of material whose ir and mass spectra were suggestive of μ-[(CH$_3$)$_2$SiH]C$_2$B$_4$H$_7$ although definitive characterization was not possible due to the extremely small quantity obtained. The material passing through the –23° trap was (CH$_3$)$_2$SiCl$_2$, in a quantity approximately equal to the starting amount, and solvent.

Reaction of Na$^+$C$_2$B$_4$H$_7^-$ with CH$_3$SiHCl$_2$. Methyldichlorosilane (3.0 mmol) was condensed at –196° into a reactor containing 7.0 mmol of Na$^+$C$_2$B$_4$H$_7^-$ in THF. The flask was warmed to room temperature, at which point a white precipitate immediately formed. After 0.5 hr the volatiles were fractionated to give a clear liquid (~2 mmol) which passed a –23° trap but was retained at –45°. This material exhibits a vapor pressure of 7.0 Torr at 23° and was characterized as μ-[CH$_3$SiH$_2$]C$_2$B$_4$H$_7$ from its ^{11}B and ^{1}H nmr, ir, and mass spectra. The mass spectrum contains a cutoff at *m/e* 122 corresponding to the ^{30}Si^{12}C$_3$^{11}B$_4$^{1}H$_{12}$$^+$ parent ion and a profile compatible with an SiB$_4$ species. The ir B–H stretching band near 2600 cm^{-1} is split, characteristic of bridge-substituted species (see above), and Si–H (2158 cm^{-1}) and cage C–H (3040 cm^{-1}) bands are also present (Table III). The bridged structure is also supported by the ^{11}B nmr spectrum (Table I) which contains only doublets, arising from terminal B–H groups, and by the ^{1}H nmr spectrum (Table II).

Reaction of Na$^+$C$_2$B$_4$H$_7^-$ with (CH$_2$)$_4$SiCl$_2$. Cyclotetramethylenedichlorosilane (3.24 mmol, 0.501 g) was condensed into a reactor containing 6.65 mmol of Na$^+$C$_2$B$_4$H$_7^-$ in THF at –196°. The reactor was warmed to 23° and maintained at that temperature for 16 hr, during which a white precipitate gradually formed. Fractionation of the volatiles through a trap at –23° gave ~2 mmol of a clear viscous liquid product having a vapor pressure of <1 Torr at 23°, which was purified by distillation *in vacuo* with mild heating. The material was characterized as μ-[(CH$_2$)$_4$SiCl]C$_2$B$_4$H$_7$ from its mass spectrum, which contains a cutoff at *m/e* 198 corresponding to the ^{30}Si^{37}Cl^{12}C$_6$^{11}B$_4$^{1}H$_{15}$$^+$ parent ion and a profile in close agreement with the calculated intensities. The ^{11}B and ^{1}H nmr spectra (Tables I and II) exhibit the usual features for a bridged C$_2$B$_4$H$_8$ derivative (see above) but the ^{1}H nmr spectrum also contains separate methylene peaks corresponding to the two types of CH$_2$ group in the organic ring (Table II). Again, the split B–H ir stretching band (~2600 cm^{-1}) is characteristic of a bridge-substituted derivative. No significant ir bands appear in the Si–H stretching region (Table III).

Thermolysis of μ-[(CH$_2$)$_4$SiCl]C$_2$B$_4$H$_7$. A sample of ~1.0 mmol of the carborane was sealed into a 5-mm Pyrex nmr tube and heated at 220° with periodic monitoring of the ^{11}B nmr spectrum. After 2.5 hr the essentially quantitative conversion to 4-[(CH$_2$)$_4$SiCl]-C$_2$B$_4$H$_7$ was evident from the nmr spectrum (Table I), which is very similar to that of other B(4)-substituted C$_2$B$_4$H$_8$ derivatives (see above and earlier references[2,7]). The ^{1}H nmr (Table II) and infrared spectra (Table III) further support the assigned structure.

Reaction of Na$^+$C$_2$B$_4$H$_7^-$ with GeH$_2$Cl$_2$. A solution of Na$^+$C$_2$B$_4$H$_7^-$ (7.0 mmol in THF) was filtered into an evacuated Pyrex reactor and cooled to –196°. Dichlorogermane (3.5 mmol) was condensed into the reactor, which was then warmed to –30°. At this temperature the solution quickly became dark red. After 0.5 hr at –30° the volatiles were fractionated through a series of traps at –23, –45, –63, and –196°, but no products other than solvent and a trace of C$_2$B$_4$H$_8$ were detected. The nonvolatile material remaining in the reactor was reddish black and crystalline in appearance, apparently air stable, and insoluble in CCl$_4$, hexane, methanol, and water. The infrared spectrum contains a B–H band but no Ge–H absorption, and the broad, poorly resolved peaks are suggestive of a polymeric structure.

Registry No. Silane, 7803-62-5; chloromethane, 74-87-3; trimethylbromostannane, 1066-44-0; trimethylchlorosilane, 1066-45-1; trimethylchlorogermane, 1529-47-1; dimethyldichlorosilane, 75-78-5; tetrachlorogermane, 10038-98-9; cyclotetramethylenedichlorosilane, 2406-33-9; methyldichlorosilane, 75-54-7; dichlorosilane, 4109-96-0; dichlorogermane, 15230-48-5; trimethyllead chloride, 1520-78-1; [Na$^+$C$_2$B$_4$H$_7^-$], 38117-50-9; [μ-(CH$_3$)$_3$SnC$_2$B$_4$H$_7$, 38117-56-5; μ-(CH$_3$)$_3$PbC$_2$B$_4$H$_7$, 38117-57-6; C$_2$B$_4$H$_7$D, 38118-31-9; μ-4-[(CH$_3$)$_3$Si]$_2$C$_2$B$_4$H$_6$, 38117-58-7; μ-D,4-(CH$_3$)$_3$SiC$_2$B$_4$H$_6$, 38194-33-1; (C$_2$B$_4$H$_6$)$_2$GeSi$_2$(CH$_3$)$_8$, 37239-40-0; μ,μ'-SiH$_2$(C$_2$B$_4$H$_7$)$_2$, 38117-59-8; μ-[(CH$_3$)$_2$SiH]C$_2$B$_4$H$_7$, 38117-60-1; μ-[CH$_3$SiH$_2$]C$_2$B$_4$H$_7$, 38117-61-2; μ-[(CH$_2$)$_4$SiCl]C$_2$B$_4$H$_7$, 38117-62-3; 4,4′-SiH$_2$(C$_2$B$_4$H$_7$)$_2$, 37889-52-4.

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Contribution from the Department of Chemistry,
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Identification of an Unstable Nonaborane (B$_9$H$_{13}$) in the Gas Phase

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Received November 20, 1972

A nonaborane, B$_9$H$_{13}$, is shown to be formed as a transient intermediate in the pyrolysis of B$_9$H$_{13}$L compounds in reactors directly coupled to a mass spectrometer. Identification is based upon the temperature dependence, time dependence, and ligand dependence of the mass spectra. Low-voltage spectra and exact mass measurements were used to support the identification. The reaction of B$_9$H$_{13}$ with B$_9$H$_{13}$L to yield B$_{18}$H$_{20}$L, the reaction of B$_9$H$_{13}$ with H$_2$ to yield B$_9$H$_{15}$, and the reaction of the pyrolysis products of B$_9$H$_{13}$S(CH$_3$)$_2$ with various boranes to yield an unusual product are reported.

The chemistry of compounds containing boron is marked by numerous examples of the importance of the Lewis acid-base concept.[2] This is particularly evident in the formal systemization of the reactions of the boron hydrides.[3] Although it is expected that intermediates produced in the reactions of boron hydrides will conform to the already established principles of the field, the identification and characterization of these unstable species can be very helpful in further developing our understanding of the reactivity of the parent compounds. Indeed, many times the progress in understanding reaction mechanisms is coupled to the progress in characterization of the important reaction intermediates.

In borane chemistry the problem of intermediates and mechanism is compounded by the reactivity of the molecular

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(1) Abstracted from the Ph.D. thesis of L. C. Ardini, University of Notre Dame, 1972. Presented in part at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971; see Abstracts, No. INOR 1.

(2) (a) A. Stock "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933; (b) R. M. Adams, Ed., "Metallo-Boron Compounds and Boranes," Interscience, New York, N. Y., 1964; (c) R. J. Brotherton and H. Steinberg, Ed., "Progress in Boron Chemistry," Vol. 1-3, Pergamon, New York, N. Y., 1970; (d) E. L. Muetterties, Ed., "The Chemistry of Boron and Its Compounds," Wiley, New York, N. Y., 1967; (e) R. L. Hughes, I. C. Smith, and E. W. Lawless, "Production of the Boranes and Related Research," Academic Press, New York, N. Y., 1967; (f) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963.

(3) R. W. Parry and L. J. Edwards, *J. Amer. Chem. Soc.*, 81, 3554 (1959).

reactants and products themselves. Thus, although a considerable amount of work designed to elucidate the identities and characteristics of these intermediates has already been published,[4] it is only by the utilization of a variety of complementary techniques that one will be able to develop a precise concept of reactivity in these systems. Relatively recently, research carried out in several laboratories has demonstrated that transient boron hydride intermediates may be directly observed in the gas phase, *e.g.*, BH_3,[5] B_4H_8,[6] B_3H_7,[7] and a triborane.[8] In a continuation of this type of approach we now report experiments concerned with investigating the existence and properties of B_9H_{13} in the gas phase. This is an intermediate for which some evidence has already been presented by others.[9-14] The results of this investigation are reported below in two related parts: the identification of the B_9H_{13} species in the gas phase and the attempted characterization of its reactivity. The former is more definitive than the latter by virtue of the nature of the question asked.

Experimental Section

The pyrolyses of $B_9H_{13}L$ compounds were investigated in two basic reactor types which are described below.

Integral Reactors. These reactors were directly coupled to the source region of an Associated Electrical Industries MS 902 high-resolution mass spectrometer. The cylindrical reactors were constructed of quartz and are illustrated in Figure 1. The smallest reactor was the commercial solid-sample probe which was heated *via* conduction from the source block. The other reactors were mounted as shown in Figure 2 and were heated independently of the source block by noninductively wound chromel wire heating coils imbedded in ceramic cement. In the former case, only the temperature of the source block itself was measured while in the latter case temperatures of the reactor walls were measured with 0.005-in. Pt–Pt–10% Rh thermocouples. The temperature measurements are only approximate and no attempt was made to assess the absolute error. The average residence time for a molecule in the gaseous state in each reactor was calculated assuming molecular flow,[15] and the times are listed in the caption of Figure 1. In the case of the standard solid-sample probe, the average residence time is ill defined and, in any case, is less than the residence time in the ion source itself. In this case the latter residence time, *ca.* 0.3 msec, was used. These times were only used in a qualitative sense and should not be construed as absolute measures of reaction time.

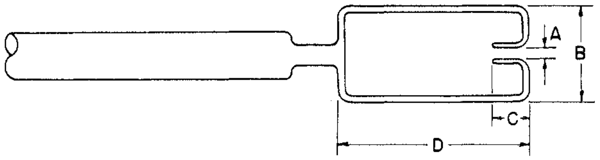

Figure 1. Cylindrical quartz reactors used in the pyrolysis of the $B_9H_{13}L$ compounds. Reactors with the following dimensions (in mm) and average residence times (in msec) were used: (1) $A = 1.7$, $B = 1.2$, $C = 0$, $D = 3.0$, $t = 0.09$ (see text); (2) $A = 1.2$, $B = 6.5$, $C = 4.0$, $D = 9.0$, $t = 1.0$; (3) $A = 1.2$, $B = 9.5$, $C = 4.8$, $D = 21$, $t = 4.2$; (4) $A = 1.1$, $B = 10.4$, $C = 9.8$, $D = 20$, $t = 11.8$. Reactor 1 is the standard solid-sample probe.

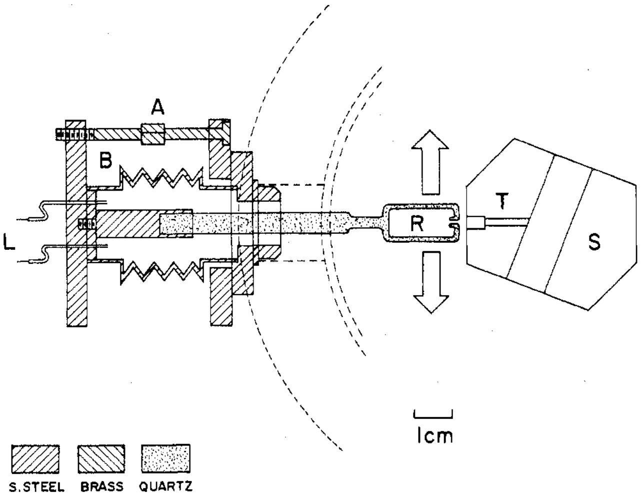

Figure 2. Scale drawing of the adapter used to mount the reactors on the MS 902 mass spectrometer. A is one of three adjusting screws and B denotes stainless steel bellows. L refers to the heater and thermocouple lead-throughs. The wires are insulated with small Teflon tubing and cemented into small holes with low vapor pressure epoxy cement. R refers to the reactors described in Figure 1 and S is the source block of the MS 902 mass spectrometer. T is a preexisting cylindrical hole in the source block whose axis crosses the electron beam.

This apparatus was designed to obtain the most direct sampling of the reactors possible while utilizing the existing vacuum envelope of the MS 902 mass spectrometer. Although rapid and continuous, the sampling conditions by no means approach those of molecular-beam sampling.[16] This is illustrated by the observation of little change in the sample ion intensity as the reactor was mechanically scanned past the round entrance hole in the ion source block (Figure 2). Thus, the species that leave the reactors are randomized in the source region before being pumped away and the ion signals observed result from these randomized species. This does not necessarily mean that the observed products were produced by pyrolysis on the metal surfaces of the source. In, fact, we have good reason to believe that such pyrolysis does not occur. With the individually heated reactors, two sources were used: one uncooled and one water cooled. There is a 50–60° difference in the normal operating temperature of the two ion sources; however, the results were essentially independent of ion source. Of course, with the solid probe, the relative residence times in the probe and ion source indicate that pyrolysis of molecules in the gaseous state would take place in the source itself. In spite of this, the results from the solid-sample probe are consistent and continuous with those from the other reactors. Therefore, it does not appear that any special catalytic source processes are involved in the production of the products upon which the major conclusions of this study are based.

For each experiment the reactors were loaded with 2–4 mg of $B_9H_{13}L$, mounted on the source and pumped on for *ca.* 1.5 hr. The base pressure in the source region was 5×10^{-7} Torr while in the analyzer region it was 5×10^{-8} Torr. After sufficient time for temperature equilibration, the mass spectrum was recorded for each reactor temperature. The oscilloscope was used as a continuous monitor at 10 times higher sensitivity. None of the $B_9H_{13}L$ compounds were completely volatile and in all reactors a tarry yellowish residue remained after pyrolysis.

The exact mass measurements were made utilizing the peak matching unit of the MS 902. Resolution (5% valley) was adjusted to *ca.* 7000 and the reference peaks used were from perfluorotributylamine and from tris(pentafluoroethyl)-*s*-triazine. The instrument was calibrated on N_2^+ and O_2^+. Appearance potential measure-

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(4) See for example A. D. Norman and R. Schaeffer, *J. Amer. Chem. Soc.*, 88, 1143 (1966), and similar work quoted in ref 2.

(5) (a) T. P. Fehlner and W. S. Koski, *J. Amer. Chem. Soc.*, 87, 409 (1965); (b) A. B. Baylis, G. A. Pressley, Jr., and F. E. Stafford, *ibid.*, 88, 2428 (1966); (c) J. H. Wilson and H. A. McGee, Jr., *J. Chem. Phys.*, 46, 1444 (1967); (d) P. S. Ganguli and H. A. McGee, Jr., *ibid.*, 50, 4658 (1969); (e) T. P. Fehlner and G. W. Mappes, *J. Phys. Chem.*, 73, 873 (1969); (f) S. J. Steck, G. A. Pressley, Jr., and F. E. Stafford, *ibid.*, 73, 1000 (1969); O. Herstad, G. A. Pressley, Jr., and F. E. Stafford, *ibid.*, 74, 874 (1970).

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ments were carried out in the usual fashion[17] using a digital voltmeter to measure the relative electron energy. Xenon was used to calibrate the voltage scale. The 30-eV spectrum was used as a monitor of gross changes in the sample level during the course of the measurements.

Hot-Cold Reactor. Larger scale pyrolyses were carried out in a hot-cold reactor.[18] In this reactor species that are volatile at the temperature of the hot surface but nonvolatile at the temperature of the cold surface rapidly condense on the latter surface after formation. Such a reactor is most useful in preparing higher molecular weight products from lower ones. The reactor used in these studies was similar to one described previously[19] with a distance of 1 cm between the inner cold surface (−78 or −40°) and the outer hot surface (100–190°). $B_9H_{13}S(CH_3)_2$ was placed in the bottom of the reactor as a powder. The second reagent was either mixed with the $B_9H_{13}S(CH_3)_2$ if it was solid or condensed in the reactor with liquid nitrogen. Hydrogen was simply expanded into the reactor. Reactions were run for 2–4 hr after which noncondensables were stripped off using liquid nitrogen. The cold finger was then allowed to warm slowly to room temperature with pumping, and volatiles were collected as they came off. Products were refractionated in the vacuum system and analyzed mass spectrometrically. In the case of the reaction with H_2, one product fractionation was carried out using the mass spectrometer for a detector of the various fractions. Standard vacuum-line techniques were used throughout.[20] All stopcocks were of the Delmar type.

Chemicals. The original samples of *i*- and *n*-$B_{18}H_{22}$ and samples of $B_9H_{13}L$ ($L = P(C_6H_5)_3$, $S(CH_3)_2$, $S(C_2H_5)_2$, C_5H_5N, $C_6H_5NH_2$, *p*-$CH_3C_6H_4NH_2$) were gifts of Drs. S. Hermanek, J. Plesek, and B. Stibr of the Institute of Inorganic Syntheses, Rez near Prague, Czechoslovakia. Subsequent samples of $B_9H_{13}S(CH_3)_2$, $B_9H_{13}C_5H_5N$, and $B_{18}H_{22}$ were prepared in this laboratory using the techniques of Hermanek and coworkers.[21] The decaborane(14) (Alfa Inorganics), the pentaborane(9) (Callery Chemical Co.), and the dimethyl sulfide (Aldrich Chemical Co.) were used without further purification. Ultrahigh-purity grade hydrogen (Matheson) was also used without purification. Diborane and F_3PBH_3 were prepared by the methods of Jeffers[22] and Parry and Bissot,[23] respectively.

Pyrolysis of $B_{19}H_{13}L$

Overview. The initial experiments consisted of a survey of the mass spectrometric behavior of the $B_9H_{13}L$ compounds available to us. The mass spectra, taken at the lowest possible temperatures, can be crudely classified into two groups: (I) those that showed considerable fragmentation to B_9 ions ($L = S(CH_3)_2$, $S(C_2H_5)_2$) and (II) those that did not (L = pyridine, aniline, *p*-toluidine). Typical spectra are shown in Figure 3. The former compounds were effective sources of B_9H_{13} whereas the latter compounds were not. Consequently, this report concentrates on the behavior of the sulfide ligand compounds and the details of the work on the other compounds may be found elsewhere.[24]

The second preliminary experiment consisted of examining the mass spectrum as a function of temperature in reactor 1. Typical results at elevated temperatures are shown in Figure 4 for $B_9H_{13}S(C_2H_5)_2$. The behavior of the parent ion region (*m/e* 188–202) with temperature is that expected for a species undergoing decomposition. In addition the production of known boron hydrides is evidenced by the appearance of their known spectra. This is illustrated by $B_{18}H_{22}$ (*m/e* 202–220) in Figure 4. The major pyrolysis products of the class I ligand compounds are $B_{18}H_{22}$, B_8H_{12}, B_6H_{10}, and small amounts of $B_{10}H_{14}$ in qualitative agreement with previous work.[11,25] Once again the production of these species, although of interest, was not the primary objective of this work and the details and interpretation may be found elsewhere.[24] The feature of greatest interest in Figure 4 is the definite increase in the intensity of the B_9 ions (*m/e* 99–112) relative to the parent ion region. The remainder of this section is focused on the identification of the origin of these ions.

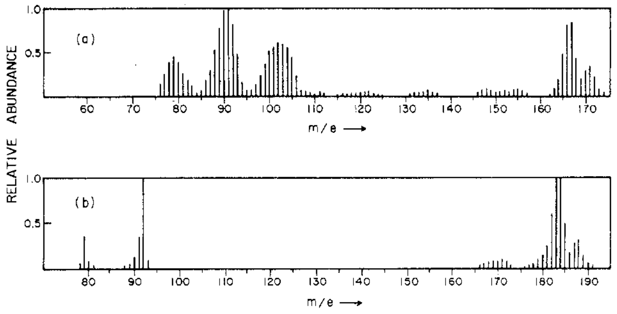

Figure 3. Partial spectra of (a) $B_9H_{13}S(CH_3)_2$ and (b) $B_9H_{13}C_5H_5N$ at 70 eV and in reactor 1 at temperatures of 55 and 100°, respectively.

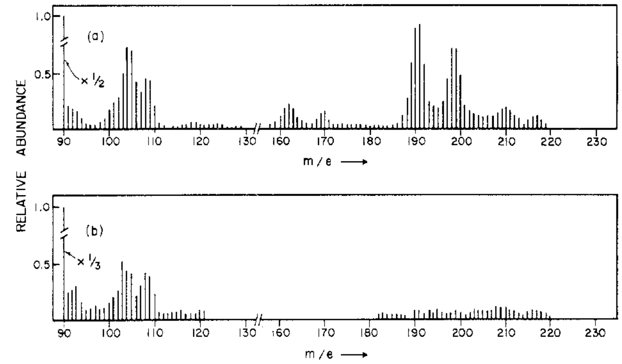

Figure 4. Partial mass spectra of $B_9H_{13}S(C_2H_5)_2$ at 30 eV and temperatures of (a) 135° and (b) 155° in reactor 1.

Identification of an Unstable Nonaborane. A more quantitative observation of the variation in the relative intensity of the B_9 region with temperature for a class I ligand compound is shown in Figure 5 where it is compared to the typically different behavior of a class II compound. The dramatic increase in the relative intensity for the class I compound at *ca.* 155° is caused by a sudden decrease in the parent ion intensity rather than a large increase in the B_9 region. Not only is there a change in the relative intensity of the B_9 ions but the intensity distribution of the B_9 region undergoes a distinct change as illustrated in Figure 6. This change is marked by a shift in intensity from the *m/e* 99–106 region to the *m/e* 106–112 region as would be expected if a hydride containing nine borons were being produced. This behavior is not consistent with assigning the increase in the relative intensity of the B_9 region to temperature-dependent fragmentation of the parent species. Also this increased relative intensity cannot be accounted for by ion fragmentation of any known higher hydrides present. Thus, the temperature dependence of the mass spectra is consistent with the formation of a nonaborane.

The variation of the relative abundances of product ion intensities as a function of average gas-phase residence time in the reactors is illustrated in Figure 7 for compounds typi-

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(17) R. W. Kiser, "Introduction to Mass Spectrometry and Its Applications," Prentice-Hall, Englewood Cliffs, N. J., 1965.

(18) M. J. Klein, B. C. Harrison, and I. J. Solomon, *J. Amer. Chem. Soc.*, **80**, 4149 (1958).

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(23) R. W. Parry and T. C. Bissot, *J. Amer. Chem. Soc.*, **78**, 1524 (1956).

(24) L. C. Ardini, Ph.D. Thesis, University of Notre Dame, 1972.

(25) There is, however, some disagreement in the interpretation of how these products arise. For example, this work shows that the production of B_8H_{12} is not coupled to the formation of $B_{10}H_{14}$ as required by the mechanism of ref 18. See L. C. Ardini, Ph.D. Thesis, University of Notre Dame, 1972.

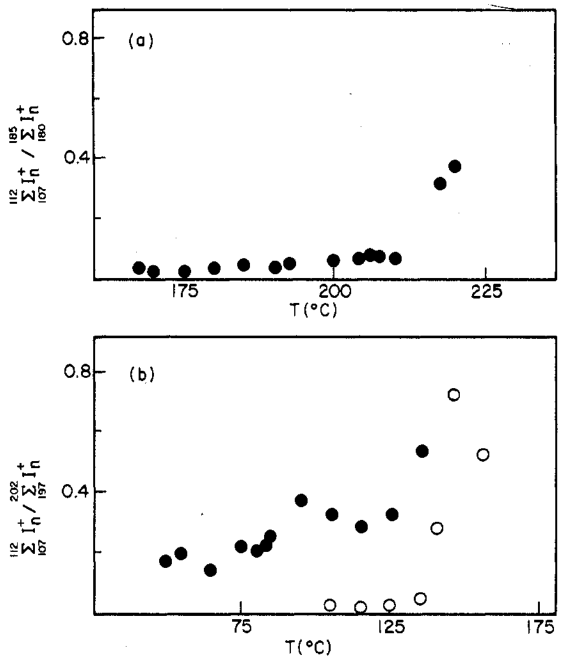

Figure 5. Variation of the sum of ion intensities in the B_9 region relative to the sum of ion intensities in the parent region *vs.* reactor temperature. Curve (a) is for L = C_5H_5N and curve (b) is for L = $S(C_2H_5)_2$. The *y* coordinates of the open circles in (b) are multiplied by a factor of 0.1. Reactor 1 (Figure 1) was used.

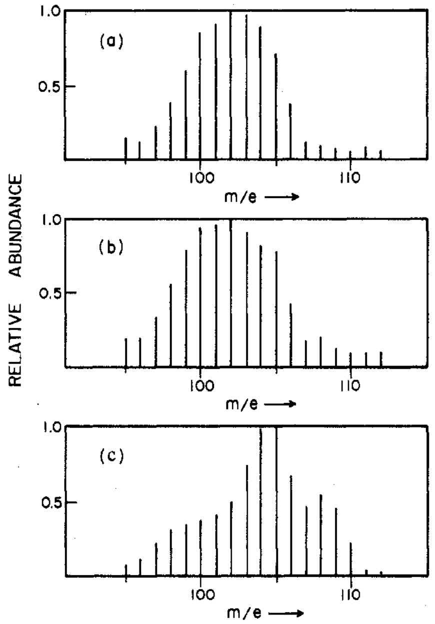

Figure 6. Mass spectra of the nonaborane region for $B_9H_{13}S(CH_3)_2$ at temperatures of (a) 55°, (b) 100°, and (c) 195° in reactor 1. Ion intensities are normalized to the most intense peak in the *m/e* 100–112 region.

cal of class I compounds. For class II compounds, the time variations in the B_9 region was that expected of fragment ions. The intensities of ions characteristic of known hydrides that are stable at these temperatures and reaction times increase with increasing time as expected for reaction products. The behavior of ions in the region *m/e* 106-112 is considerably different for class I compounds. The relative intensities of these ions decrease sharply with increasing reaction time. Again, this behavior is consistent with the production of an unstable nonaborane in the pyrolysis of class I compounds.

The variation in the production of the B_9 hydride with the nature of the ligand L is consistent with the solution chemistry of these compounds[21] and with the initial decomposition reaction being

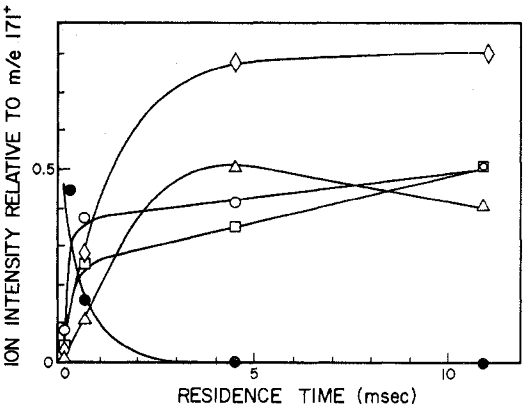

Figure 7. Plot of the relative intensities of selected ions as a function of reactor residence time for the pyrolysis of $B_9H_{13}S(CH_3)_2$ at a reactor temperature of 75–85°. The symbols are as follows: ●, I_{110^+}/I_{171^+}; ○, I_{210^+}/I_{171^+}; □, I_{116^+}/I_{171^+}; △, $(I_{71^+}/I_{171^+}) \times 0.1$; ◇, $(I_{96^+}/I_{171^+}) \times 0.1$; characteristic of B_9H_{13}, $B_{18}H_{22}$, $B_{10}H_{14}$, B_6H_{10}, and B_8H_{12} respectively. The solid curve for I_{110^+}/I_{171^+} represents an exponential decay with a half-life of 0.5 msec.

$$B_9H_{13}L \rightarrow B_9H_{13} + L \qquad (1)$$

Maximum amounts of the B_9 hydride were produced from $B_9H_{13}S(CH_3)_2$ and $B_9H_{13}S(C_2H_5)_2$; no evidence was found for the production of the nonaborane from $B_9H_{13}C_5H_5N$ or $B_9H_{13}(p\text{-}CH_3C_6H_4NH_2)$ and some evidence, *i.e.*, production of $B_{18}H_{22}$ and characteristic ion intensity changes in the B_9 region, was found for the production of very small quantities of the nonaborane from $B_9H_{13}C_6H_5NH_2$. However, it is evident from the time and temperature behavior of the product abundances and the formation of significant amounts of nonvolatile material that decomposition paths other than that represented by reaction 1 are available. For relatively weakly bound ligands it appears that reaction 1 competes favorably with the other undefined pathways while for more strongly bound ligands it does not. It must be noted, however, that none of these compounds is a particularly clean source of the nonaborane.except at very short residence times.

Some ancillary evidence for the production of a discrete nonaborane results from two added observations. The appearance of doubly charged ions in the B_9^{2+} region was observed to accompany the increase in the relative intensity of the B_9^+ ions with temperature. Such doubly charged ions provide support for the view that the latter ions result from ionization of a nonaborane. Finally, the appearance potential of the *m/e* 112 ion was measured as a function of temperature. Although the results were somewhat ambiguous, the ionization efficiency curves in the temperature range where the nonaborane is produced can be interpreted in terms of a superposition of two ionization processes. Presumably one corresponds to the direct ionization of the nonaborane whereas the other corresponds to ion fragmentation of $B_9H_{13}L^+$.

Stoichiometric Identification of the Nonaborane. The mass spectrum of the B_9 region at low electron energy is shown in Figure 8. The high mass cutoff corresponds to $^{11}B_9H_{13}^+$; thus the hydride must contain at least 13 hydrogen atoms. The spectrum also "strips"[26] to yield a monoisotopic spectrum in which the $B_9H_{13}^+$, $B_9H_{11}^+$, and, $B_9H_9^+$ ions are

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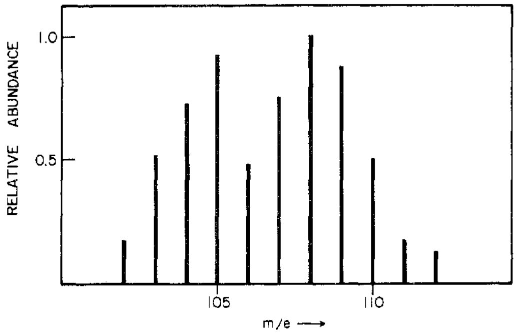

Figure 8. Mass spectrum of the nonaborane region at 12 eV for the pyrolysis of $B_9H_{13}S(C_2H_5)_2$ in reactor 1 at 145°.

most prominent. Once again this is behavior typical of that exhibited by boron hydrides.[26]

The exact mass of the ion at *m/e* 112 was determined and the results are shown in Table I. The conditions of this work prevented the attainment of the accuracy which the instrument is capable of producing; however, the results are good enough to eliminate the possibility of an alkylborane and other less probable impurities. In addition the peak matching capability of the instrument was used to search for the $^{11}B_9H_{14}^+$ ion. None was observed. If the nonaborane observed in this work were n-B_9H_{15}, for example, we should have been able to observe the *m/e* 113 ion reported by Schaeffer, *et al.*[10] Therefore, it is clear that the identity of the unstable boron hydride being produced is B_9H_{13}. Although nonaboranes with lower hydrogen contents, *i.e.*, B_9H_{11}, cannot be excluded on the basis of our evidence, Figure 8 indicates that they cannot be present at levels greater than that of B_9H_{13}.

Partial Characterization of B_9H_{13}

The fact that B_9H_{13} is produced by the thermal decomposition of $B_9H_{13}L$ *via* reaction 1 along with the short half-life of B_9H_{13} at fairly low temperatures (Figure 7) indicates that this species may have some of the characteristics of free borane (BH_3). Thus, the possibility of synthesizing some unusual higher hydrides was explored.

Reactions with $B_9H_{13}L$. The copyrolysis of $B_9H_{13}S(CH_3)_2$ with various $B_9H_{13}L$ compounds was carried out in reactor 1. For $L \neq S(CH_3)_2$, in addition to the normal products noted above, ions corresponding to $B_{18}H_xL^+$ were observed at temperatures between 100 and 170°. These results are summarized in Table II and the relative intensities in the high-mass region for $B_{18}H_xP(C_6H_5)_3^+$ are shown in Figure 9. The observation of the $B_{18}H_xL^+$ ions depended on having sources of both B_9H_{13} and $B_9H_{13}L$ present.

The exact mass of the *m/e* 480 ion peak from $B_{18}H_xP(C_6H_5)_3$ was measured with results as shown in Table III. The results indicate that the peak is probably an unresolved doublet of $^{11}B_{18}{}^{12}C_{18}{}^{31}P^1H_{35}^+$ and $^{11}B_{17}{}^{10}B^{12}C_{17}{}^{13}C^{31}P^1H_{35}^+$. $^{11}B_{17}{}^{10}B^{12}C_{18}{}^{31}P^1H_{36}^+$ is ruled out as there is no corresponding $^{11}B_{18}$ peak and $^{11}B_{18}{}^{12}C_{17}{}^{13}C^{31}P^1H_{34}^+$ is also ruled out because there is little hydrogen fragmentation. Ions corresponding to $^{11}B_{18}H_{22}P(C_6H_5)_3^+$ were sought but not found. The parent ion envelope in the region *m/e* 471-480 corresponds to a $^{10}B/^{11}B$ statistical distribution equal within experimental error to that expected for a very strong $B_{18}H_{20}P(C_6H_5)_3^+$ ion with little hydrogen fragmentation.[26] As all of the ligand compounds we have examined showed observable parent ions and, as the $B_{18}H_{20}P(C_6H_5)_3^+$ ion exhibits little hydrogen fragmentation, the $B_{18}H_xL^+$ ions observed probably arise from the compound $B_{18}H_{20}L$. If so, this constitutes the first observation of a substituted octadecaborane molecule.

Table I. Mass Measurement of *m/e* 112 in the Pyrolysis of $B_9H_{13}S(CH_3)_2$

Ion	Mass	
	Calcd	Calcd – obsd[a]
$^{11}B_9{}^1H_{13}^+$	112.1855	−0.0014
$^{11}B_8{}^{12}C^1H_{12}^+$	112.1683	−0.0186
$^{11}B_8{}^{10}B^1H_{14}^+$	112.1969	0.0100

[a] $^{12}CF_3$ used for peak matching.

Table II. Abundance of the $B_{18}H_xL$ Product in the Copyrolysis of $B_9H_{13}S(CH_3)_2$ with $B_9H_{13}L$

L	$\Sigma B_{18}H_xL^+/\Sigma B_9H_xL^+$	$\Sigma B_{18}H_xL^+/\Sigma B_{18}H_x^+$	T,[a] °C
$S(CH_3)_2$	0[b]	0[b]	
$S(C_2H_5)_2$	0.01	0.02	125
C_5H_5N	0.01	0.004	150
$C_6H_5NH_2$	0.03	0.18	145
p-$CH_3C_6H_4NH_2$	~0.01	*c*	95
$P(C_6H_5)_3$	0.07	0.18	165

[a] Temperature at which $B_{18}H_xL$ first appears. [b] No $B_{18}H_xL^+$ ions observed in the pyrolysis of pure $B_9H_{13}S(CH_3)_2$. [c] Obscured by $B_9H_{13}L$.

Table III. Mass Measurements of *m/e* 480 in the Copyrolysis of $B_9H_{13}S(CH_3)_2$ and $B_9H_{13}P(C_6H_5)_3$

Ion	Mass		
	Calcd	Calcd – obsd[a]	Calcd – obsd[b]
$^{11}B_{18}{}^{12}C_{18}{}^{31}P^1H_{35}^+$	480.4151	−0.0044	−0.0121
$^{11}B_{17}{}^{10}B^{12}C_{18}{}^{31}P^1H_{36}^+$	480.4266	0.0071	−0.0006
$^{11}B_{17}{}^{10}B^{12}C_{17}{}^{13}C^{31}P^1H_{35}^+$	480.4221	0.0026	0.0051
$^{11}B_{18}{}^{12}C_{17}{}^{13}C^{31}P^1H_{34}^+$	480.4107	−0.0088	−0.0165
$^{11}B_{17}{}^{12}C_{18}{}^{13}C^{31}P^1H_{33}^+$	480.3935	−0.0260	−0.0337
$^{11}B_{17}{}^{12}C_{19}{}^{31}P^1H_{34}^+$	480.3980	−0.0215	−0.0292
$^{12}C_9{}^{19}F_{15}{}^{14}N_3^+$	434.9961	0.0077	

[a] $^{12}C_9{}^{19}F_{14}{}^{14}N_3^+$ used for peak matching, calibrated on O_2^+/N_2^+. [b] $^{12}C_9{}^{19}F_{14}{}^{14}N_3^+$ used for peak matching, calibrated on $^{12}C_9{}^{19}F_{15}{}^{14}N_3^+$.

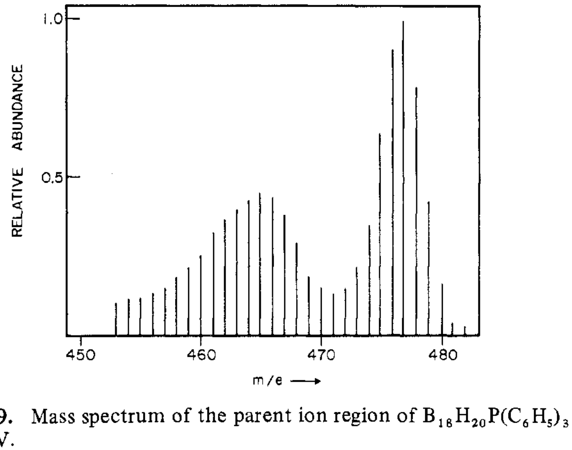

Figure 9. Mass spectrum of the parent ion region of $B_{18}H_{20}P(C_6H_5)_3$ at 70 eV.

We have also considered the possibility that the ions observed result from an ion-molecule reaction such as

$$B_9H_x^+ + B_9H_{13}L \rightarrow B_{18}H_{20}L^+ + (13 + x - 20)H_2 \tag{2}$$

There are two major reasons for ruling out this explanation of the observations. First the $B_{18}H_xL^+$ ions are not observed in the pyrolysis of $B_9H_{13}S(CH_3)_2$ alone even though both $B_9H_x^+$ and $B_9H_{13}S(CH_3)_2$ are present in the ion source. Second, copyrolysis of $B_9H_{13}O(C_4H_9)_2$ with $B_9H_{13}P(C_6H_5)_3$ followed by extraction of the product with diethyl ether and separation of the remaining components by tlc produced a solid[27] which, when mass spectrometrically analyzed in this laboratory, produced $B_{18}H_{20}P(C_6H_5)_3^+$ ions in the absence of any intense $B_9H_x^+$ ions. Clearly in this case the ion-molecule reaction (eq 2) is not possible. Therefore, we conclude that $B_{18}H_{20}L$ is being produced in this system.

Reaction with H_2. As B_9H_{15} apparently yields B_9H_{13} by loss of H_2[9] and as B_4H_8 produced in the thermal decomposition of B_4H_8CO adds H_2 to yield B_4H_{10},[28] we investigated the possibility that B_9H_{13} possessed this type of reactivity. $B_9H_{13}S(CH_3)_2$, *ca.* 1 mmol, was pyrolyzed in the presence of H_2, *ca.* 3 mmol, in the hot-cold reactor. Then the H_2 was removed and the products fractionated. The major volatile products (with the exception of $S(CH_3)_2$) were B_6H_{10}, *ca.* 3 μmol, and B_9H_{15}, *ca.* 1 μmol. If the fractionation procedure was not carefully done, hydrogen was generated and only B_6H_{10} was observed. More precise product analysis resulted from using the mass spectrometer to observe the products as the fractionation proceeded. The products and the temperatures at which they first became evident are as follows: pentaborane, $S(CH_3)_2$, −75°; hexaborane, −72°; nonaborane, −42°; octaborane, −20°; decaborane, −8°. The observation of the last two products seemed to accompany the decomposition of the nonaborane above −28°. The volatility of the nonaborane and the apparent instability coupled with the observed decomposition products correspond more closely to the characteristics of *i*-B_9H_{15} than to those of *n*-B_9H_{15}.[9] The simplest explanation of these results is that reaction 3 takes place. Considering the conditions of

$$B_9H_{13} + H_2 \rightarrow B_9H_{15} \qquad (3)$$

the experiments this must be a very efficient reaction. This is another indication of the very reactive nature of the B_9H_{13} species produced in this work.

Reactions with Other Boranes. One of the characteristic reactions of BH_3 is the addition to stable boranes.[8] Both to characterize further the reactivity of B_9H_{13} and to investigate the possibility of producing some new boranes with more than 10 borons, the copyrolysis of $B_9H_{13}S(CH_3)_2$ with BH_3PF_3, B_2H_6, B_5H_9, and $B_{10}H_{14}$ were carried out. All reactions were run in the hot-cold reactor and a summary of the results is contained in Table IV. All volatile products were formed in low yields but sufficient quantities were produced for their characterization by volatility and mass spectrum. No new higher hydrides were identified as volatile products or were found in the nonvolatile fraction. The possible reasons for this are discussed below.

Table IV. Typical Results of the Copyrolysis of $B_9H_{13}S(CH_3)_2$ with Other Boranes

Borane	Cold bath, °C	Hot bath, °C	Time, hr	Major volatile products[a]
BH_3PF_3	−78	105	5	H_2, PF_3, B_5H_9, B_6H_{10}
B_2H_6	−78	80	1	H_2, B_5H_9, B_8H_{12}
B_5H_9	−40	100	2	H_2, $B_{10}H_{16}$
B_5H_9 + Hg	−40	100	2	H_2
B_5H_9 + $S(CH_3)_2$	−40	100	2	H_2, $BH_3S(CH_3)_2$, $B_{10}H_{12}S(CH_3)_2$, $B_{10}H_{14}$
$B_{10}H_{14}$	25	100	4	H_2, $BH_3S(CH_3)_2$, B_5H_9, B_6H_{10}

[a] At 25°. $B_{18}H_{22}$ was present in the solid remaining in the reactor. All products found were in low yield.

One of the products observed is very interesting even though its origin is baffling. In the copyrolysis of $B_9H_{13}S(CH_3)_2$ with B_5H_9, a borane with the molecular formula $B_{10}H_{16}$ was produced. This species was purified by fractionation. The mass spectrum was similar to that published previously for a $B_{10}H_{16}$.[29] The structure of the $B_{10}H_{16}$ produced in the present work is not known and it may well be one of the isomers of the known $B_{10}H_{16}$.[30-32] The physical properties of the present species (solid at room temperature,[30] passing a −28° slush bath readily,[30] separated from B_5H_9 only with difficulty[33]) indicate that it would be the 1,1′ isomer. On the other hand our $B_{10}H_{16}$ may be the unknown icosahedral borane. The production of this species depended on the presence of both $B_9H_{13}S(CH_3)_2$ and the borane in the reactor. However, neither this product nor the other observed products necessarily result directly or through the intermediacy of B_9H_{13} because the pyrolysis of $B_9H_{13}S(CH_3)_2$ involves more than the simple production of B_9H_{13} (see above). Therefore, these particular experiments do not yield any conclusive information on the reactivity of B_9H_{13}.

This apparent lack of reactivity in terms of addition to boranes need not be conclusive, however. The B_9H_{13} is produced at very low pressures and, in this reactor, must interact with the stable borane in short time. Also the addition product may be unstable or of so low a volatility that it is lost in the solid residue. Finally, the reaction system, by necessity, contains free ligand in substantial amounts. It is known that BH_3 reacts 10^2-10^3 times faster with free ligands than it does with stable hydrides.[34,35] Thus it is possible that in this system only reactions of B_9H_{13} that have rates comparable to reaction 4 will be observed.

$$B_9H_{13} + L \rightarrow B_9H_{13}L \qquad (4)$$

In summary, then, B_9H_{13} exhibits several characteristics of a type that may be associated with a reactive site such as is present in BH_3. It has a very short lifetime. It reacts readily with molecular hydrogen to form B_9H_{15} probably in the iso form. Finally, it reacts with other ligand compounds to yield $B_{18}H_{20}L$.

Registry No. B_9H_{13}, 12008-51-4; $B_9H_{13}S(CH_3)_2$, 32357-02-1; $B_9H_{13}S(C_2H_5)_2$, 32356-99-3; $B_9H_{13}NC_5H_5$, 32357-07-6; $B_9H_{13}NH_2C_6H_5$, 38118-27-3; $B_9H_{13}NH_2C_6H_4CH_3$-*p*, 38118-28-4; $B_9H_{13}P(C_6H_5)_3$, 32235-80-6; $B_{18}H_{20}P(C_6H_5)_3$, 37239-41-1; H_2, 1333-74-0; B_9H_{15}, 19465-30-6; BH_3PF_3, 14931-39-6; B_2H_6, 19287-45-7; B_5H_9, 19624-22-7; $B_{10}H_{14}$, 17702-41-9; $B_{10}H_{16}$, 12430-42-1.

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