exchange resin using acetonitrile as eluent. The acetonitrile was removed in vacuo and the residue sublimed at 40-45°C to obtain 0.76 g (4.3% yield, mp 145-146°C).

The infrared spectrum (KBr phase) includes absorptions at \( \lambda_{\text{max}} \) 2545 (vs), 1570 (m), 1470 (s), 1345 (s), 1375 (m), 1320 (m), 1200 (w), 1260 (w), 1070 (m), 1060 (m), 1010 (s), 990 (s), 970 (s), 930 (m), 905 (m), 810 (m), 780 (m), 755 (m), 725 (s), 700 (m), 675 (s), 640 (w), 440 (m), and 390 (w) cm\(^{-1}\).

The proton nmr spectrum (CDC\(_3\) solution) shows only a broadened resonance at \( \tau \approx 2.4 \) due to the C,H\(_2\) group. The boron nmr spectrum at 70.6 MHz (chloroform) exhibits resonances at \( \gamma(B) \) in parentheses \(-4.4 \) (1 B, 140 Hz), 1.7 (2 B, 170 Hz), 5.6 (2 B, 165 Hz), 14.2 (2 B, 150 Hz), 17.7 (1 B, 155 Hz), and 23.3 ppm (2 B, 150 Hz), externally referenced to BF\(_3\)-O(C\(_2\)H\(_5\)).


The proton nmr spectrum (CH\(_3\)\(_2\)Nbh\(_3\)H\(_3\)) includes absorptions at \( \lambda_{\text{max}} \) 1070 (m), 1060 (m), 1010 (s), 990 (s), 970 (s), 930 (m), 905 (m), 810 (m), 780 (m), 755 (m), 725 (s), 700 (m), 675 (s), 640 (w), 440 (m), and 390 (w) cm\(^{-1}\).

The proton nmr spectrum (CH\(_3\)\(_2\)NB\(_3\)H\(_3\)) includes absorptions at \( \lambda_{\text{max}} \) 3020 (m), 2500 (vs), 1475 (vs), 1440 (m), 1430 (m), 1500 (s), externally referenced to BF\(_3\)-O(C\(_2\)H\(_5\)).

The infrared spectrum of (CH\(_3\)\(_2\))NB\(_3\)H\(_3\)AsCH\(_3\)) indicates absorptions at \( \lambda(B) \) 935 (s), 725 (s), 680 (s), 550 (w), 520 (w), 465 (m), 430 (m), and 415 (m) cm\(^{-1}\).

The proton nmr spectrum of CH\(_3\)\(_2\)NB\(_3\)H\(_3\)AsCH\(_3\)) consists of a very sharp singlet at 6.66 (CH\(_3\)) and a multiplet centered at 2.7 (CH\(_3\)).

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Chemical and Nuclear Magnetic Resonance Studies of the B\(_3\)H\(_{12}^-\) and B\(_3\)H\(_{12}^2\)Ions

A. R. SIEIDLE, G. M. BODNER, A. R. GARBER, and L. J. TODD

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The 70.6-MHz \(^{11}B\) nmr spectra of labeled B\(_3\)H\(_{12}^-\) derivatives indicate that a rearrangement process occurs during the formation of this thiaborane from decaborane(14). Treatment of B\(_3\)H\(_2\)S(C\(_6\)H\(_6\)) or B\(_3\)H\(_6\) with ammonium polysulfide forms B\(_3\)H\(_{12}^-\). Similar rearrangement of labeled molecules is observed in these latter two chemical transformations. A unified mechanism which explains all the observed rearrangement reactions is proposed.

Introduction

Exclusive of the carboranes, the chemistry of nine-atom boranes and heteroatom boranes may be divided into three broad categories: (1) synthesis and reactions of the two neutral, isomeric B\(_3\)H\(_3\) hydrides,\(^7\)\(^8\)(2) reductive reactions of decaborane to form B\(_3\)H\(_{12}^-\)\(^9\) B\(_3\)H\(_{14}^-\), and B\(_3\)H\(_{13}^-\) ligand species.\(^1\)\(^2\)\(^11\) (3) Insertion of heteroatoms into the B\(_3\) framework to form B\(_3\)H\(_{12}^-\)S\(_2\) and B\(_3\)H\(_{12}^-\)NH\(_2\)\(^12\) and metalloboranes such as (R\(_3\)P\(_2\))Pt(B\(_3\)H\(_{12}^-\)ligand)\(^13\) and (CO)\(_3\)Mn[(B\(_3\)H\(_{12}^-\)].\(^14\) We have recently reported specific positional assignments of the \(^{11}B\) nuclear magnetic resonance spectra of complex boron hydride species such as B\(_{10}H\(_{13}^-\), B\(_{10}H\(_{15}^-\),\(^15\) and B\(_{10}H\(_{13}^-\)ligand.\(^16\) This paper reports the results of a 70.6-MHz \(^{11}B\) nmr spectral study of B\(_3\)H\(_{12}^-\), B\(_3\)H\(_{12}^2\), and their labeled derivatives.

Experimental Section

The \(^{11}B\) nmr spectra were measured on equipment consisting of a pulsed nmr apparatus built in this department operating at 70.6 MHz, a Varian 51.7-kG superconducting magnet, and a 20K Nicolet 1080 series computer. Additional details have been reported elsewhere.\(^1\)\(^8\) The \(^{11}B\) nmr spectra were externally referenced to BF\(_3\)-O(C\(_2\)H\(_5\)).


sulfur were removed by filtration through Celite. Concentration of the filtrate under vacuum afforded the product as white crystals. An additional crystallization from aqueous acetonitrile gave 0.12 g (33%) of (C₆H₅)₂NBrB₂H₆S. Anodic oxidation of (C₆H₅)₂NBrB₂H₆S in 45% yield.

Sulfur were removed by filtration through Celite. Concentration of the filtrate under vacuum afforded the product as white crystals. Anodic oxidation of (C₆H₅)₂NBrB₂H₆S in 45% yield.

The product was isolated by filtration, vacuum dried, and stored in the cold under nitrogen. Yields of the (C₆H₅)N⁺[B₂H₆S] and (C₆H₅)₂N⁺ salts were typically 70–80%. The salts contained a trace of an impurity, observed as a shoulder on the +14.4 ppm peak in the ¹¹B nmr. Identification of this feature as due to an impurity is confirmed by its absence in the ¹¹B nmr spectrum of (Ph₃PCH₂)B₂H₆ prepared from B₂H₆·S(C₆H₅)₂ and Ph₃P=CH₂. The infrared spectrum of (C₆H₅)₃N[B₂H₆] (KBr) contained bands at 2990 (w), 2500 (s), 1470 (m), 1410 (m), 990 (w), 945 (m), 880 (w), 787 (w), 680 (w) cm⁻¹. 'H nmr (CD₂CN): in addition to peaks due to the cation, a broad singlet at +1.1 ppm appeared which is assigned to the bridge protons. This procedure was used to convert B₂H₆·S(C₆H₅)₂ to (C₆H₅)₃N⁺[B₂H₆] in 45% yield.

Synthesis of B₂H₆·S(C₆H₅)₂ from (C₆H₅)₂N[B₂H₆H₄]. A stream of dry hydrogen chloride was passed into a suspension of 0.2 g of (C₆H₅)₂N[B₂H₆H₄] in 5 ml of diethyl sulfide. An exothermic reaction occurred and the solid dissolved. The solvent was removed under reduced pressure and the residue extracted with 30 ml of diethyl ether. The extract was filtered and the filtrate evaporated. The residue was crystallized from dichloromethane-hexane to give crystalline B₂D₄H₄·S(C₆H₅)₂.

Results and Discussion

¹¹B Nmr Studies of B₉H₁₂S⁻. Treatment of decaborane with aqueous ammonium polysulfide results in partial degradation of the decaborane framework and sulfur atom insertion by an unknown mechanism to form B₉H₁₂S⁻ in high yield. The ⁷⁰.₆-MHz ¹¹B nmr spectrum of CsB₉H₁₂S in acetonitrile (Figure 1) consists of six resonances of relative areas 1:2:1:1:2:1 reading upfield. The pattern of the nmr spectrum is consistent with the solid-state structure of B₉H₁₂⁻ S⁻ found in an X-ray crystallographic study of (PPh₃)₃Au[B₉H₁₀S] which is shown in Figure 2.¹⁹ The numbering system employed in Figure 2 and for B₉H₁₀S⁻ departs from that used previously¹⁷ and is essentially the same as in decaborane. This allows easy reference to the labeled decaborane derivatives used in this work.

The triplet of unit area at +150.0 ppm (J₁₁B = 110 Hz) can be assigned by inspection to B(9) to which two terminal hydrogens are bonded. Upon irradiation at the bridge proton frequency (+1.85 ppm at 220 MHz), the doublets of relative areas 1:2:1:2:1:2 reading upfield. These two resonances must then be due to B(5,7) and B(8,10) which are directly bonded to the two bridge hydrogens and which would be expected to be weakly spin coupled to these nuclei. The remaining doublet of area 2 at +36.6 ppm must therefore be due to B(1,3).

The ⁷⁰.₆-MHz ¹¹B nmr spectrum of CsB₉D₄H₄S prepared from 1,2,3,4-B₁₀D₁₀H₄ is shown in Figure 3. The doublet resonances at +36.6 and −4.0 ppm in the spectrum of B₉H₁₀S⁻ appear to be almost completely collapsed to singlets in Figure 3. In addition the resonances at +33.4 and +11.3 ppm show partial collapse to singlets and those at +14.9 and +7.9 ppm appear unaffected. Thus, there is some but not complete scrambling of the deuterium label during the formation of B₉D₄H₈S⁻.

The ¹¹B nmr spectrum of CsB₉D₄H₄S prepared from μ₄-S·6,7,8,9,10-B₁₀D₁₀H₄ is shown in Figure 4. Barring rearrangement or H-D exchange, it was anticipated that this spectrum would contain singlets at +7.9 and +33.4 ppm due to B-D groups at B(5,7) and B(8,10) and a singlet at +15 ppm due to a BD₂ group at position B(9). Exchange of terminal hydrogens with the water used for crystallization of the labeled compounds was excluded by the observation that recrystallization of CsB₉H₁₂S from hot D₂O resulted in no incorporation of terminal deuterium by infrared analysis. However, reference to Figure 4 shows that, again, some redistribution of the deuterium label has occurred but that the process is not random. These results may be accounted for by postulating the existence of a boron hydride intermediate prior to sulfur atom insertion which has effective C₃₅ symmetry. Such a tautomerase'ing structure has been postulated for B₉H₁₄⁺ on the basis of its ¹¹B nmr spectrum.²⁰,²¹ The gross geometry of our proposed intermediate is shown in Figure 5. The sets of boron atoms in the B₉ fragment which are equivalently related by the C₃ axis are B(1,3,4), B(5,7,9), and B(2,8,10). Sulfur atom insertion can occur at any of three equivalent points.

located off the mirror plane of symmetry passing through the sulfur, B(2), B(4) and B(9). Sulfur atom insertion into the structure of this compound must await a single-crystal X-ray investigation.

Figure 4. The 70.6-MHz $^1$B nmr spectrum of CsB$_9$D$_4$H$_8$S obtained from $\mu_3$-5,6,7,8,9,10-B$_{10}$H$_{14}$H$_4$.

The spectrum of (C$_2$H$_5$)$_4$N[BrB$_9$H$_{11}$S], prepared from 2-BrB$_9$H$_{13}$, is shown in Figure 7. The singlet of unit area at +1.85 ppm. We therefore conclude that during the formation of B$_3$D$_4$H$_6$S$^-$ in alkaline H$_2$O, H for D exchange of one deuterium atom at B(9) occurred to give a B(D)H unit. The $^{11}$B nmr spectrum of CsB$_9$D$_4$H$_8$S, Figure 3, may also be assigned on the basis of the postulated effective C$_{3v}$ intermediate just described.

The spectrum of (C$_2$H$_5$)$_4$N[BrB$_9$H$_{11}$S], prepared from 2-BrB$_9$H$_{13}$, is shown in Figure 7. The singlet of unit area at +24.6 ppm may be assigned to the bromine-substituted boron atom. However, the presence of eight discernible resonances in this spectrum reveals that the bromine must be located off the mirror plane of symmetry passing through the sulfur, B(2), B(4) and B(9). Sulfur atom insertion into a bromine-containing C$_{3v}$ intermediate would in principle form 1-BrB$_9$H$_{12}$S$^-$ (or the enantiomeric 3-BrB$_9$H$_{12}$S$^-$) and 4-BrB$_9$H$_{12}$S$^-$ in a 2:1 ratio. Careful examination of the reaction products failed to disclose the presence of a second isomer in addition to the isolated isomer which we believe to be 1-BrB$_9$H$_{12}$S$^-$.

Possible Intermediates in the Formation of B$_9$H$_{12}$S$^-$. The labeling experiments described above led to the expectation that B$_9$H$_{12}$S$^-$ which has the required effective C$_{3v}$ symmetry of the postulated intermediate was an intermediate in the formation of B$_9$H$_{12}$S$^-$. This also seemed reasonable since B$_9$H$_{13}$ was formed by degradation of BrB$_9$H$_{14}$ in aqueous alkaline solution.

Other B$_9$ intermediates were then considered which could plausibly form under the reaction conditions, namely, B$_9$H$_{13}$, ligand species and B$_9$H$_{12}$ which is derived from the former by deprotonation and loss of the ligand.

Treatment of either B$_9$H$_{13}$SC$_2$H$_2$ or (CH$_3$)$_3$NB$_9$H$_{12}$ in acetonitrile with aqueous ammonium polysulfide formed B$_9$H$_{12}$S$^-$ in about 45% yield. A similar reaction between 4-BrB$_9$H$_{13}$SC$_2$H$_2$, in which the position of substitution is known from previous nmr studies, formed BrB$_9$H$_{12}$S$^-$ which had a $^{11}$B nmr spectrum identical with the BrB$_9$H$_{12}$S$^-$ derivative synthesized from 2-BrB$_9$H$_{13}$.

Based upon these experiments we suggest that B$_9$H$_{13}$ might be transformed to B$_9$H$_{12}$S$^-$ through a series of reactions like:

- $^+$Br$_4$H$_{14}$ + OH$^-$ → $^+$Br$_8$H$_{12}$ + H$_2$O

and our postulated mechanism (vide supra), we propose that the product of this reaction is 1-BrB$_9$H$_{12}$S$^-$. More definitive evidence concerning the structure of this compound must await a single-crystal X-ray investigation.

Figure 5. The proposed effective C$_{3v}$ intermediate and its relationship to starting material and product.

Figure 6. The 70.6-MHz $^1$B nmr spectrum of CsB$_9$D$_4$H$_8$S obtained from D$_2$O-OD$^-$ exchange of CsB$_9$H$_{14}$S.

Figure 7. The 70.6-MHz $^1$B nmr spectrum of (C$_2$H$_5$)$_4$N[BrB$_9$H$_{11}$S] obtained from 2-BrB$_9$H$_{13}$. 

22) There is also a second possible bromine-containing intermediate which, after sulfur atom insertion would result in the formation of 4-BrB$_9$H$_{12}$SO (or the enantiomeric 2-BrB$_9$H$_{12}$SO) and 2-BrB$_9$H$_{12}$S$^-$. The reasons for rejecting this second possibility are given in the next section (see ref 23).

23) This experimental result strongly suggests that only one of the two possible BrB$_9$ intermediates (see ref 22) is formed in this reaction. Based on the known structure of 4-BrB$_9$H$_{12}$SC$_2$H$_2$, and our postulated mechanism (vide supra), we propose that the product of this reaction is 1-BrB$_9$H$_{12}$S$^-$. More definitive evidence concerning the structure of this compound must await a single-crystal X-ray investigation.
The intermediate \([\text{B}_{10}\text{H}_{13}(\text{S}_{2})]^{2-}\) may be considered as a member of the \(\text{B}_{10}\text{H}_{14}^{2-}\) ligand class of molecules as are the anions \(\text{B}_{10}\text{H}_{14}^{-}\) and \(\text{B}_{10}\text{H}_{13}(\text{CN})^{-}\). The \([\text{B}_{9}\text{H}_{13}(\text{S}_{2})]^{2-}\) intermediate may be viewed as a member of the \(\text{B}_{9}\text{H}_{13}\) ligand class of which \(\text{B}_{9}\text{H}_{13}(\text{SCN})^{-}\) is an example. It is pertinent to note that decaborane in aqueous sodium hydroxide solution at room temperature is relatively stable with regard to further degradation to \(\text{B}_{9}\) species. In contrast, the reaction of decaborane with aqueous polysulfide is quite brisk. This suggests that the polysulfide ion plays an active, nucleophilic role in the degradation process leading to the elision of one boron atom and labilizes the boron framework to further attack.

Previous studies of the \(^{11}\text{B}\) nmr spectra of labeled derivatives of \(\text{B}_{10}\text{H}_{12}^{2-}\) ligand \(^{24}\) and \(\text{B}_{9}\text{H}_{13}\) ligand \(^{17}\) compounds did not reveal any label interchanges or scrambling. We have therefore investigated the \(^{11}\text{B}\) nmr spectra of \(\text{B}_{9}\text{H}_{12}^{-}\) derivatives obtained from labeled \(\text{B}_{9}\text{H}_{13}(\text{SC}_{2}\text{H}_{5})_{2}\) molecules in search of the point where labeled position interchange might occur.

\(^{11}\text{B}\) Nmr Studies of the \(\text{B}_{9}\text{H}_{12}^{-}\) Ion. The \(^{11}\text{B}\) nmr spectrum of \(\text{B}_{9}\text{H}_{12}^{-}\), obtained at an unspecified but low field strength, has been reported previously.\(^{25}\) An ethanol solution of \(\text{B}_{9}\text{H}_{13}\text{S}(\text{C}_{2}\text{H}_{5})_{2}\) was mixed with an aqueous solution of tetraethylammonium hydroxide to form \((\text{C}_{2}\text{H}_{5})_{4}\text{N}\)[\(\text{B}_{9}\text{H}_{12}\)]. The 70.6-MHz \(^{11}\text{B}\) nmr spectrum of this salt is illustrated in Figure 8. The spectrum consists of four doublets at +10.0, +14.4, +34.2, and +52.0 ppm of relative areas 3:3:2:1, respectively. The spectrum of \(\text{B}_{9}\text{D}_{4}\text{H}_{8}\) prepared in the same manner starting from \(1,2,3,4-\text{B}_{10}\text{D}_{4}\text{H}_{10}\) is shown in Figure 9A along with a line-narrowed \(^{26}\) spectrum of the sample (Figure 9B). Comparison of the spectra in Figures 8 and 9 indicates that doublets at +10.0, +14.4, and +52.0 ppm have collapsed to singlets as a result of deuteration. Thus two resonances are observed within each of the two low-field multiplets of area 3. This information suggests that the \(^{11}\text{B}\) nmr spectrum of \(\text{B}_{9}\text{H}_{12}^{-}\) contains at least six doublets in a 1:2:2:1:2:1 ratio reading upfield.\(^{27}\) Attempts to determine the solid-state structure of \(\text{B}_{9}\text{H}_{12}^{-}\) by X-ray methods have been frustrated by disorder problems.\(^{28}\) Based on the crystal structure of \(\text{B}_{9}\text{H}_{13}\text{(CH}_{3}\text{CN})\),\(^{29}\) the facile interconversion of \(\text{B}_{9}\text{H}_{13}\text{S}(\text{C}_{2}\text{H}_{5})_{2}\) and \(\text{B}_{9}\text{H}_{12}^{-}\), and the observed pattern of resonances in the \(^{11}\text{B}\) nmr spectrum of \(\text{B}_{9}\text{H}_{12}^{-}\), it is reasonable to assume that \(\text{B}_{9}\text{H}_{12}^{-}\) has the same overall arrangement of boron atoms as was found in \(\text{B}_{9}\text{H}_{13}\text{(CH}_{3}\text{CN})\). In an earlier study it was observed that \(\text{B}_{9}\text{H}_{12}^{-}\) could be converted back to the \(\text{B}_{9}\text{H}_{13}\text{(Lewis base)}\) derivative with hydrogen chloride and a Lewis base.\(^{10}\) We therefore treated the \((\text{C}_{2}\text{H}_{5})_{4}\text{N}[\text{B}_{9}\text{D}_{4}\text{H}_{8}]\) described above with \(\text{HCl}\) in diethyl sulfide to form \(\text{B}_{9}\text{D}_{4}\text{H}_{9}\text{S}(\text{C}_{2}\text{H}_{5})\). The \(^{11}\text{B}\) nmr spectrum of this product is presented in Figure 10. Comparison of this spectrum with the 80.2-MHz \(^{11}\text{B}\) nmr spectrum of \(\text{B}_{9}\text{H}_{13}\text{S}(\text{C}_{2}\text{H}_{5})_{2}\) published earlier\(^{17}\) also shows that partial interchange of deuterium-labeled positions has occurred.

(27) In Figure 9B, the peak marked with an X is due to an impurity in the sample as was determined by alternate synthesis of the compound. See the Experimental Section.
occurred. The doublet resonances centered at -4 and +39.2 ppm due to B(4) and B(1,3) appear completely collapsed. The resonances at -16.5 and +15 ppm due to B(2) and B(8,10) appear partially collapsed and the other two doublets due to B(5,7) and B(9) are unchanged. These results are consistent with the existence of a C₃ᵥ intermediate which is causing the partial scrambling of the labeled boron atoms.

Treatment of 4-BrB₉H₁₂S(C₂H₅)₂ with aqueous ethanolic tetraethylammonium hydroxide at room temperature produced (C₂H₅)₄N[BrB₉H₁₁] and the ¹¹B nmr spectrum of this product is presented in Figure 11. The appearance of at least seven resonances in this spectrum suggests that the bromine atom in the product is located at a position which is not on the mirror plane passing through B(2), B(4), and B(9). Therefore rearrangement of the bromine label (possibly as shown in Figure 12) has occurred in this case also.

While these observations do not serve as proof concerning our proposed mechanism for the formation of B₉H₁₂S⁺ from decaborane, the generation of similarly "rearranged" labeled molecules in these transformations strongly suggests the existence of a common reaction intermediate with effective C₃ᵥ symmetry (possibly a B₉H₄⁺ species) in these processes. Further studies concerning the mechanism of formation of B₉H₁₂S⁺ are in progress.

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Registry No. (C₂H₅)₄N[B₉BrH₁₁], S(C₂H₅)₁₁, 51292-99-0; B₉BrH₁₁, S(C₂H₅)₁₁, 51292-00-6; (C₂H₅)₄N[B₉BrH₁₁], S, 51293-01-7; C₂H₅B₉H₁₁, S, 51358-27-1; (C₂H₅)₄N[B₉H₁₁], 51644-40-5; (C₂H₅)₄N[BrB₉H₁₁], 51666-81-0; ¹¹B, 14798-13-1.

Contribution from the Department of Chemistry, Tufts University, Medford, Massachusetts 02155

Some By-Products of the Oxidative Coupling of Decahydrodecaborate(2⁻), B₁₀H₁₀(₂⁻)

Z. B. CURTIS, C. YOUNG, R. DICKERSON, KWAN K. LAI, and A. KACZMARCZYK

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The involvement of ions other than the primary oxidizing agents in the oxidation of B₉H₁₂⁺ produces a variety of substituted species in addition to B₉H₁₂⁺ and B₉H₁₂⁺. Fe(NO₃)₃ yields B₉H₁₂NO⁻; FeCl₃ yields 1,6,8-B₉H₃Cl₃⁻ and 1,6- (or 2,4)-B₉H₃Cl₂⁻; KClO₃ yields B₉H₃Cl⁺ and a free radical. The effects of temperature, reagent concentration, solvent, acidity, and reaction time on the yields of the principal by-products were explored.

Introduction

Over the years, we and other researchers investigating the oxidative coupling of B₁₀H₁₀²⁻ have observed extraneous bands in the infrared spectra of the expected products, blue and purple colors, and other evidence of side reactions. Wiesboeck assumed that the blue color produced by Fe(NO₃)₃ is due to the same nitroso derivative as the one made with gaseous oxides of nitrogen. He did not isolate the colored material, and the blue color produced by Fe(NO₃)₃ is due to the same region of the visible spectrum, as we decided to isolate and characterize the colored species in our reactions. In one system the colored species turned out to be the B₉H₁₀H₂O⁻⁻ ion, in another it was a free radical. The extraneous infrared bands were found to belong to partially halogenated decahydrodecaborates. Since the published halogenation methods are unsuitable for the synthesis of specific ions having fewer than eight chlorines, due to the very rapid substitution rate, it seemed worthwhile to explore conditions under which the yield of such chlorinated species is optimized. Moreover, as the molecular structure of one of our products (B₁₀H₃Cl₂⁻) had already been determined by X-ray crystallography, it seemed only proper that the synthesis be published too.

Experimental Part

Reagents and Techniques. Salts of B₉H₁₂⁺ were prepared in this laboratory from decaborane; all other chemicals were reagent grade. The infrared spectra of samples pressed into KBr pellets were recorded on a Perkin-Elmer Model 337 spectrophotometer. The visible spectra were recorded on a Cary 14 spectrophotometer. The ¹¹B nmr spectra were obtained at a frequency of 19.25 MHz on a Varian DA-60 spectrometer. Samples were considered free of B₉H₁₂⁺ when the uv spectrum showed no traces of the intense bands at 2320 and 2930 A and free of B₉H₁₂⁺ in the absence of the hydrogen-bridge ir band at 1870 cm⁻¹. Overall purity was also ascertained with the aid of tlc. For the halogenated species the best results were obtained on basic alumina with diisobutylene-2-propanol-water (5:4:1) or acetone-acetone-water (2:1) as eluents.

B₉H₁₆NO⁻⁻. Procedure A. To solutions of (Et,N)₂[B₉H₁₆] in 15 ml of water weighed samples of Fe(NO₃)₃·9H₂O (uncrushed lumps) were added without stirring and the mixtures were left standing at room temperature. Filtration removed a purple solid which was washed with four 25-ml aliquots of water and dried for 24 hr over P₂O₅. The dry solid was washed repeatedly with dry acetonitrile-tritton-water (5:4:1) or acetone-acetone-water (2:1) mixture.

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