

magnetic susceptibility measurements.

Our attempts to measure the molar conductance of $A_2[V(O_2)_3F]$ in water were unsuccessful. The values obtained were higher than that expected for a 2:2 type electrolyte. It has been generally observed by us⁷ and also by others¹³ that owing to their instability the molar conductances of many peroxyvanadium(V) compounds cannot be measured. Thus, the higher conductance values in the present case are not too surprising.

The IR spectra of the series of three salts resemble each other very closely (Table II), indicating that the compounds are similar both structurally and stoichiometrically. The spectra of the compounds showed absorptions in two characteristic regions, viz., at 850–855 cm^{-1} and at 470–475 cm^{-1} . Each spectrum shows only one strong absorption in the 850–855- cm^{-1} region, which has been unambiguously assigned¹⁶ as the ν_{-O-O-} mode of coordinated peroxy groups. A single absorption in this region suggests that all three peroxy ligands are bonded to the vanadium(V) center in an analogous fashion. Since the ν_{-O-O-} absorptions occur exactly in the region stipulated for the triangularly bonded peroxy groups, we infer that all three peroxy ligands in the complexes are bonded in a triangular bidentate manner. The absorptions in the comparatively lower region, i.e., 470–475 cm^{-1} , are straightforward and have been assigned as the ν_{V-F} modes arising from the presence of fluoride ion coordinated to the vanadium(V) center. This compares very well with the ν_{V-F} values observed in the cases of various fluorovanadate species.^{7,17} The three extra

vibrations at 3158 (m), 3040 (s), and 1400 (s) cm^{-1} in the spectrum of $(NH_4)_2[V(O_2)_3F]$ have been assigned to the ν_3 , ν_1 , and ν_4 modes of NH_4^+ .

In an attempt to study the effect on the basicity of peroxy ligands as a function of the number of peroxy groups coordinated to the vanadium(V) center, we compared the IR spectra of $A_2[V(O_2)_3F]$ with those of $A_2[VO(O_2)_2F]$ compounds, recorded under identical conditions. It is interesting to note that, while ν_{-O-O-} absorptions for $A_2[VO(O_2)_2F]$ compounds lie in the region 870–895 cm^{-1} , those of $A_2[V(O_2)_3F]$ compounds lie between 850 and 855 cm^{-1} . The lowering of the values must be attributed to the lowering of $-O-O-$ bond order of the coordinated peroxy groups in the latter case. In other words, removal of further π_p density from O_2^{2-} to the vanadium appears to have taken place in the case of $A_2[V(O_2)_3F]$ which has been facilitated by the attachment of a fluoride ligand to V^{5+} . This observation enables us to infer that the basicity of coordinated peroxy ligands increases with the increase in the number of such ligands coordinated to vanadium(V) and lend support to the proposition made by Quilitzsch and Wieghardt⁵ from their studies in solution.

Thus, it appears from our present work that the peroxy ligands are triangularly bonded to V^{5+} and the complex species $[V(O_2)_3F]^{2-}$ may have a heptacoordinated monomeric structure but the probability of a polymeric structure through a weak V–F–V bridging can not also be totally ruled out.

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Registry No. $[NH_4]_2[V(O_2)_3F]$, 82865-19-8; $Na_2[V(O_2)_3F]$, 82865-20-1; $K_2[V(O_2)_3F]$, 82865-21-2; V_2O_5 , 1314-62-1; NH_4F , 12125-01-8; NaF , 7681-49-4; KF , 7789-23-3; H_2O_2 , 7722-84-1.

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Stereochemical Nonrigidity in Nine-Vertex Polyhedral Boranes: Dimethyl Sulfide Derivatives of Nonahydranonaborate(2-)¹

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Reaction of nonahydranonaborate, $B_9H_9^{2-}$, with acetic anhydride/dimethyl sulfoxide yielded both isomers of $B_9H_8SMe_2^-$. Variable-temperature 1H and ^{13}C NMR studies revealed these to exhibit the first example of intramolecular rearrangement of a nine-boron cluster. The activation barrier of this dynamic process has been found to be 22 kcal/mol. Disubstitution by prolonged reaction time followed by workup and recrystallization yielded a single isomer of $B_9H_7(SMe_2)_2$ identified by X-ray diffraction work as the 1,5-isomer. At ambient temperatures and above, dynamic behavior of this isomer was observed which suggested its equilibration with both the 4,5- and 1,8(9)-isomers. 1H NMR (90 MHz) spectral data indicated coalescence at 130 °C due to rapid cage rearrangement with an activation barrier of 19 kcal/mol. This evidence for structural nonrigidity and the possible mechanism involved are discussed in light of known dynamic processes in cluster chemistry.

Introduction

Structural nonrigidity in boron cluster compounds provides a useful model for fluxional behavior of coordination compounds in general and cluster compounds in particular.^{2a,b} Especially appropriate is the family of polyhedral boranes,

$B_nH_n^{2-}$, ranging in geometry from the six-vertex octahedron to the twelve-vertex icosahedron.^{2c,d} An intriguing range of fluxionality exists. While $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ have high rearrangement barriers and are stereochemically rigid under normal conditions,^{2c,d} $B_8H_8^{2-}$ has been shown to be nonrigid at 30 °C with an estimated activation barrier of only 12 kcal/mol.³ More dramatically, $B_{11}H_{11}^{2-}$ has high fluxionality and its limiting solution spectrum was not observed even at -90 °C.⁴ Although the intermediate $B_9H_9^{2-}$ species should

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(2) (a) E. L. Muetterties, *Tetrahedron*, **30**, 1595 (1974); (b) E. L. Muetterties and B. F. Beier, *Bull. Soc. Chim. Belg.*, **84**, 397 (1975); (c) E. L. Muetterties and W. H. Knoth, "Polyhedral Boranes", Marcel Dekker, New York, 1968; (d) V. I. Stanko, V. A. Brattsev, and S. P. Kuyazev, *Russ. Chem. Rev. (Engl. Transl.)*, **48**, 130 (1979).

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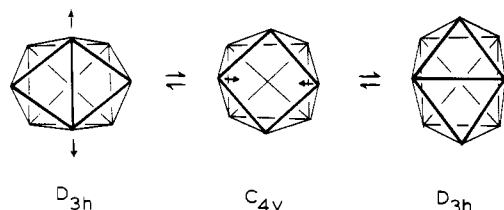


Figure 1. $D_{3h} = C_{4v} = D_{3h}$ rearrangement of a nine-vertex polyhedron.

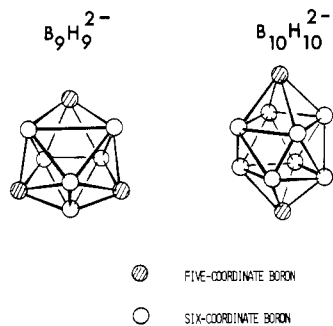


Figure 2. $B_9H_9^{2-}$ and $B_{10}H_{10}^{2-}$ polyhedra.

also be susceptible to polyhedral rearrangement,^{2c} the parent $B_9H_9^{2-}$ maintains its tricapped-trigonal-prism (D_{3h}) geometry up to 250 °C in solution.⁵ Muettterties and Guggenberger have suggested electronic factors to be operative in raising its activation barrier.^{2b,6} The most reasonable rearrangement intermediate or transition state would have the monocapped-square-antiprism (C_{4v}) geometry (see Figure 1), and this has been shown to be electronically degenerate, making the $D_{3h} = C_{4v} = D_{3h}$ process spin disallowed. Recently, King also proposed symmetry arguments for the rigidity of $B_9H_9^{2-}$.⁷ Literature reports on other nine-vertex clusters have suggested fluxional behavior, although no definitive studies are available. For example, B_9Br_9 has a single ^{11}B solution NMR signal down to -60 °C though this may be a result of accidental overlap.⁸ The metal clusters Sn_9^{4-} and Bi_9^{5+} have C_{4v} and D_{3h} structures, respectively.⁹ Rudolph has reported prima facie evidence for fluxional behavior of Sn_9^{4-} using ^{119}Sn NMR, but no limiting spectrum was obtained.¹⁰ A recent report of a nine-vertex rhodium cluster, $Rh_9P(CO)_{21}^{2-}$, also mentioned possible solution fluxionality.¹¹

Previous work in polyhedral borane chemistry has suggested that substitution of the parent dianion may be effective in altering the rearrangement barrier.¹² We have attempted to prepare derivatives of $B_9H_9^{2-}$ in order to examine their structural rigidity. An additional impetus for this work was to discover the extent of site selectivity during substitution reactions on the nine-vertex cluster. On both $B_9H_9^{2-}$ and $B_{10}H_{10}^{2-}$ two types of sites are available: the five-coordinate capping borons and the six-coordinate prismatic borons (Figure 2). Ground-state molecular orbital calculations by Lipscomb have predicted the lower coordinate capping sites to be more

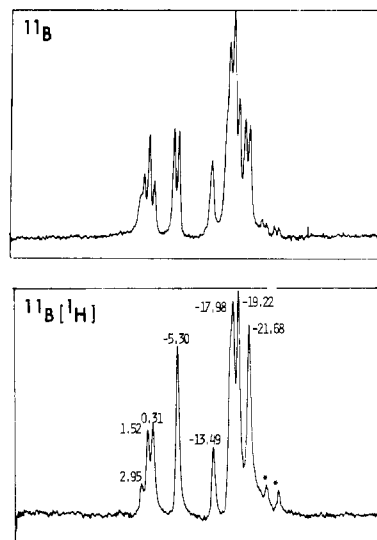


Figure 3. ^{11}B NMR (127 MHz) spectra of $(PPN)B_9H_8SMe_2$ in CH_2Cl_2 (asterisks refer to small amounts of $B_{10}H_9SMe_2^-$ impurity).

attractive toward electrophiles.¹³ Considerable experimental evidence in $B_{10}H_{10}^{2-}$ derivative chemistry supports this premise, but a significant number of violations have also been reported.^{2c} We would expect the smaller $B_9H_9^{2-}$ to provide a more stringent test for these predictions due to the greater discrepancy in ground-state electronic populations between its five- and six-coordinate sites.¹³

Results

Muettterties first reported the synthesis of dimethyl sulfide derivatives of $B_{10}H_{10}^{2-}$ using HCl/Me_2SO as the reagent.¹⁴ Due to the sensitivity of $B_9H_9^{2-}$ to strong protic acids, we chose to use the acetic anhydride/ Me_2SO system first described by Kaczmarczyk in preparing analogous $B_{12}H_{12}^{2-}$ compounds.¹⁵ We found that $Na_7B_9H_9 \cdot xH_2O$ reacted smoothly with this reagent at room temperature to give high yields of $B_9H_8SMe_2^-$ isolated as Rb , NMe_4 , and PPN (bis(triphenylphosphine)nitrogen(1+)) salts.

Reaction of either $B_9H_9^{2-}$ or $B_9H_8SMe_2^-$ with acetic anhydride/ Me_2SO for 2 days at ambient temperature yielded the neutral disubstituted $B_9H_7(SMe_2)_2$ derivative, which can be readily recrystallized from benzene/hexane.

Characterization of Products. $B_9H_8SMe_2^-$. Room-temperature 1H NMR spectra of $PPN^+B_9H_8SMe_2^-$ in $CDCl_3$ exhibited methyl singlets at 2.78 and 2.12 ppm (relative areas 1:2) indicative of production of both possible isomers. By analogy to known $B_{10}H_9SMe_2^-$ isomers,¹⁴ a tentative assignment of the 2.78-ppm resonance to an SMe_2 group at a five-coordinate capping boron (the 4-isomer) and the 2.12-ppm signal to substitution at a six-coordinate prismatic boron (the 1-isomer) can be made. The ^{13}C NMR spectrum also showed two distinct methyl carbons at 28.42 and 26.53 ppm in the same ratio.

Confirmation of the above assignments using ^{11}B NMR at 28.7 MHz is difficult due to overlapping peaks. However, at 127 MHz, the assignment of the product to be a 1:2 mixture of the 4- and 1-isomers can indeed be validated (Figure 3). Among the low-field resonances, we can assign the singlet at +2.95 and doublet at +0.31 ppm ($J_{B-H} = 148$ Hz, relative intensities 1:2) to belong to the three five-coordinate capping borons of the 4-isomer. The doublets at +0.31 ($J_{B-H} = 148$

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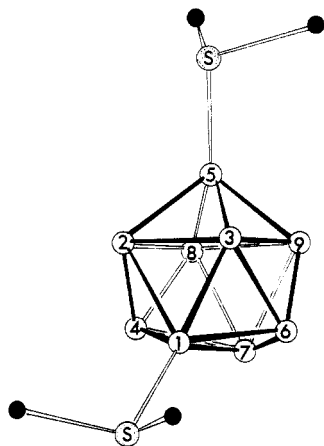


Figure 4. Molecular structure of 1,5-B₉H₇(SMe₂)₂.

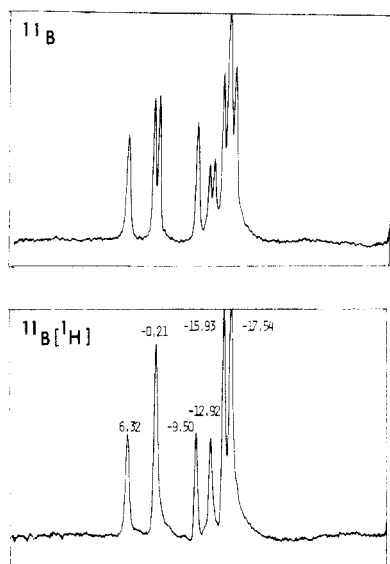


Figure 5. ¹¹B NMR (127 MHz) spectra of 1,5-B₉H₇(SMe₂)₂ in acetone.

Hz) and -5.3 ppm ($J_{\text{B-H}} = 140$ Hz, relative areas 1:2) can be assigned to the capping borons of the 1-isomer with the singlet at -13.49 ppm assigned to the substituted prismatic boron. The relative amounts of the 4- vs. the 1-isomer can be calculated to be 1:2, consistent with the ¹H and ¹³C NMR results. Repeated fractional recrystallization and preparative TLC failed to separate these isomers.

B₉H₇(SMe₂)₂. A single-crystal X-ray diffraction study of the recrystallized product identified it as the 1,5-isomer with a SMe₂ group at each type of boron site (Figure 4).¹⁶ Freshly prepared solutions of the 1,5-isomer in CDCl₃ exhibited two methyl singlets (2.84, 2.24 ppm) of equal areas when kept at 10 °C or below. The ¹¹B NMR at 127 MHz in acetone-*d*₆ also confirmed its initial solution structure (Figure 5). Assignments can be made as follows: singlet at +6.32 (substituted B(5)), doublet at -0.21 (B(4), B(6); $J_{\text{B-H}} = 148$ Hz), singlet at -9.50 (substituted B(1)), doublet at -12.92 (B(7); $J_{\text{B-H}} = 143$ Hz), doublet at -15.93 (B(2) and B(3); $J_{\text{B-H}} \approx 164$ Hz), and doublet at -17.54 (B(8), B(9); $J_{\text{B-H}} \approx 180$ Hz).

Variable-Temperature NMR Studies. B₉H₇(SMe₂)₂⁻. Above ambient temperature, the ratio of the two methyl resonances in the 90-MHz ¹H NMR spectrum slowly changed from 1:2 to about 1:5 at 130 °C. Concurrently, broadening of both signals led to eventual coalescence into a broad signal at 2.22

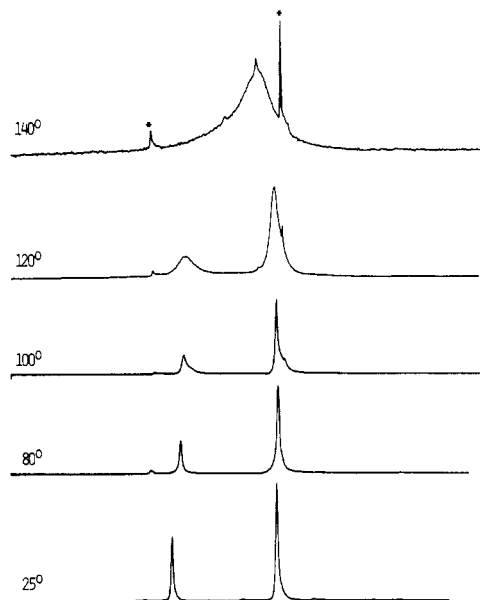


Figure 6. Temperature dependence of the 90-MHz ¹H NMR spectra of (PPN)B₉H₈SMe₂ in C₂D₂Cl₄ (asterisk denotes decomposition product).

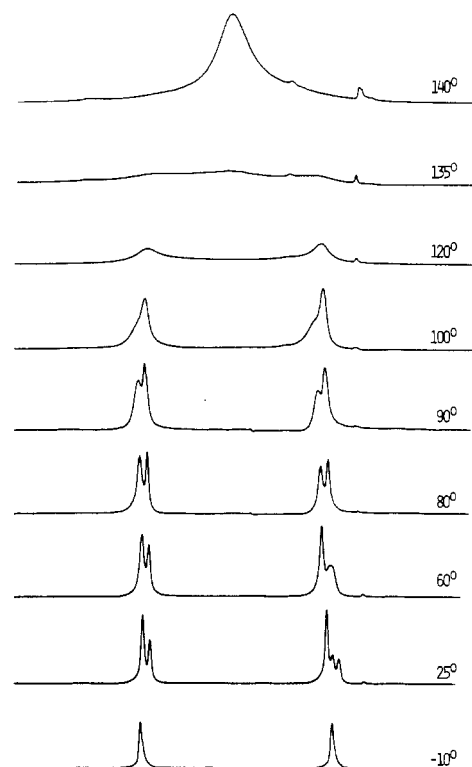


Figure 7. Temperature dependence of the 90-MHz ¹H NMR spectra of 1,5-B₉H₇(SMe₂)₂ in C₂D₂Cl₄.

ppm at 145 °C (Figure 6). These spectral changes were reversible between 25 and 145 °C, but above 150 °C significant irreversible decomposition occurred as a persistent new signal at 2.08 ppm appeared. Complete decomposition with effervescence occurred at 160 °C. The ¹³C NMR spectrum showed similar temperature dependence though the ¹¹B spectral data at 28.7 MHz was uninformative, showing only general broadening and collapsing into a broad signal at higher temperatures.

B₉H₇(SMe₂)₂. As freshly prepared solutions of the 1,5-isomer were allowed to stand at room temperature in C₂D₂Cl₄, weak new signals appeared in the ¹H NMR spectrum at 2.79 (singlet) and two equal peaks centered at 2.19 ppm. At 60

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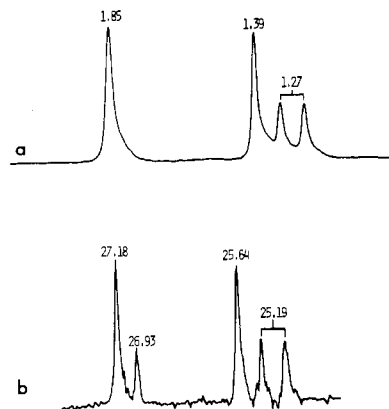


Figure 8. (a) ^1H NMR (90 MHz) spectrum of an aged solution of 1,5- $\text{B}_9\text{H}_7(\text{SMe}_2)_2$ in C_6D_6 . (b) $^{13}\text{C}\{^1\text{H}\}$ NMR (22.5 MHz) spectrum of the same solution.

$^\circ\text{C}$, the two equal signals had coalesced into a broad singlet. At higher temperatures, the relative intensities of the new signals continued to increase, and above 100°C , they became the major resonances. Broadening of the signals was followed by coalescence at 130°C .

The temperature dependence of these ^1H spectra is shown in Figure 7. These spectral changes were found to be reversible between 25 and 130°C . Cooling below 25°C , however, did not regenerate the original two-singlet spectrum.

Solvent dependence of the 90-MHz ^1H NMR spectrum of 1,5- $\text{B}_9\text{H}_7(\text{SMe}_2)_2$ was also observed. The splitting of the two equal signals centered at 2.19 ppm is 2.7 Hz at ambient temperature in CDCl_3 and 1.6 Hz in CD_2Cl_2 , and it is not resolved in $\text{Me}_2\text{SO}-d_6$ or acetone- d_6 . An aromatic-solvent-induced shift (ASIS) is observed in C_6D_6 (Figure 8a), where upfield shifts occurred for all five methyl resonances, with additional changes in relative intensities. The two equal signals are now split by 6.8 Hz.

The $^{13}\text{C}\{^1\text{H}\}$ NMR spectra in CDCl_3 and $\text{C}_2\text{D}_2\text{Cl}_4$ parallel the observed ^1H NMR spectral behavior. Initial methyl signals at 27.83 and 26.27 ppm were joined by new resonances at 27.64 ppm (singlet) and two equal signals centered at 25.89 ppm upon standing. In C_6D_6 , the relative intensities of the four signals now at 27.18 (s), 26.93 (s), 25.64 (s), and 25.19 ppm (two singlets) are 1:0.3:1:0.97, respectively (Figure 8b). This is confirmed also by ^1H NMR spectral integration.

The temperature dependence of the ^{11}B NMR at 28.7 MHz is much less informative. Broadening of all signals occurred with formation of a single broad resonance above 140°C .

Discussion

$\text{B}_9\text{H}_8\text{SMe}_2^-$. The ^1H , ^{13}C , and ^{11}B NMR spectra confirmed the formation of both possible isomers in a statistical distribution (4-isomer:1-isomer = 1:2). On the strength of these data, it first appeared that the substitution proceeded without discrimination between the two sites. The variable-temperature data, however, rendered site selectivity arguments moot.

We interpret the data as supportive of slow equilibration of the 1- and 4-isomers at ambient temperatures. The rearrangement became rapid (NMR time scale) at above 130°C ; concurrently, the equilibrium increasingly favored the 1-isomer. A calculated activation barrier of about 22 ± 1 kcal/mol can be obtained from the coalescence temperature.

$\text{B}_9\text{H}_7(\text{SMe}_2)_2$. There are three possible nonvicinal isomers for $\text{B}_9\text{H}_7(\text{SMe}_2)_2$ (Figure 9). The X-ray result and the NMR data establish the 1,5-isomer as the only isolated product. In order to monitor the product distribution before workup and recrystallization, we followed the reaction of $\text{PPN}^+\text{B}_9\text{H}_8\text{SMe}_2^-$ with $(\text{CD}_3\text{CO})_2\text{O}$ and $\text{Me}_2\text{SO}-d_6$ using ^1H NMR. It was found that all three isomers (1,5, 4,5, and 1,8(9)) were simultaneously formed in their equilibrium ratio. Therefore,

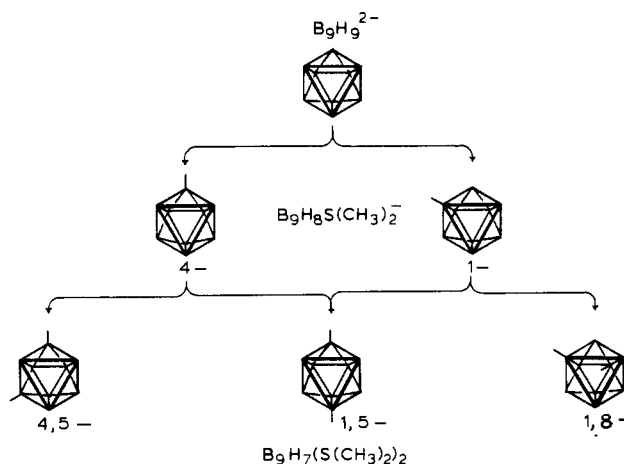


Figure 9. Possible substitution isomers of $\text{B}_9\text{H}_9^{2-}$.

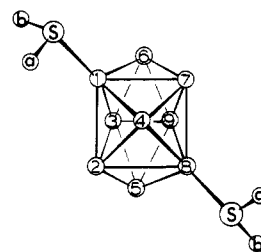


Figure 10. 1,8-isomer of $\text{B}_9\text{H}_7(\text{SMe}_2)_2$ viewed down its C_2 axis.

the recrystallization process apparently favored the 1,5-isomer, resulting in its preferential formation in the solid state.

We propose the following interpretation for the variable-temperature spectral data. Above 10°C , small concentrations of both 4,5- and 1,8(9)-isomers exist in equilibration with the 1,5-species. The two equal new signals centered at 2.19 ppm can be assigned to the 1,8(9)-isomer due to its dissymmetry (Figure 10), with collapse of the peaks above 60°C by rapid pyramidal inversion about the sulfur centers. Similar spectral behavior has been reported for the dissymmetric 2,7(8)-isomer of $\text{B}_{10}\text{H}_8(\text{SMe}_2)_2$.¹⁴ At higher temperatures, the equilibria increasingly favor the 1,8(9)- and 4,5-isomers over the 1,5-isomer. At 130°C and above the cage rearrangement becomes rapid on the NMR time scale. We estimate an activation barrier of 19 ± 1 kcal/mol from the coalescence temperature. The intramolecular nature of the process was supported by the kinetic data and exchange experiments using $\text{B}_9\text{H}_7(\text{S}(\text{C}-\text{D}_3)_2)_2$. From kinetic data, the rate constant of cage rearrangement can be calculated to be about $2 \times 10^{-6} \text{ s}^{-1}$ at 25°C .

The inequivalence of the two sets of new peaks (0.3:0.97) in C_6D_6 rules out the possibility of a single new species, e.g., a nido structure, being responsible for all the new signals. We have not considered the existence of vicinal isomers for two reasons. One is the lack of precedence in the well-developed derivative chemistry of $\text{B}_{10}\text{H}_{10}^{2-}$ except for amino substituents.^{2c,d} Steric factors should make vicinal $\text{B}_9\text{H}_7\text{L}_2$ species similarly unfavorable. A second reason is that, in all polyhedral boranes and carborane rearrangements, higher temperatures have favored nonvicinal isomers over vicinal ones.^{12,2d} The increasing proportion of the new isomers with increasing temperature in a $\text{B}_9\text{H}_7(\text{SMe}_2)_2$ solution is only consistent with their being nonvicinal isomers.

We believe these to be the first examples of structural nonrigidity for a nine-boron cluster. It is reasonable that derivatization has lowered the rearrangement barrier and that the monosubstituted $\text{B}_9\text{H}_8\text{SMe}_2^-$ isomers have a slightly higher barrier than the disubstituted $\text{B}_9\text{H}_7(\text{SMe}_2)_2$. It is also likely that replacement of the cage hydrides with SMe_2 groups may

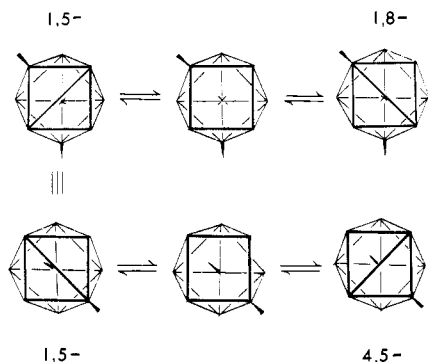


Figure 11. DSD mechanism for interconversion of the three isomers of $B_9H_7(SMe_2)_2$.

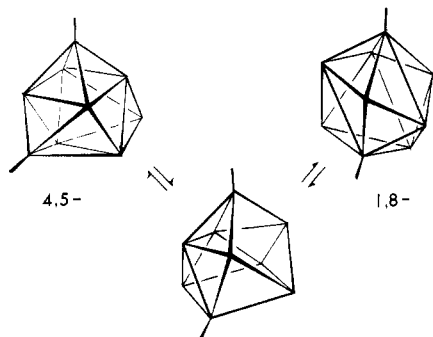


Figure 12. Alternate mechanism for direct interconversion of the 1,8- and 4,5-isomers of $B_9H_7(SMe_2)_2$.

eliminate the degeneracy in the " C_{4v} " rearrangement intermediate or transition state proposed to account for the structural rigidity of B_9H_9 .⁶

Mechanism

Muetterties has proposed a simple $D_{3h} \rightleftharpoons C_{4v} \rightleftharpoons D_{3h}$ sequence for the rearrangement of a nine-boron cage based on Lipscomb's diamond \rightarrow square \rightarrow diamond (DSD) mechanism.^{2c,17} This process can interchange two capping five-coordinate borons with two prismatic six-coordinate vertices. Simple distortions that are normal cage vibrations can result in the postulated " C_{4v} " intermediate or transition state. This mechanism readily accounts for the equilibration of the two isomers of $B_9H_9SMe_2^-$ (Figure 1). It can also explain the equilibration of 1,5- $B_9H_7(SMe_2)_2$ with either the 4,5- or the 1,8(9)-isomer (Figure 11). At the high-temperature limit, equilibration of the predominant 4,5- and 1,8(9)-isomers can still occur via the 1,5-isomer though an intermediate (or transition state) with two square faces of C_s cage symmetry may also directly interconvert the two species (Figure 12). Alternate pathways cannot be ruled out but will involve more extensive disruptions of cage bonding.

Experimental Section

All reactions were performed under a nitrogen atmosphere in Schlenk glassware. Acetic anhydride and Me_2SO were obtained from Baker and degassed before use. Deuterated solvents for NMR were purchased from Stohler and Aldrich. $Rb_2B_9H_9$ was prepared according to literature methods.¹⁸ $Na_2B_9H_9 \cdot xH_2O$ was obtained by ion exchange of $Rb_2B_9H_9$. $(PPN)Cl$ was purchased from Alfa.

Infrared spectra were recorded as KBr wafers on a Perkin-Elmer 283 spectrophotometer. The 1H NMR spectra were obtained on a JEOL FX-90Q NMR spectrometer with D-lock. Variable-temperature spectra were recorded in $C_2D_2Cl_4$ with ethylene glycol as a chemical shift thermometer.¹⁹ Both 1H and ^{13}C chemical shifts were

referenced to internal Me_4Si . ^{11}B NMR spectra were obtained at 28.7 MHz with external $BF_3 \cdot Et_2O$ as reference. Spectra at 127 MHz were recorded at UCLA.

TLC was performed to monitor reaction progress using Baker PEI-F cellulose with 6 N NH_4NO_3 as eluting solvent and $PdCl_2/HCl$ as the visualizing agent. Elemental analyses were by the UNH Instrumentation Center and Schwarzkopf Analytical Co., Woodside, NY.

The free energy of activation for $B_9H_7(SMe_2)_2$ at coalescence (T_c) was calculated with use of the Eyring equation:²⁰

$$\Delta G_c^* = 2.3RT_c [10.32 + \log (T_c/k_c)]$$

where $k_c = \pi(\Delta\nu)/2^{1/2}$ is the rate constant for exchange at the coalescence temperature and $\Delta\nu$ is the frequency difference at the slow-exchange limit.

For $B_9H_9SMe_2^-$, a modification of the above by Shanan-Atidi and Bar-Eli was used.²¹

Kinetic runs for 1,5- $B_9H_7(SMe_2)_2$ were performed at 40.4, 47.1, 52.0, and 59.9 $^{\circ}C$. Isomerization rates were obtained from integrated peak areas of the 1H NMR spectra. Rate constants were obtained graphically.²²

$(NMe_4)B_9H_8SMe_2^-$. An amount of 0.95 g (3.4 mmol) of $Rb_2B_9H_9$ was converted to $Na_2B_9H_9 \cdot xH_2O$. The white powder was dissolved in 20 mL of Me_2SO and 10 mL of acetic anhydride. After 4 h of stirring at room temperature, the reaction mixture was poured into 250 mL of 2-propanol and NMe_4OH (27% in EtOH) added to precipitate $(NMe_4)B_9H_8SMe_2^-$ as a white solid. Yields were 80–90%. Anal. Calcd for $C_6H_{26}NB_9S$: C, 9.50; H, 5.54. Found: C, 9.41; H, 5.63. Its infrared spectrum contained bands at 2500 (s), 1054 (m), 1000 (m), 955 (s), 885 (w), and 725 (w) cm^{-1} .

$PPN^+B_9H_8S(CH_3)_2^-$. Six milliliters of acetic anhydride was added dropwise to a degassed solution of 2.35 mmol $Na_2B_9H_9 \cdot xH_2O$ in 6 mL of dimethyl sulfoxide. After 4 h of stirring, the solution was poured into 100 mL of 2-propanol and filtered through Celite. A solution of 4.2 g (7.4 mmol) of $(PPN)Cl$ in 25 mL of 2-propanol was added dropwise to precipitate $PPN^+B_9H_8S(CH_3)_2^-$. The crude product was filtered and stirred in 50 mL of ethanol overnight to remove residual $(PPN)Cl$. Two recrystallizations from methylene chloride/absolute ethanol gave needlelike crystals of pure $PPN^+B_9H_8S(CH_3)_2^-$ (50% yield). The infrared spectrum recorded in KBr includes absorptions at 3080, 3000, 2500, and 2450 cm^{-1} due to the anion. The lower half of the spectrum includes the cation absorptions. Anal. Calcd for $(PPN)B_9H_8S(CH_3)_2$: C, 64.64; H, 6.28; N, 1.98; S, 4.54. Found: C, 64.34; H, 6.36; N, 2.05; S, 4.69.

$B_9H_7(S(CH_3)_2)_2$. A 4.5-mL quantity of acetic anhydride was added to a degassed solution of 500 mg (1.8 mmol) of $Rb_2B_9H_9$ in 4.5 mL of dimethyl sulfoxide. After 24 h of stirring, the solution was filtered through Celite into 160 mL of 2-propanol. Crude $RbB_9H_8S(CH_3)_2$ (90 mg) was filtered from this solution, and the filtrate was concentrated to 10 mL with a rotary evaporator. Ten milliliters of a saturated aqueous solution of NH_4Cl was added to the residue to precipitate 1.24 mmol of crude $B_9H_7(S(CH_3)_2)_2$. Recrystallization with benzene/hexane yielded clear, X-ray-quality crystals. The infrared spectrum in KBr included absorptions at 3000 (w), 2900 (w), 2500 (vs), 1425 (s), and 1350 (w) cm^{-1} as well as 1050, 1000, 975, 880, 860, 840, and 800 (m) cm^{-1} . Anal. Calcd for $B_9H_7(S(CH_3)_2)_2$: C, 21.10; H, 8.32; B, 42.59; S, 28.00. Found: C, 21.10, H, 8.58; B, 42.47; S, 28.13.

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Registry No. $(NMe_4)(B_9H_8SMe_2)$, 1-isomer, 83044-18-2; $(NMe_4)(B_9H_9SMe_2)$, 4-isomer, 83044-16-0; $(PPN)(B_9H_8SMe_2)$, 4-isomer, 83044-15-9; $(PPN)(B_9H_9SMe_2)$, 1-isomer, 83044-17-1; $[B_9H_7(SMe_2)_2]$, 1,5-isomer, 81343-16-0; $[B_9H_7(SMe_2)_2]$, 4,5-isomer, 82963-25-5; $[B_9H_7(SMe_2)_2]$, 1,8-isomer, 82963-26-6; $Na_2B_9H_9$, 82978-72-1; $Rb_2B_9H_9$, 12046-63-8; Me_2SO , 67-68-5.

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