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Polydeltahedral Thiaboranes

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Pyrolysis of the *nido*-thiaboranes 6-SB_9H_{11} and 7-$SB_{10}H_{12}$ gives, in addition to the *closo*-thiaboranes 1-SB_9H_9 and 1-$SB_{11}H_{11}$, respectively, a variety of isomeric polydeltahedral thiaboranes, clusters linked through a B–B two-center bond. 2,2′-, 2,6′-, and 6,6′-(1-SB_9H_8)$_2$ are formed from 6-SB_9H_{11}. Three isomeric forms of (1-SB_9H_8)(1′-$SB_{11}H_{10}$) are obtained from 7-$SB_{10}H_{12}$, the best characterized of which appears to be either the 2,2′ or the 2,7′ isomer. Copyrolysis of 1,7-$C_2B_{10}H_{12}$ and 6-SB_9H_{11} gives three isomers of (1-SB_9H_8)(1′,7′-$C_2B_{10}H_{11}$) but more definitive structural characterization is rather tenuous. Complete structural characterization is also lacking for the two (1-SB_9H_8)(2′,3′-$C_2B_9H_{10}$) isomers formed upon copyrolysis of 6-SB_9H_{11} and 7,9-$C_2B_9H_{13}$. However, the carboranyl thiaboranes also are believed to be B–B linked clusters. There is no evidence for polydeltahedral thiaboranes where the B–B link involves a vertex of order other than 5. For instance, the 1-SB_9H_8 moiety was not found to link through the axial boron.

Introduction

An interesting expansion of the scope of borane chemistry is the linkage of various clusters to form "polypolyhedra". Two polyhedra of either the same or different cage size joined by either multicenter or, more generally, two-center B–B or B–C bonds are known. The first reported example was 1,1′-$(B_5H_8)_2$ (two pentaborane molecules joined apically by a B–B bond[1]). The 1,2′-$(B_5H_8)_2$ and 2,2′-$(B_5H_8)_2$ isomers are also known.[2] The existence of other open frameworks joined by B–B bonds, e.g., $(B_4H_9)_2$,[3] $(B_5H_8)(B_6H_9)$,[4] and $(B_5H_8)(B_{10}H_{13})$,[4] among others, has been suggested. Numerous examples of linked deltahedral[5] (closo) cages are known, most involving 10-, 11-, and 12-vertex clusters. Closo frameworks have been joined by B–B bonds [10,10′-(1-$B_9CH_9)_2^{2-}$], and the three isomers of $(B_{10}H_9)_2^{4-}$,[6] by B–H–B bonds [$B_{24}H_{23}^{3-}$],[7] by multicenter bonds [$B_{20}H_{18}^{2-}$],[8] by C–C bonds [$(B_{10}C_2H_{11})_2$],[9] and by B–C bonds [$B_9C_2H_{10}$–$B_{10}C_2H_{11}$].[10] Also known is a limited number of novel structures which amount to the joining of two clusters by a common face, i.e., $B_{20}H_{16}$ (two decaborane units joined along their open faces),[11] or edge, i.e., *n*-$B_{18}H_{22}$[12] or *i*-$B_{18}H_{22}$[13] (two decaborane units sharing a common edge) and $B_{14}H_{20}$ (two B_8H_{12} fragments with a cisoid fusion).[14]

The methods of coupling have been varied and include chemical oxidation, electrochemical oxidation, pyrolysis, deuterium activation, Lewis acid–base complexation, and electrical discharge. Pyrolysis appears to be a rather general route to the coupling of neutral boranes and was used for the preparation of the polydeltahedral thiaboranes reported here.

Results and Discussion

$(SB_9H_8)_2$ Molecules. During the pyrolytic closure of 6-SB_9H_{11}, three $(SB_9H_8)_2$ isomers are formed,[15,16] 2,2′-(1-SB_9H_8)$_2$, Ia, 2,6′-(1-SB_9H_8)$_2$, Ib, and 6,6′-(1-SB_9H_8)$_2$, Ic (see Figure 1 for numbering convention). The ^{11}B NMR and infrared spectra (Tables I and II, respectively) of these compounds or of their mixtures are remarkably similar to those of the parent 1-SB_9H_9 and show no evidence of B–H–B bridge hydrogen signals. Since the ultraviolet absorption maxima are identical for 1-SB_9H_9 and 2,2′-(1-SB_9H_8)$_2$ and since the molar extinction coefficients differ by a factor of 2 [8100 and 16 160 l. mol^{-1} cm^{-1}, respectively], it is felt that the SB_9H_8 moieties are linked by a two-electron, two-center bond with no electron delocalization between clusters.

Table I. ^1H and ^{11}B NMR Data[a]

Ia, 2,2′-(1-SB_9H_8)$_2$:[b] −71.6, d (2), $J_{BH} = 175$; 2.9, s (2); 4.7, d (2), $J_{BH} = 180$; 6.3, d (4), $J_{BH} = 175$; 18.2, d (4), $J_{BH} = 156$; 19.2, d (4), $J_{BH} = 156$

Ib 2,6′-(1-SB_9H_8)$_2$:[b] −72.2, d (1), $J_{BH} = 150$; −69.5, d (1), $J_{BH} = 150$; 6.0, d (8), $J_{BH} = 180$; 18.3, d (4), $J_{BH} = 155$; 19.1, d (4), $J_{BH} = 160$

IIb, 2,2′- or 2,7′-(1-SB_9H_8)-(1′-$SB_{11}H_{10}$):[c] −71.1, d (1), $J_{BH} = 165$; −20.1, d (1), $J_{BH} = 150$; 0.5, s (1); 2.4, d (5), $J_{BH} = 180$;[c] 5.5, d (8), $J_{BH} = 160$;[c] 18.1, d (2), $J_{BH} = 150$; 19.0, d (2), $J_{BH} = 140$

IIIa, (1-SB_9H_8)(1,7-$C_2B_{10}H_{11}$):[b,e] −71.5, d (1), $J_{BH} = 160$; 5.9, d, $J_{BH} = 160$; 9.2, d, $J_{BH} = 165$; 12.3, d, $J_{BH} = 155$; 15.7, d, $J_{BH} = 155$; 18.6, d, $J_{BH} = 150$; 19.0, d, $J_{BH} = 160$ [^1H NMR: −2.94, s (1); 2.56, s (1)][d]

[a] The chemical shift data are given in ppm relative to $Et_2O \cdot BF_3$ [minus values downfield] followed by a description of the multiplet [d = doublet], its relative intensity (in parentheses), and observed coupling constants given in Hz. [b] Determined in benzene-d_6 at 70.6 MHz. [c] Determined in benzene-d_6 at 86.6 MHz. [d] Determined at 100 MHz in $CDCl_3$ with shifts relative to internal TMS. [e] Relative intensities were difficult to determine in the upfield region because of extensive overlap. See text for discussion.

Table II. Infrared Spectra[a]

Ia, 2,2′-(1-SB_9H_8)$_2$:[b] 2596 vs, 2542 vs, 1900 vw, 1745 vw, 1000 vw, 945 vs, 905 sh, 898 s, 880 m, 868 sh, 848 m, 832 m, 809 s, 748 w, 738 w, 724 m, 715 s, 680 s, 670 sh, 613 vs, 606 vs, 557 w, 536 s, 458 w

Ib, 2,6′-(1-SB_9H_8)$_2$:[b] 2595 vs, 2542 vs, 1905 vw, 1745 vw, 1200 w, 995 w, 952 vs, 940 sh, 898 w, 885 w, 839 w, 822 m, 807 s, 775 m, 763 w, 740 m, 685 s, 665 sh, 634 w, 608 m, 573 w, 540 m, 462 vw

IIb, (1-SB_9H_8)(1-$SB_{11}H_{10}$):[b] 2592 vs, 2545 vs, 1009 s, 949 s, 906 m, 885 w, 870 m, 840 w, 832 w, 816 sh, 808 m, 755 w, 723 s, 685 m, 634 m, 617 w, 587 w, 563 w, 541 w

IIIa, (1-SB_9H_8)(1,7-$C_2B_{10}H_{11}$):[c] 3055 m, 2594 vs, 2553 vs, 1255 w, 1237 vw, 1057 m, 1015 m, 984 w, 950 s, 895 w, 881 w, 835 sh, 809 m, 719 s, 691 m, 642 w, 616 w, 601 w, 554 m

[a] Band positions are reported in cm^{-1} with relative intensities given by s = strong, m = medium, w = weak, v = very, sh = shoulder. [b] Determined as a Nujol mull. [c] Determined in a KBr matrix.

Here the equivalent atoms in sets B(2,3,4,5) and B(6,7,8,9) (see Figure 1) are designated as the upper equatorial belt (ub) and the lower equatorial belt (lb), respectively; the unique boron at position 10 is termed axial (ax). There are six distinct ways to couple two 1-SB_9H_8 units through a B–B bond. The three possible ways involving an axial boron (ax–ax, ax–lb, and ax–ub) should exhibit a distinctive low-field singlet in the ^{11}B NMR arising from the unique axial boron without a terminal hydrogen. Since no low-field singlets are observed in either the isolated compounds or their mixtures, only equatorially coupled dimers are produced in the 450 °C pyrolysis. The three equatorially linked isomers are identified by a combination of x-ray crystallography[17] and NMR spectroscopy.

The ^{11}B NMR spectrum of 2,6′-(1-SB_9H_8)$_2$, Ib, is distinct from those of Ia and Ic. The two axial borons are in different environments in Ib and two low-field doublets of intensity 1

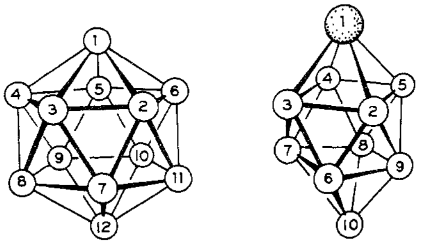

Figure 1. Proposed structures and numbering conventions. The polydeltahedral clusters described in the text are proposed to be based on various combinations of the deltahedra shown here. Each deltahedral vertex represents BH, CH, S, or B depending on the molecule under consideration and the position of the B–B link joining the clusters.

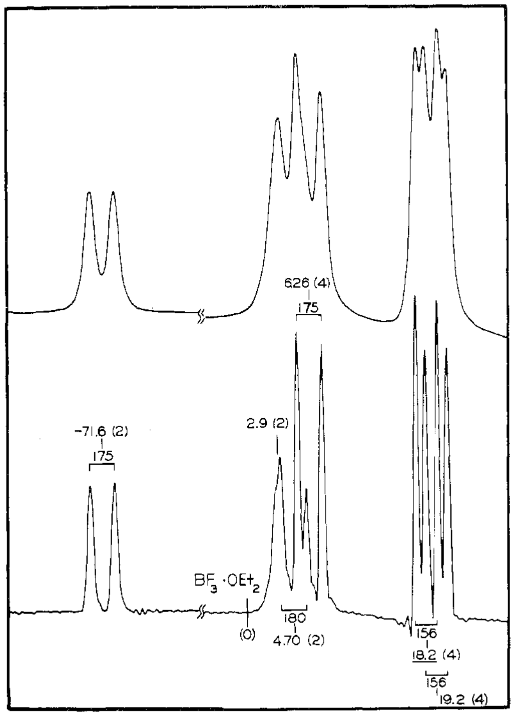

Figure 2. The 70.6-MHz ^{11}B NMR spectrum of 2,2′-$(1\text{-}SB_9H_8)_2$. The lower trace is line narrowed. (Solvent is benzene-d_6, coupling constants are given in Hz over or under brackets, and chemical shifts are followed by relative intensities in parentheses.)

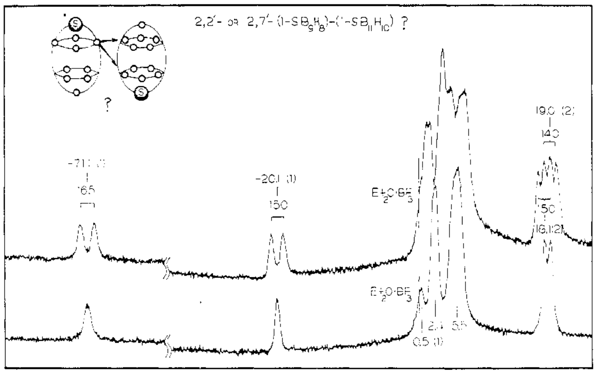

Figure 3. Possible structures and the 86.6-MHz ^{11}B NMR spectrum of 1-SB_9H_8(1′-$SB_{11}H_{10}$). The lower trace is ^1H decoupled. (Solvent is benzene-d_6, coupling constants are given in Hz over or under brackets, and chemical shifts are followed by relative intensities in parentheses.)

each are observed (see Table I). Distinction between Ia and Ic cannot be based on the appearance of the low-field axial boron resonance since in both of these isomers the two axial borons are equivalent and only one low-field doublet of intensity 2 is observed. Definitive assignment of Ia was made by x-ray crystallography.[17]

Assignment of the ub, lb, and ax signals in the ^{11}B NMR spectrum of Ia is possible (Table I) in view of the crystal structure. The 70.6-MHz spectrum with its line-narrowed derivative is shown in Figure 2. Three signal regions (all slightly perturbed from those of 1-SB_9H_9) are seen with greater detail derived upon line narrowing. The low-field doublet of intensity 2 is readily assigned to the unique axial borons. The grouping of signals near +5 ppm [a singlet of intensity 2 (2.9 ppm), a doublet of intensity 2 (4.7 ppm), and a doublet of intensity 4 (6.3 ppm)] can be assigned to the upper belts which contain the borons participating in the exodeltahedral B–B bond and giving rise to the singlet. The remaining distinct signal region around 18 ppm [two doublets of intensity 4 each at 18.2 and 19.2 ppm] gives the predicted pattern for the lower belt. However, assignment of a particular signal to a given set of borons within the lower belt is not possible. Extrapolation of these assignments to the ^{11}B NMR spectrum of 1-SB_9H_9 is straightforward.

(1-SB_9H_8)(1-$SB_{11}H_{10}$) Molecules. The 450 °C pyrolysis of 7-$SB_{10}H_{12}$ gives 1-$SB_{11}H_{11}$[26] and a less volatile component identified as $S_2B_{20}H_{18}$ by mass spectroscopy. The less volatile material consists of three isomers produced in a 1:8:4 relative abundance as shown by gas chromatography and mass spectroscopy (GC–MS) (isomers IIa, IIb, and IIc, respectively, given in order of increasing retention time). The relative amounts of these isomers vary with the temperature of the pyrolysis (at 360–370 °C the distribution is 1:3:2). The ^{11}B NMR of the mixture of isomers exhibits poor resolution due to extensive overlap in the region characteristic of the equatorial belts of both 1-SB_9H_9 and 1-$SB_{11}H_{11}$, suggesting that the isomers are (1-SB_9H_8)(1-$SB_{11}H_{10}$) molecules. The regions typical of the axial boron resonance for both cages are sufficiently resolved to give pertinent structural information which, as in the case of the isolated forms of $(1\text{-}SB_9H_8)_2$, shows that the axial boron of the SB_9H_8 moiety is not part of a B–B bond. However, one of the three isomers (either IIa or IIc; vide infra) shows a singlet at −18.6 ppm suggesting a B–B link through the axial boron of the icosahedral thiaborane.

The 86.6-MHz ^{11}B NMR spectrum (Figure 3) of IIb (isolable by gas chromatography) contains a low-field doublet of intensity 1, typical of the axial boron in 1-SB_9H_8, at −71.1 ppm. Another low-field doublet of intensity 1 is seen at −20.1 ppm, only slightly shifted from the position of resonance of the axial boron of 1-$SB_{11}H_{11}$ (−19.2 ppm). The high-field overlapping doublets of intensity 2 each (+18.1 and +19.0 ppm) are typical of lower belt boron environments in 1-B_9H_8S groups (vide supra). The absence of asymmetry in the appearance of the latter doublets as well as their symmetric collapse upon ^1H decoupling suggests that the *upper* belt contains the boron participating in the B–B bond joining the cages. The signals grouped around +4 ppm are typical of upper belt borons of a 1-SB_9H_8 unit and both the upper and lower belts of a $SB_{11}H_{10}$ unit. Proton decoupling indicates the presence of a singlet at +0.5 ppm. The presence of low-field doublets excludes axial coupling and isomer IIb apparently is either 2,2′-(1-SB_9H_8)(1′-$SB_{11}H_{10}$) or 2,7′-(1-SB_9H_8)(1′-$SB_{11}H_{10}$) (see Figures 1 and 3).

(1-SB_9H_8)(1′,7′-$C_2B_{10}H_{11}$) Molecules. The copyrolysis of 6-SB_9H_{11} and 1,7-$C_2B_{10}H_{12}$ at 450 °C also appears to produce linked deltahedra. GC–MS shows, besides the three $(1\text{-}SB_9H_8)_2$ isomers, three isomeric compounds containing dicarbaborane moieties; the latter isomers (IIIa, -b, and -c in order of retention time) dominate the mixture approximately 3:1 over the $(SB_9H_8)_2$ isomers. The 70.6-MHz ^{11}B NMR spectrum of IIIa, isolated in pure form, is given in Table I. The low-field doublet at −71.5 ppm again indicates an ub- or lb-substituted 1-SB_9H_9 molecule. Extensive overlap of the other boron environments hinders a certain interpretation of the spectrum. Only six distinct signals are observed in the upfield region, two of which are equal-intensity doublets at 18.6 and 19.0 ppm (typical of an unsubstituted lower belt in the 1-SB_9H_8 moiety). The position of substitution on the meta carborane cage cannot be precisely determined, but the fact that two C–H resonances typical of carboranes are seen in the ^{1}H NMR data (Table I) implies that linkage is through a boron atom and is unsymmetrical with respect to the carbons within the icosahedral framework. Only two nonequivalent boron positions satisfying these requirements exist within a meta carborane framework, i.e., the 4(6,8,11) and the 5(12) positions (see Figure 1 for numbering convention). The former would render all boron environments unique; the latter would yield an expected 1:1:2:2:2:2 pattern (all doublets except for one singlet of intensity 1). The observation of fewer signals than expected for either case precludes a definitive assignment of 4- vs. 5-substitution of the carborane. In summary, the data appear to be most consistent with either 2,4′- or 2,5′-(1-SB_9H_8)(1′,7′-$C_2B_{10}H_{11}$).

Data concerning the nature of the linkage of all three (1-SB_9H_8)(1,7-$C_2B_{10}H_{12}$) isomers are not available because of separation problems. Presumably the meta carboranyl group does not undergo intramolecular isomerization because of the high barrier which exists (1,7-$B_{10}C_2H_{12}$ does not undergo isomerization to the 1,12 isomer until over 600 °C).[18] Whether axial substitution of the thiaboranyl group has occurred for certain isomers and whether the linkage is a B–C bond for certain isomers are not known. ^{11}B NMR spectra of the mixtures were not determined.

The copyrolysis of SB_9H_{11} and $C_2B_9H_{13}$ produces a variety of products. The more volatile products are, of course, 1-SB_9H_9[16] and 2,3-$C_2B_9H_{11}$.[19] Among the less volatile materials produced, as shown by GC–MS, are the three 1-SB_9H_8 isomers previously discussed, two isomers of mass 266, and two isomers of mass 274. The two species of mass 266, which compose about 3% of the mixture of the less volatile materials, are most likely "dimers" of 2,3-$C_2B_9H_{11}$, i.e., $(C_2B_9H_{10})_2$. One isomeric form of the latter, composed of two $C_2B_9H_{10}$ units coupled by a C–C bond, has been reported;[20] however, the isomers reported presently are probably joined by a B–B bond.[28] The (1-SB_9H_8)$_2$ isomers compose about 45% of the mixture and the remaining 52% is a mixture of the two species of mass 274 in a relative abundance of 1:2. Because the infrared spectrum of the mixture resembles a superpositioning of the spectra of $(SB_9H_8)_2$ and 2,3-$C_2B_9H_{11}$, the species of mass 274 are most likely (1-SB_9H_8)(2,3-$C_2B_9H_{10}$) isomers. B–B linkage is suggested (vide infra), though the exact point of attachment is not known. The mixture was not separated, nor were NMR spectra taken.

General Considerations. Each particular pyrolytic coupling reaction produces several isomers. Three of the six possible (1-SB_9H_8)$_2$ molecules are formed at 450 °C in a relative abundance of 1:2:2 for the ub–ub, ub–lb, and lb–lb isomers, respectively. Statistically the relative abundance of the ax–ax, ax–lb, ax–ub, lb–lb, ub–ub, and ub–lb isomers would be 1:4:4:16:16:32, respectively. Failure to observe axial substitution does not preclude formation of such isomers with subsequent isomerization to the observed mixture. A series of two diamond–square–diamond (dsd) motions[21] will interchange the axial boron with a lower belt boron, while first shifting the sulfur to an equatorial position and then back to the axial position. A series of four dsd motions will scramble any boron position within the bicapped-square-antiprism geometry, always returning the sulfur to an axial position.

Since the observed 1:2:2 abundance of isomers is not a statistical distribution, it is most likely an equilibrium distribution. When either pure 2,2′-(1-SB_9H_8)$_2$ or an equimolar mixture of the 2,6′ and 6,6′ isomers was subjected to conditions identical with those of the pyrolysis in which it was formed, 50–60% of the material was recovered as a 1:2:2 mixture of the three (1-SB_9H_8)$_2$ isomers. No other volatile products were formed.

Two possible explanations most readily account for the thermal isomerization. The first is skeletal rearrangement, perhaps via a dsd mechanism, forming the observed distribution and reflecting the thermodynamically preferred isomers at these conditions.

The second possibility is a homolytic scission of the B–B bond joining the two clusters, formation and rearrangement of the resulting 1-SB_9H_8 radicals to a distribution reflecting their relative stabilities, and subsequent recombination. In contrast to the first intramolecular mechanism, the second is primarily an intermolecular process. However, because substitution of a given SB_9H_8 cage is exodeltahedral, isomerization of (1-SB_9H_8)$_2$ cannot be characterized readily as either intra- or intermolecular.

Among the various bond types present in linked cages the B–B bond (79 kcal)[22] is the weakest and would be expected to rupture in preference to B–B–B three-center bonds (estimated strength 91 kcal),[22] B–H bonds (91 kcal)[22] and C–H bonds (99 kcal).[23] Following their formation, the $SB_9H_8\cdot$ radicals could undergo skeletal rearrangement or an intramolecular hydrogen migration. The relative abundance of the various isomeric forms of $SB_9H_8\cdot$ would depend on their relative stability. Two distinctly different radicals can exist, one with the radical center located on the axial boron having four nearest-neighbor atoms and the other with the radical center on an equatorial boron, necessarily having five nearest-neighbor atoms. In general, a radical is stabilized by its ability to delocalize the unpaired electron.[24] A vertex of order 5 has a greater degree of bond delocalization than does a vertex of order 4. In terms of two- and three-center bonds, more canonical structures are associated with an order 5 boron than with one of order 4.[25] Thus the ability of an equatorial boron in $SB_9H_8\cdot$ to delocalize an upaired electron should be greater than that of a lower order axial boron. If the difference in stability is sufficiently large, few if any $SB_9H_8\cdot$ radicals having the radical centered on the axial boron would exist. Subsequent recombination, either in the gas phase or on the glass wall of the reaction tube could yield only equatorially substituted 1-SB_9H_9 cages.

Although an intermolecular mode of isomerization of B–B linked thiaborane clusters is implicated by the preceding arguments, verification of these prejudices awaits definitive experimental evidence. We anticipate that if isomerization is effected with a normal sample of $(SB_9H_8)_2$ to which an amount of isotopically enriched sample, $(SB_9H_8)^*{}_2$, has been added, scrambling will occur and form some $SB_9H_8(SB_9H_8)^*$.

If one assumes that the formation of the linked clusters described here involves free-radical intermediates, even those incorporating a carborane moiety are suggested to be B–B linked.[28] The formation of a B-centered radical would be more favorable than that of a C-centered radical both on the basis of bond energy (BH weaker than CH) and on the enhanced ability of B sites to delocalize the radical center.

Finally, it should be clear that the terms "axial" and "equatorial" are derived from molecular symmetry and do not connote the order of a vertex. Unlike the case of 1-SB_9H_9, axial and equatorial sites need not have a different vertex order. For instance, note the B–B link from the axial boron of the 1-$SB_{11}H_{10}$ moiety to an equatorial site of the 1-SB_9H_8 moiety, both vertices of order 5. Thus, the crux of the arguments presented above regarding radical stability revolves around vertex order. We have not been able to find evidence for polydeltahedral thiaboranes where the B–B link involves a vertex of order other than 5. This is in contrast to the case of the polydeltahedral clusters formed upon pyrolysis of C_2B_4 and C_2B_5 carboranes.[28]

Experimental Section

General Data. Infrared spectra were determined on a Perkin-Elmer 457 as either KBr disks or Nujol mulls on KBr plates. The infrared spectral data are listed in Table II. The ^{11}B NMR spectra were recorded on a Varian HA-100 and a JEOL JNH-PS-100 operating at 32.1 MHz, a Varian HR-200 operating at 70.6 MHz (Indiana University), and a Brucker 270 operating at 86.3 MHz (University of Wisconsin). ^{11}B NMR spectra from the latter three instruments were obtained using a pulsed Fourier transform mode. Proton NMR spectra were obtained on a Varian T-60 and a JEOL JNH-PS-100. Chemical shifts are reported relative to external $(C_2H_5)_2O{\cdot}BF_3$ and internal $Si(CH_3)_4$ for ^{11}B and ^1H, respectively. Ultraviolet spectra were recorded on a Cary 14. The mass spectra were obtained on an Associated Electronic Industries MS-902. Gas chromatograms and preparative GC separations were performed on a Varian Aerograph Series 2700 having a thermal conductivity bridge detector and employing a 5-ft × $^1/_4$-in. stainless steel column packed with 1.5% OV-101 on Chromosorb G (100–120 mesh). GC–MS analyses were obtained on a AEI MS-30 double-beam instrument with a Pye Series 104 chromatograph using a 5-ft × $^1/_4$-in. column (SE 30, 3%). Solvents were reagent grade and were used without further purification. Brinkman precoated silica gel TLC plates (Siliplate P2OF-22, F-254, 20 × 20 cm, 2 mm thick) were employed for preparative TLC separation. Samples for NMR analysis were prepared from dried solvents, sealed under nitrogen, and stored at −78 °C prior to analysis.

$(1\text{-}SB_9H_8)_2$ Isomers. The various $(SB_9H_8)_2$ isomers were formed as secondary products during the pyrolysis of SB_9H_{11} to form 1-SB_9H_9. Refer to the preparation of SB_9H_9 for exact details regarding this pyrolysis.[16,26] The less volatile $(SB_9H_8)_2$ separated from the more volatile 1-SB_9H_9 and condensed in the pyrolysis tube about 10 cm above the furnace. The crude yellow solid was scraped from the cooled tube (25 °C) with no special precaution for air and moisture protection. Typically 7.91 g (56.3 mmol) of SB_9H_{11} yielded 0.630 g (2.30 mmol) of $(SB_9H_8)_2$ isomers (8.1%).

The 2,2′-$(1\text{-}SB_9H_8)_2$, Ia, was separated from the other isomers by preparative silica gel TLC plates. Approximately 150 mg of crude dimer, dissolved in a minimal volume of CH_2Cl_2, was streaked onto each plate. The plates were eluted with pentane–CH_2Cl_2 (9:1) giving two bands as seen under ultraviolet light. The leading band, R_f 0.41, was Ia and the broad second band, R_f 0.28, was composed of Ib and Ic. From the original crude mixture of 650 mg, 60 mg of pure Ia was obtained by extraction of the leading bands from several plates with CH_2Cl_2. Evaporation of the solvent gave small clear crystals, mp 159.5–161 °C (uncor in a sealed capillary).

The low-resolution mass spectrum of 2,2′-$(1\text{-}SB_9H_8)_2$ exhibits typical boron envelopes with a m/e cutoff of 278 corresponding to $^{11}B_{18}{}^1H_{16}{}^{32}S_2{}^+$ and a weaker cutoff of correct relative intensity at m/e 280 corresponding to $^{11}B_{18}{}^1H_{16}{}^{32}S^{34}S^+$. The ultraviolet spectrum exhibits a single absorption at 2140 Å (ϵ 16160 l. mol^{-1} cm^{-1}) in Spectrograde heptane.

The broad band appearing on the preparative TLC plates (vide supra) was extracted with CH_2Cl_2 and the extract taken to dryness on a rotary evaporator, yielding 375 mg of the original 650 mg streaked onto the plates. Isolation of 2,6′-$(1\text{-}B_9H_8S)_2$, Ib, was achieved by preparative gas chromatography under the following conditions: column temperature of 210 °C, the flow of 65 cm^3/min, and injection of mixture as a concentrated CH_2Cl_2 solution. Retention times were as follows: Ia, 1.0 (3.0 min); Ib, 1.42 (4.25 min); Ic, 1.67 (5.0 min). Trace amounts of Ia were present. Resolution of the second and third peaks was not complete because of the large amount of material injected during preparative separation. Ib was obtained in a purity greater than 95% by a second pass through the chromatograph. Ten milligrams of Ib (mp 151.5–153 °C, uncor, sealed capillary) was recovered in this manner. The low-resolution mass spectrum exhibited the proper cutoffs with correct relative intensities at m/e 278 and 280 corresponding to $^{11}B_{18}{}^1H_{16}{}^{32}S_2{}^+$ and $^{11}B_{18}{}^1H_{16}{}^{32}S^{34}S^+$.

Copyrolysis of 6-SB_9H_{11} and 1,7-$C_2B_{10}H_{12}$. The apparatus was the same as that described for the synthesis of 1-SB_9H_9.[16,26] The pyrolysis tube was charged with 7.96 g (55.2 mmol) of 1,7-$C_2B_{10}H_{12}$ and 7.78 g (55.3 mmol) of SB_9H_{11}, thoroughly mixed together. The pyrolysis was performed at 450 °C in a manner identical with the SB_9H_9 synthesis and gives 12.1 g of material on the sublimator cold finger. Gas chromatography showed this material to be about 63% meta carborane and 37% 1-SB_9H_9. From the inner wall of the pyrolysis tube, about 15 cm above the furnace, 750 mg of pale yellow solid was removed. Gas chromatography conditions identical with those described for the isolation of Ib (except for a column temperature of 190 °C) showed six major components, three of which were the $(SB_9H_8)_2$ isomers previously described. The other three were isomers of molecular formula $B_{19}H_{19}C_2S$, as shown by GC–MS. The retention times were as follows: Ia, 1.00 (~3.7 min); IIIa, 1.27 (~4.7 min); Ib, 1.48 (~5.5 min); IIIb, 1.62 (~6.0 min); Ic, 1.78 (~6.6 min); IIIc, 1.97 (~7.3 min). Fifteen milligrams of white, crystalline IIIa was isolated with 95% purity by preparative gas chromatography. The low-resolution mass spectrum of IIIa showed typical boron envelopes with the parent envelope cutoff at m/e 284 corresponding to $^{11}B_{19}{}^1H_{19}{}^{12}C_2{}^{32}S^+$ and a weaker cutoff of correct relative intensity at m/e 286 corresponding to $^{11}B_{19}{}^1H_{19}{}^{12}C_2{}^{34}S^+$.

Copyrolysis of $C_2B_9H_{13}$ and SB_9H_{11}. 7,9-$C_2B_9H_{13}$ was prepared by protonating 7,9-$C_2B_9H_{12}{}^-$ with 85% phosphoric acid under a layer of benzene.[19] Rotary evaporation of the benzene and room-temperature sublimation of the resulting residue yielded pure 7,9-$C_2B_9H_{13}$. A 1.68-g amount (11.9 mmol) of SB_9H_{11} and 1.60 g (11.9 mmol) of $C_2B_9H_{13}$ were thoroughly mixed in a nitrogen atmosphere and placed in the pyrolysis tube. The pyrolysis at 450 °C was performed in the usual manner and 1.91 g of material was deposited on the sublimator cold finger. This material was composed of 1-SB_9H_9 and 2,3-$C_2B_9H_{11}$ in a 1:1 ratio. Approximately 85 mg of a less volatile yellow material was collected from the inner wall of the pyrolysis tube 16 cm above the furnace. This material was sublimed in vacuo at 75 °C to yield 75 mg of a white solid. The GC–MS and infrared spectrum of the latter were determined. The important features of both are described in the Results and Discussion. No attempt at separation was made.

$(1\text{-}SB_9H_8)(SB_{11}H_{10})$. Besides $SB_{11}H_{11}$, three $(1\text{-}SB_9H_8)(B_{11}H_{10}S)$ isomers were formed during the pyrolysis of $SB_{10}H_{12}$ at 450 °C.[26,27] These isomers were deposited on the inside wall of the pyrolysis tube 10–20 cm above the furnace opening. From the pyrolysis of 2.04 g of $SB_{10}H_{12}$, 75 mg of this less volatile material was obtained. It was sublimed in vacuo at 90 °C to yield 68 mg of white solid. The GC–MS of this material demonstrated that it was a mixture of three isomers which exhibited the following retention times (column temperature 220 °C, flow rate 75 ml/min: IIa, 1.00 (~6.1 min); IIb, 1.33 (~8.1 min); IIc, 1.52 (~9.3 min). An 18-mg amount of IIb was isolated by preparative gas chromatography affording crystals which melted at 210–210.5 °C (uncor) in a sealed capillary. The infrared spectrum of IIb is described in Table II. The low-resolution mass spectrum exhibited typical boron envelopes. The most intense feature was the parent envelope having an m/e cutoff at 302 corresponding to $^{11}B_{20}{}^1H_{18}{}^{32}S_2{}^+$ and a less intense cutoff of correct relative intensity at m/e 304 corresponding to $^{11}B_{20}{}^1H_{18}{}^{32}S^{34}S^+$.

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Registry No. Ia, 54748-44-6; Ib, 54748-45-7; Ic, 54748-46-8; IIb, 59388-91-9; IIIa, 59388-90-8; 1-SB_9H_9, 41646-56-4; 6-SB_9H_{11}, 12447-77-7; 1,7-$C_2B_{10}H_{12}$, 16986-24-6; ^{11}B, 14798-13-1.

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Kinetics and Mechanism of Trimethylamine–Fluoroborane Hydrolysis

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Hydrolysis of trimethylamine–fluoroborane occurs via acid-independent and acid-catalyzed pathways each of which is first order in substrate. Below 0.5 M HCl, the acid-catalyzed reaction is first order in a_{H^+}. The logarithm of the observed rate constant, which is linear with pH from about 0.1 to 0.5 M HCl, continues linear with the Hammett acidity function, H_0 (slope = 1.1 at 25 °C), in concentrated acid solutions up to 6 M H_2SO_4. Thus, the rate is described by the expression $-d[Me_3N{\cdot}BH_2F]/dt = [Me_3N{\cdot}BH_2F][k_1 + k_2h_0]$. Rates are about 30% faster in water than in deuterium oxide over a range of acidity from 0.1 M HCl to 3 M H_2SO_4. It is suggested that the uncatalyzed reaction may proceed via the rate-limiting loss of F^- from the coordination sphere of boron analogous to the previously proposed mechanism for hydrolysis of iodo-, bromo- and chloroborane–amines. An A-1 mechanism is suggested for the acid-catalyzed pathway involving the preequilibrium protonation of substrate at fluorine with subsequent rate-determining loss of HF via dissociative activation. This susceptibility of the fluoro derivative to acid-catalyzed hydrolysis bears analogy to the aquation chemistry of cobalt(III) complexes containing highly electronegative coordinated ligands.

Introduction

Effects of iodide, bromide, chloride, and, more recently, cyanide ion as boron-bonded substituents on the kinetics and mechanism of hydrolysis of borane–amine addition compounds have been subjects of previous investigation.[1,2] A study of the particular effect of fluoride was precluded due to the unavailability of the appropriate substrate. In a more recent period, however, VanPaasschen and Geanangel[3] have succeeded in preparing and characterizing both the mono- and difluoroborane adducts of trimethylamine and this has prompted us to extend the investigation of such substituent effects by exploring the hydrolysis behavior of the monofluoro derivative, $Me_3N{\cdot}BH_2F$. Further incentive for such a study was based upon previously noted similarities in the apparent mechanisms of hydrolysis of substituted amine–boranes with those of selected transition metal complexes,[1,2] e.g., of Co(III), where, unlike that of the higher halo derivatives, the aquation of certain fluoroammine complexes has been found to be highly susceptible to acid catalysis.[4,5] It was, therefore, of interest to examine the possibility of an analogous divergent influence of fluoride on the mechanism of hydrolytic decomposition of amine–haloboranes.

Experimental Section

Materials. Trimethylamine–fluoroborane, prepared via the reaction of HF with trimethylamine–borane in benzene and displaying the previously reported analytical and spectral properties,[3] was supplied by Dr. R. A. Geanangel and co-workers (University of Houston). All reagents were of analytical grade and supplied by Baker, Matheson Coleman and Bell, or Allied Chemical Co. Vitex starch was obtained from G. F. Smith Co. Deuterium oxide (99.8% isotopic purity) and 98% D_2SO_4 in D_2O were obtained from Diaprep Inc. of Aldrich Chemical Co. Deuterium chloride was prepared from D_2O and benzoyl chloride by the method of Brown and Groot.[6] Aqueous solutions of sulfuric acid and hydrochloric acid were prepared using deionized water and analytical concentrations of all acid solutions were determined by routine titration with solutions of NaOH which had been standardized with potassium hydrogen phthalate.

Kinetic Studies. In a typical run, a 0.05–0.10-g (0.55–1.1-mmol) sample of trimethylamine–fluoroborane was weighed in an iodine flask and suspended in a constant-temperature bath for about 5 min. To this sample was added about 100 ml of the desired acid solution which had been brought to temperature equilibrium in the same bath. The time of mixing was taken as t_0, and complete solution was obtained usually in about 0.5 min. At various time intervals, 10-ml portions of solution were withdrawn and added to previously prepared solutions containing KIO_3 and KI. The hydride content was determined iodometrically using 0.02 N $Na_2S_2O_3$ as previously described for comparable studies of the hydrolysis of amine–boranes.[7] The temperature was controlled to ±0.1 °C using a Sargent Thermonitor or Freas Precision constant-temperature bath. The rate of decomposition of substrate was studied in various media including water, dichloroacetate buffer solutions, aqueous HCl (0.05–3.0 M), aqueous HCl containing KCl as added electrolyte, aqueous sulfuric acid (1.5–6.0 M), DCl in D_2O, D_2SO_4 in D_2O, and aqueous sodium hydrogen sulfate. Values of H_0 of concentrated acid solutions (>0.5 M HCl; >1.0 M H_2SO_4) containing no added electrolyte were obtained by interpolation using the data of O'Connor.[8] The D_0 values for selected solutions of D_2SO_4 in D_2O and H_0 values for various solutions at different temperatures were obtained from Rochester.[9] Three solutions containing respectively 0.60, 1.2, and 1.8 M HCl were adjusted to constant ionic strength (μ = 3.0) by the addition of potassium chloride. Values of H_0 for such solutions were obtained by spectrophotometric measurements using a Cary 15 recording spectrophotometer and employing the indicators *p*-nitroaniline (mp 147–147.5 °C) and *o*-nitroaniline (mp 71 °C). Both indicators had been recrystallized from H_2O and their concentrations ranged from 1.4 to 1.7 mM in these determinations.

In a separate study, a 0.28-g sample of $(CH_3)_3N{\cdot}BH_2F$ was dissolved in 100 ml of 0.46 M DCl in D_2O at 25 °C. After 15 h, corresponding to about 1 half-life for hydrolysis of the substrate, the unreacted fluoroborane was extracted with four 25-ml portions of Et_2O. The solution was then dried over anhydrous $MgSO_4$, the liquid decanted from the solid residue, and ether removed by evaporation