryoscopically in benzene: calcd, 162; found, 165. The ultraviolet spectrum (acetonitrile solution) contained λ_{max} (ϵ) at 253 (400) and 198 mμ (4150). The proton nmr spectrum (benzene solution) showed a broad doublet centered at τ 7.85 (J_{PCH} = 14 cps).

1,7-$B_{10}H_{10}CHP$ (II).—One gram of I was sealed into an evacuated Carius tube (25 × 2 cm) and maintained at 550° for 8 hr. The product mixture was sublimed at 50–60° (0.01 mm) to obtain 60–65% yield by weight of sublimate. Gas chromatographic analysis indicated that the product was a 99:1 mixture of II and I, respectively. The 1,7 isomer was further purified by crystallization from *n*-hexane, mp 325–327°. The infrared spectrum of II (CCl_4 solution) contained absorptions at λ_{max} 3055 (w), 2595 (vs), 1134 (m), 1058 (m), 996 (s), 720 (w), and 665 (w) cm^{-1}. The ultraviolet spectrum of II (acetonitrile solution) contained λ_{max} (ϵ) at 245 mμ (265). The proton nmr spectrum (benzene solution) contained a broad singlet at τ 7.52.

1,12-$B_{10}H_{10}CHP$ (III).—One gram of I was sealed into an evacuated, thick-wall tube and heated at 650° for 19 hr. The pyrolyzate was sublimed giving 0.5 g of a 1:1 mixture of II and III as indicated by glpc. Column chromatography on alumina with pentane as eluent gave pure III, mp 314–315.5°. The infrared spectrum (CCl_4 and CS_2 solutions) included absorptions at λ_{max} 3057 (m), 2580 (s, b), 1145 (m), 1069 (m), 1059 (m, sh), 988 (m), 888 (w), 786 (w), 731 (s), and 679 (m) cm^{-1}. The proton nmr spectrum of III (benzene solution) contained a broad singlet at τ 7.30.

7,8-$B_9H_{10}CHP^-$ (IV). (A) **Piperidinium Salt.**—A solution of 5.00 g (0.03 mol) of I in 50 ml of piperidine was heated at 60° for 6 hr and then the solvent was removed *in vacuo*. Methanol was slowly added to the oily solid products until gas evolution ceased. The product was then recrystallized from methanol–water, mp 307–308°, to give 5.7 g of $C_5H_{10}NH_2[7,8\text{-}B_9H_{10}CHP]$ (80% yield). The infrared spectrum of the piperidinium salt exhibited absorptions at λ_{max} 3200 (s), 3122 (m), 2962 (m), 2930 (m), 2870 (w), 2560 (vs), 1573 (s), 1470 (m), 1450 (m), 1404 (m), 1383 (m), 1293 (m), 1154 (m), 1077 (m), 1020 (s), 990 (sh), 940 (m), 906 (m), 855 (w), 641 (m), 540 (w), and 426 (m) cm^{-1}. The proton nmr spectrum in dimethyl sulfoxide-d_6 consisted of a sharp singlet (2 H), a broad, poorly resolved multiplet (4 H), a broad singlet (6 H), and a broad doublet (1 H; J = 26 cps) centered at τ 5.31, 6.6, 8.2, and 8.86, respectively.

(B) **Tetramethylammonium Salt.**—The piperidinium salt of IV was dissolved in acetone and treated with aqueous tetramethylammonium chloride solution until precipitation was complete. The solid was collected by filtration and recrystallized from acetone–methanol. The ^1H nmr spectrum of the tetramethylammonium salt (acetone-d_6) consisted of a sharp singlet (12 H) and a broad doublet (1 H; J = 26 cps) at τ 6.56 and 8.86, respectively.

7,9-$B_9H_{10}CHP^-$ (V). (A) **Piperidinium Salt.**—This compound was prepared from II in precisely the same manner as the corresponding salt of IV. The piperidinium salt of V was obtained in 90% yield, mp 296–297°. The infrared spectrum included absorptions at λ_{max} 3200 (s), 2962 (m), 2560 (s), 1467 (m), 1383 (m), 1293 (m), 1154 (m), 1089 (m), 1070 (m), 1025 (m), 990 (s), 905 (m), 855 (w), and 750 (w) cm^{-1}.

(B) **Tetramethylammonium Salt.**—Sodium metal (1.9 g, 0.08 g-atom) was allowed to react with 80 ml of ethanol and then 4.50 g (0.027 mol) of 1,7-$B_{10}H_{10}CHP$ was added to the mixture. After reflux for 20 hr, the solvent was removed under vacuum at room temperature. The residues were treated with water and 0.95 g (21%) of II was recovered from the insoluble solids. The water-soluble material was treated with tetramethylammonium chloride. The precipitate was collected and recrystallized from acetone–methanol giving 3.37 g (53% yield) of $(CH_3)_4N[7,9\text{-}B_9H_{10}CHP]$. The tetramethylammonium salt of V exhibited absorptions at λ_{max} 3018 (w), 2540 (vs), 1480 (s), 1416 (m), 1090 (m), 1080 (m), 1036 (w), 991 (s), 948 (s), 878 (w), 752 (w), 738 (w), and 438 (w) cm^{-1}. The proton nmr spectrum (acetone-d_6) showed a sharp singlet at τ 6.53 (12 H) and a broad singlet at τ 8.1 (1 H).

7,8-$B_8H_{10}CHPCH_3$ (VI).—To a solution of $(CH_3)_4N[7,8\text{-}B_9H_{10}CHP]$ (2.25 g, 0.01 mol) in 100 ml of THF was added methyl iodide (1.42 g 0.01 mol) and then the mixture was refluxed for 1 hr. The solvent was removed under vacuum at room temperature and the product was sublimed from the residues at 60° (0.01 mm) to give 0.61 g (40% yield) of VI, mp 108–109°. The infrared spectrum of VI (chloroform solution) contained absorptions at λ_{max} 3040 (w), 3005 (w), 2912 (w), 2560 (vs), 1400 (w), 1292 (w), 1123 (w), 1012 (m), 988 (m), and 965 (m) cm^{-1}. The low-voltage mass spectrum cut off at *m/e* 168 corresponding to the $^{11}B_9{}^1H_{14}{}^{12}C_2{}^{31}P^+$ parent ion. The proton nmr spectrum of VI ($CDCl_3$ solution) consisted of a sharp doublet (J = 11 cps; 3 H) centered at τ 7.75 and a broad singlet (1 H) at τ 7.9.

7,9-$B_9H_{10}CHPCH_3$ (VII).—This compound was prepared from V by the exact procedure used to prepare VI. 7,9-$B_9H_{10}CHPCH_3$ was obtained in 94% yield, mp 112–113°. The infrared spectrum (CS_2 solution) showed absorptions at λ_{max} 3010 (w), 2932 (m), 2552 (vs), 1402 (w), 1285 (w), 1157 (w), 1084 (m), 1057 (m), 1014 (w), 975 (s), 930 (m), 910 (m), 892 (m), 872 (m), 847 (m), 750 (m), 739 (s), 678 (w), and 600 (w), cm^{-1}. The low-voltage mass spectrum of VII cut off at *m/e* 168 corresponding to the $^{11}B_9{}^1H_{14}{}^{12}C_2{}^{31}P^+$ parent ion. The osmometric molecular weight in acetone was found to be 175 (calcd, 166). The proton nmr spectrum ($CDCl_3$ solution) showed a broad singlet (1 H) at τ 7.6 and a sharp doublet (J = 12 cps; 3 H) at τ 8.03.

7,9-$B_9H_{10}CHPH$ (VIII).—A column of acid ion-exchange resin (Amberlite IR-120H) with fivefold excess exchange capacity was thoroughly washed with acetonitrile. An acetonitrile solution of 1.50 g (0.0067 mol) of $(CH_3)_4N[7,9\text{-}B_9H_{10}CHP]$ was slowly passed though the column. The column was washed with additional acetonitrile until the eluent no longer reduced silver nitrate. The solvent was removed under vacuum at room temperature and the solid products were sublimed at 50° (0.01 mm) to give 0.93 g (91% yield) of 7,9-$B_9H_{10}CHPH$, mp 206–210° dec.

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[18] The time required to form the white solid depends upon the purity of the carborane reagent (6–48 hr).

[19] D. E. Hyatt, F. R. Scholer, L. J. Todd, and J. L. Warner, *Inorg. Chem.*, **6**, 229 (1967).

VIII was dissolved in water and titrated with sodium hydroxide to a phenolphthalein end point (calcd equiv wt, 152; found, 159). The infrared spectrum of VIII (CS_2 solution) exhibited absorptions at λ_{max} 3040 (w), 2595 (vs), 2400 (w), 1140 (m), 1080 (s), 1060 (s), 980 (sh), 970 (s), 931 (m), 895 (m), 875 (m), 846 (m), 745 (sh), 733 (s), and 684 (m) cm^{-1}. The low-voltage mass spectrum cut off sharply at *m/e* 154 corresponding to the $^{11}B_9{}^1H_{11}{}^{12}C^{31}P^+$ parent ion.

1,2-$B_{10}H_9BrCHP$ (IX).—To a refluxing solution containing 1,2-$B_{10}H_{10}CHP$ (1.0 g, 0.0062 mol) and aluminum chloride (0.9 g, 0.0068 mol) in 50 ml of carbon disulfide was added dropwise over 1–5 hr a solution of bromine (0.94 g, 0.0058 mol) in 25 ml of carbon disulfide. Reflux was continued for 2 hr after addition. The mixture was filtered and the solvent was removed under vacuum. The resulting tan solid was extracted with three 50-ml portions of boiling hexane. Concentration and cooling of the extract gave pure 1,2-$B_{10}H_9BrCHP$, mp 244.5–245.5°. Both tlc and glpc suggested that the product was a single isomer. The mass spectrum of IX at low electron voltage (10 eV) cut off at *m/e* 244 corresponding to a parent ion of composition $^{11}B_{10}{}^1H_{10}{}^{12}C^{31}P^{81}Br^+$. The infrared spectrum (CS_2 solution) included absorptions at λ_{max} 3040 (m), 2590 (s), 1110 (w), 980 (w), 960 (m), 925 (w), 905 (w), 835 (w), 825 (s), and 725 (m) cm^{-1}. The proton nmr spectrum of IX (acetone-d_6) contained a broad peak at τ 5.75.

1,2-$B_{10}H_8Br_2CHP$ (X).—The procedure used in this synthesis was the same as for IX. Reaction of 0.0062 mol of 1,2-$B_{10}H_{10}CHP$ and 0.0068 mol of aluminum chloride with 0.0117 mol of bromine in carbon disulfide solution gave 1.03 g (52% yield) of 1,2-$B_{10}H_8Br_2CHP$, mp 255–256°. The mass spectrum at low electron voltage (15 eV) cut off at *m/e* 324 corresponding to a parent ion of composition $^{11}B_{10}{}^1H_9{}^{12}C^{31}P^{81}Br_2{}^+$. The infrared spectrum of X (CS_2 solution) included absorptions at λ_{max} 3040 (m), 2605 (s), 1085 (m), 965 (m), 950 (m), 935 (s), 825 (s), and 725 (m) cm^{-1}. The proton nmr spectrum of X (acetone-d_6) contained a broad doublet at τ 5.78.

1,2-$B_{10}H_7Br_3CHP$ (XI).—This derivative was prepared by the same procedure described above for IX and X except that 2.9 mol of bromine was used for each mole of 1,2-$B_{10}H_{10}CHP$. The product was recrystallized from *n*-hexane, mp 352–353°. The mass spectrum at low voltage (13 eV) cut off at *m/e* 404 corresponding to a parent ion of composition $^{11}B_{10}{}^1H_8{}^{12}C^{31}P^{81}Br_3{}^+$. The infrared spectrum contained peaks at λ_{max} 3030 (m), 2600 (s), 1125 (m), 1045 (w), 990 (w), 980 (m), 970 (m), 940 (w), 930 (m), 890 (w), 875 (m), 850 (s), 830 (w), 780 (w), 720 (w), 665 (m), 485 (m), 420 (w), and 370 (w) cm^{-1}. The proton nmr spectrum of XI (acetone-d_6) contained a broad doublet at τ 5.6.

1,7-$B_{10}H_9BrCHP$ (XII).—This compound was prepared by the same procedure used for IX. The analytical sample was recrystallized from *n*-pentane, mp 226–227.5°. The high-resolution mass spectrum contained a peak at *m/e* 244.0613 (calcd, 244.0613) corresponding to a parent ion of composition $^{11}B_{10}{}^1H_{10}{}^{12}C^{31}P^{81}Br^+$. The infrared spectrum of XII contained absorptions at λ_{max} 3030 (m), 2590 (s), 1140 (w), 1135 (m), 1045 (w), 1000 (w), 975 (w), 925 (m), 827 (w), 810 (s), 780 (w), 737 (m), 730 (w), 665 (w), and 450 (m) cm^{-1}.

1,7-$B_{10}H_8Br_2CHP$ (XIII).—This derivative was prepared by the same procedure used for X. The analytical sample was recrystallized from low-boiling (60–68°) petroleum ether, mp 234–235°. Both tlc and glpc suggested that XIII was a single isomer. The mass spectrum at low voltage (10.5 eV) cut off at *m/e* 324 corresponding to a parent composition $^{11}B_{10}{}^1H_9{}^{12}C^{31}P^{81}Br_2{}^+$. The infrared spectrum of XIII included absorptions at λ_{max} 3040 (m), 2600 (s), 1145 (m), 1055 (m), 1015 (s), 940 (s), 915 (m), 880 (m), 845 (m), 825 (s), 795 (m), 750 (m), and 465 (s) cm^{-1}.

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Nuclear Magnetic Resonance Study of Aminoboranes and Related Nitrogen–Boron Compounds

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Proton and boron magnetic resonance spectroscopy has been applied to the study of a number of aminoboranes in which restriction of rotation about the nitrogen–boron bond is expected to be present. The magnetic anisotropy of the cyclopropyl and vinyl groups has been shown to lead to differential shielding of vicinal substituents when restriction is present. In a number of B-vinyl compounds, the results can be explained by conjugation and restricted rotation about both the N–B and the B–C_{vinyl} bonds with only one isomer present. In (cyclopropylamino)dimethylborane and in (methylphenylamino)phenylvinylborane, but not in the other B-vinyl compounds, the nonequivalence of the methyl substituents could be removed either by raising the temperature or by using dimethyl sulfoxide as the solvent. The lack of temperature and solvent effects indicates an increased barrier to rotation about the N–B bond contributed by the vinyl substituent. In a number of aminoboranes and related nitrogen–boron compounds, the ^{11}B chemical shifts can be described fairly well in terms of a set of additive substituent contributions. These contributions depend on the mesomeric effect of the substituent rather than on its electronegativity. Steric effects seem to be important insofar as they influence the amount of double-bond character between the boron and the substituents.

Introduction

Restricted rotation about the nitrogen–boron bond in several aminoboranes, resulting from partial double-bond character, was demonstrated previously by nuclear magnetic resonance spectroscopy with a barrier to rotation about the N–B bond of 10–20 kcal/mol. For example, the spectrum of (methylphenylamino)-dimethylborane at room temperature shows two B-methyl peaks, which correspond to the differently shielded boron methyls *cis* and *trans* to the anisotropic