

smaller volumes near the downstream end of the experimental section than did the products of low-temperature runs. Since quantities of product with significantly different reaction times were closest together following high-temperature runs, the lowering of calculated rate constants due to mixing would be largest for these runs, even if the extent of mixing were the same for all runs. From the pressure histories it seems likely that the extent of mixing, if any, would have increased with increasing reflected shock temperature: this would increase the error at the high end of the temperature range. We cannot assess the magnitude of mixing except to note that it was not extensive enough to introduce detectable amounts of driver gas into the product samples. However, as mixing should have no significant effect on the comparative rate analysis, this could explain the small divergence between comparative and absolute rate results in the 1100–1175° region and the resulting difference in activation energy values.

From our data and the arguments discussed above, we feel that the activation energy for *tert*-butyl alcohol decomposition to isobutene and water lies somewhere between 63.0 and 66.2 kcal/mol. Because the 66.2-kcal/mol value results in the best internal consistency among the many comparative rate experiments discussed in this report and leads to deduced parameters for a number of reactions that agree well with extrapolations of low-temperature work,^{10,11,26} we favor the higher end of the acceptable range.

Acknowledgment. We would like to thank the Sloan Foundation, the Carter-Wallace Foundation, and the Colgate University Research Council for financial support. The shock tube was donated to us by the Cabot Corporation. We would also like to thank Dr. Wing Tsang for suggesting the cyclohexene decyclization as the standard reaction for this comparative rate study.

Boron-11 Nuclear Magnetic Resonance Chemical Shift Assignments for Monohalogenated Decaborane(14) Isomers

Richard F. Sprecher,*^{1a} Brian E. Aufderheide,^{1a} George W. Luther III,^{1b} and James C. Carter^{1b}

Contribution from the Departments of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213, and University of Pittsburgh, Pittsburgh, Pennsylvania 15213. Received December 18, 1973

Abstract: Boron-11 nmr chemical shifts have been assigned for all possible isomers of monochloro-, monobromo-, and moniododecaborane(14) using the ¹¹B–¹¹B double resonance technique. The properties of 5-chlorodecaborane(14) and 6-iododecaborane(14) were reported for the first time. Chemical shifts are found to depend on the halogen and the site of substitution in a regular manner. All shift trends are dominated by the influence of the 2p orbital size on the paramagnetic shielding term (σ_p). It was suggested that a small σ_p accounts for the shielding of B₂ and B₃ relative to the rest of the cage.

Theories of the origin of the nmr chemical shift have been proposed by Saika and Slichter,^{2a} Karplus and Das,^{2b} and Pople.³ In all of those treatments, the shielding at a particular atom was found to be separable into a diamagnetic atomic term, a paramagnetic atomic term, and a term due to neighboring atoms. Applications of these theories to ¹³C chemical shifts by Karplus and Pople,⁴ Pople,⁵ and Cheney and Grant,⁶ to ¹¹B chemical shifts by Boer, *et al.*,⁷ to ¹⁴N chemical shifts by Kent and Wagner,⁸ to ¹⁷O chemical shifts by Moniz and Poranski,⁹ and to ¹⁹F chemical shifts by Saika and Slichter^{2a} and Karplus and Das^{2b} has resulted in confirmation of the theory and explanation of many em-

pirical correlations. The theory has been extended to include the effects of bonding through d orbitals by Jameson and Gutowsky,¹⁰ who also discussed periodicities in the ranges of chemical shifts in terms of an explicit dependence of the paramagnetic term on the nuclear charge. A recent study of decaborane(14) by Laws, *et al.*,¹¹ gives a detailed picture of the electronic structure of the molecule but unfortunately does not give much attention to the problem of ¹¹B chemical shifts.

I. Discussion

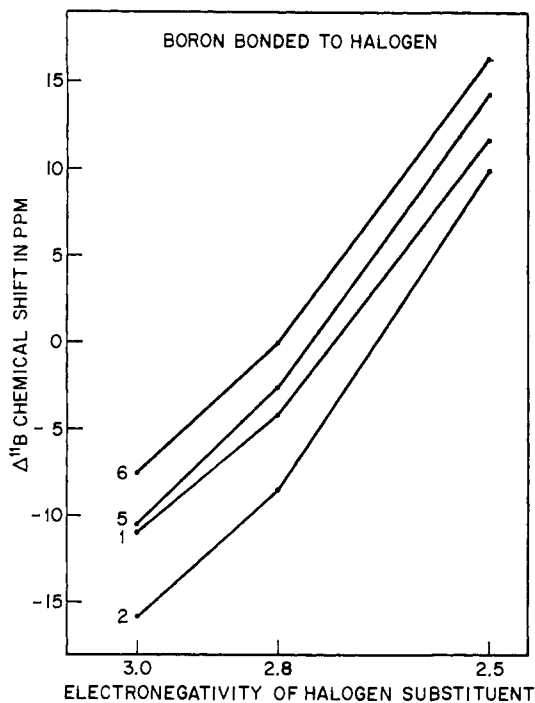
We have assigned all ¹¹B nmr chemical shifts for all of the monochloro-, monobromo-, and moniododecaboranes, using a double resonance technique,¹² and have compared the shifts with those of the parent compound. In order to explain the trends we see, one must assume that the contribution of the paramagnetic part of the

- (1) (a) Carnegie-Mellon University; (b) University of Pittsburgh.
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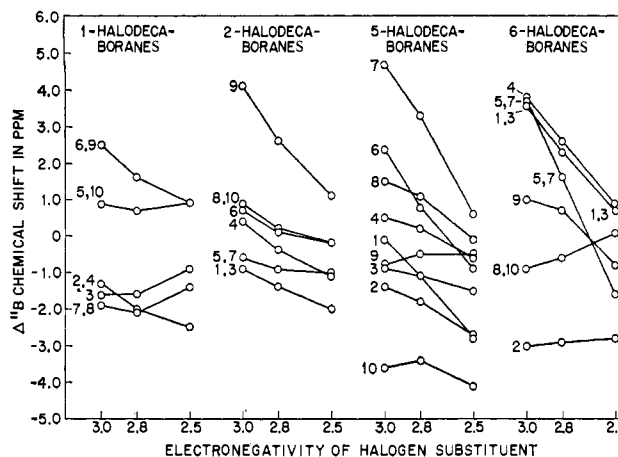
Table I. ^{11}B Chemical Shifts for Halogen-Substituted Decaborane(14) Isomers as 0.1 M Solutions in CH_2Cl_2 Referenced by External Replacement to 0.1 M TMB in CH_2Cl_2

	B ₁	B ₂	B ₃	B ₄	B ₅	B ₆	B ₇	B ₈	B ₉	B ₁₀
Decaborane(14)	6.2	54.2	6.2	54.2	17.7	7.8	17.7	17.7	7.8	17.7
1-Chlorodecaborane(14)	-4.8	52.9	4.6	52.9	18.6	10.3	15.8	15.8	10.3	18.6
2-Chlorodecaborane(14)	5.3	38.3	5.3	54.6	17.1	8.5	17.1	18.6	11.9	18.6
1-Bromodecaborane(14)	2.0	52.2	4.6	52.2	18.4	9.4	15.6	15.6	9.4	18.4
2-Bromodecaborane(14)	4.8	45.6	4.8	53.8	16.8	7.9	16.8	17.9	10.4	17.9
1-Iododecaborane(14)	17.8	51.7	5.3	51.7	18.6	8.7	16.3	16.3	8.7	18.6
2-Iododecaborane(14)	4.2	64.0	4.2	53.1	16.7	7.6	16.7	17.5	8.9	17.5
5-Chlorodecaborane(14)	6.1	52.8	5.3	54.7	7.1	10.2	22.4	19.2	7.0	14.1
6-Chlorodecaborane(14)	9.8	51.2	9.8	58.0	21.4	0.3	21.4	16.8	8.8	16.8
5-Bromodecaborane(14)	5.1	52.4	5.1	54.4	15.0	8.6	21.0	18.8	7.3	14.3
6-Bromodecaborane(14)	8.5	51.3	8.5	56.8	19.3	7.7	19.3	17.1	8.5	17.1
5-Iododecaborane(14)	3.4	51.5	4.7	53.6	31.9	6.9	18.3	17.6	7.3	13.6
6-Iododecaborane(14)	6.9	51.4	6.9	55.1	16.1	24.1	16.1	17.8	7.0	17.8

**Figure 1.** The chemical shift of the halogen-substituted boron in the halodecaboranes relative to the shift of the equivalent boron in decaborane(14). Positive Δ corresponds to an upfield shift.

shielding tensor dominates the trends. The detailed shift data and assignments are presented in Table I. Chemical shifts relative to equivalent atoms in decaborane(14) are presented in Figures 1 and 2. For want of a simple correlation, the data are presented as functions of the electronegativity of the halogen.

Shielding of the Substituted Boron. Inspection of Figure 1 immediately reveals a trend of increasing shielding of the substituted atom in the order $\sigma(\text{B-Cl}) < \sigma(\text{B-Br}) < \sigma(\text{B-I})$. This trend should be explicable in terms of the anisotropic susceptibility of the halogen atom and an induced paramagnetic shielding at the substituted boron atom. Pople¹³ has calculated the principal components of the susceptibility tensor for ^{19}F . From his equations and values of $\langle r^{-3} \rangle$ given by Jameson and Gutowsky¹⁰ for the other halogens, one can readily infer that the anisotropies of the atomic susceptibilities ($\Delta\chi$) will be in the order $\Delta\chi(\text{F}) > \Delta\chi(\text{Cl}) > \Delta\chi(\text{Br}) > \Delta\chi(\text{I})$, if we assume that the contribution from

(13) J. A. Pople, *J. Chem. Phys.*, **37**, 60 (1962).**Figure 2.** The chemical shift of the nonsubstituted borons relative to the shift of the equivalent boron in decaborane(14). Positive Δ corresponds to an upfield shift.

the filled d and f orbitals is small. Because $\Delta\chi(\text{X})$ is in the sense of excess diamagnetism along the B-X bond axis, we must expect shielding at boron in the order $\sigma(\text{B-F}) > \sigma(\text{B-Cl}) > \sigma(\text{B-Br}) > \sigma(\text{B-I})$. Such is not the case and we look to the induced paramagnetic term for an explanation. As noted by Karplus and Pople,⁴ an electronegative substituent can contribute to a paramagnetic shielding (σ_p^{AA}) through the polarity parameter¹⁴ and through changes in the dimension of the 2p orbital on the atom induced by changes in the orbital population. While the first effect is expected to be small⁴ and yields the trend $|\sigma_p^{\text{AA}}(\text{B-Cl})| < |\sigma_p^{\text{AA}}(\text{B-Br})| < |\sigma_p^{\text{AA}}(\text{B-I})|$, the second effect can be expected to be significant. The influence of $\langle r^{-3} \rangle_{2p}$ changes on ^{13}C shifts is well documented.⁴⁻⁶ While ^{11}B shifts should be less sensitive to orbital population changes because of the smaller effective Z for ^{11}B , the term must still be important. The effect of the electronegativity of the halogen on $\langle r^{-3} \rangle_{2p}$ leads to paramagnetic terms in the order $|\sigma_p^{\text{AA}}(\text{B-Cl})| > |\sigma_p^{\text{AA}}(\text{B-Br})| > |\sigma_p^{\text{AA}}(\text{B-I})|$, which agrees with the observed trend. Substitution of I for H leads to shielding of the substituted boron and is readily explained by the observation that $\Delta\chi(\text{H})$ must be zero.¹³ Thus, B-X must be shielded relative to B-H. Part of this shielding is canceled by σ_p^{AA} and the superposition of the opposing trends leads to a roughly linear correlation of $\Delta\delta$ with electronegativity as seen in Figure

(14) C. A. Coulson, "Valence," Oxford University Press, New York, N. Y., 1952.

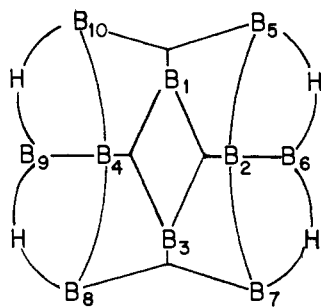


Figure 3. Numbering scheme and topological representation for decaborane(14) (B = B-H).

1. The smaller dependence on the site of substitution parallels a trend in the variance of $\Delta\delta$ for the unsubstituted atoms. As we will show later, this may relate to interactions between the nonbonding orbitals on the halogen and the bonding orbitals in the cage.

Shielding of the Unsubstituted Borons. In the average excitation energy approximation, one generally assumes the mean excitation energy does not vary in the series under consideration. We feel this approximation is justified here, for although decaborane(14) has low-lying nonbonding orbitals,¹⁵ the electron-deficient nature of the bonding results in 16 unoccupied levels *vs.* 8 occupied levels in a minimum basis set calculation. Thus perturbation of a few unoccupied levels is not likely to affect ΔE strongly. Of greater consequence could be the perturbation of an occupied bonding level. We assume that such a perturbation could arise from interactions between the nonbonding orbitals on the halogen substituent and the cage framework orbitals. Such interactions would lead to an alteration of the orbital populations relative to those in decaborane(14) and would primarily lead to changes in σ_p^{AA} according to the principles given by Pople.³ If the net result is a donation of electron density to the cage, then we would expect the magnitude of the donation to be in the order Cl > Br > I because the overlap between the 2s,p orbitals on B and the *ns,p* orbitals on X decreases with increasing *n*. The result is an increase of $\langle r^{-3} \rangle$ and $|\sigma_p^{AA}|$ with increasing *n*. We expect then to see a general shielding in the order $\sigma(\text{Cl}) > \sigma(\text{Br}) > \sigma(\text{I})$. Such a trend is seen in the mean shift values ($\overline{\Delta\delta}$) for substitution at a particular site as shown in Table II. The shifts also show a variation in the sensitivity to the site of substitution and the halogen substituent as indicated by the variance (k_2) of the shift from the mean value.

The sensitivity toward substitution of chlorine for

Table II. Mean ¹¹B Shifts Relative to Equivalent Atoms in Decaborane(14)^a

Site	Cl[0.37] ^b	Br[0.39]	I[0.35]
1	-0.13 (3.39) ^c	-0.58 (2.81)	-0.57 (2.20)
2	0.44 (2.46)	-0.21 (1.52)	-0.73 (0.96)
5	0.26 (5.77)	-0.28 (3.69)	-1.40 (2.29)
6	1.62 (6.96)	0.78 (3.33)	-0.48 (1.67)

^a The shift of the substituted boron is not included in the calculation. ^b Hammett σ for halogens from J. Hine, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1962, p 87. ^c k_2 (variance as defined by E. S. Keeping, "Introduction to Statistical Inference," Van Nostrand, Princeton, N. J., 1962, p 36).

(15) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963.

hydrogen at B₅ or B₆ would seem to be reflecting the electron deficient nature of that part of the cage. However, interaction between the halogen *n* orbitals and open three-center boron bonds should be stronger than the corresponding interaction with closed three-center bonds. In addition, $\langle r^{-3} \rangle_{2p}$ is more sensitive to change in orbital population when that population is small. Because all of these effects are expected to yield the same trends, we decline to single out one of them without detailed calculations. The regular decrease in k_2 on going through the series Cl, Br, and I is as we expect on the basis of decreasing overlap between the halogen *n* orbitals and the cage. The relative insensitivity to substitution at B₁ coupled with a strong correlation of that $\overline{\Delta\delta}$ with the Hammett σ leads us to suspect an inductive component to the trends but we would not expect it to be a long-range effect,⁶ and it is certainly not a dominant one in the B₂-, B₅-, and B₆-substituted series.

Examination of Figure 2 reveals a regular pattern in the direction of the shifts relative to decaborane(14). Atoms directly attached to the substituted site tend to be deshielded and those with one atom intervening tend to be shielded. Long-range effects are also obvious with the most striking being the behavior of B₉ on Cl substitution at B₂. A full explanation of these data must await a detailed quantum mechanical treatment.

Shielding in Decaborane(14). We feel that enough qualitative trends are available to allow us to suggest an origin for the decaborane(14) shifts. Calculations by Lipscomb¹⁵ and Laws, *et al.*,¹¹ show a charge density in the algebraic order 2, 4 << 1, 3 < 5, 7, 8, 10 < 6, 9. Increasing electron density will result in expansion of the 2p orbitals with a resultant decrease in $|\sigma_p^{AA}|$. If this effect outweighs the tendency of the bond order and charge density matrix elements to increase $|\sigma_p^{AA}|$, then the net result of increased electron density will be shielding. We suggest that this effect is the primary contribution to the shielding of B₂ and B₄ relative to the rest of the cage. Accordingly, B₁ and B₃ are slightly deshielded relative to our expectations. This can be rationalized in terms of a small paramagnetic contribution at B₁ and B₃ from local circulation on B₂ and B₄.

II. Results

Syntheses. Decaborane(14) has C_{2v} symmetry and can be topologically represented by the diagram in Figure 3. Four different monosubstituted decaborane isomers are possible if one of the nonbridged hydrogens is replaced by some functional group. There are three halogenation reactions known, each of which produces varying mixtures of the four possible monohalo isomers. An uncatalyzed reaction of iodine with decaborane(14) produces a mixture of 1- and 2-monoiodinated species.¹⁶ An AlCl₃-catalyzed reaction between decaborane(14) and bromine or chlorine produces corresponding mixtures of 1- and 2-brominated or 1- and 2-chlorinated decaboranes.¹⁷ A mixture of decaborane isomers halogenated at the 5 and 6 borons is obtained from the reaction of the anhydrous hydrogen halide with a decaborane dialkyl sulfide diligand, B₁₀H₁₂(SR₂)₂.¹⁸ The

(16) M. Hillman, *J. Amer. Chem. Soc.*, **82**, 1096 (1960).

(17) L. Zakharkin and V. Kalinin, *Zh. Obshch. Khim.*, **36**, 2160 (1966).

(18) B. Štíbr, J. Plešek, and S. Heřmánek, *Collect. Czech. Chem. Commun.*, **34**, 194 (1969).

ligand is made by direct combination of decaborane(14) and the dialkyl sulfide. In most cases, these halogenation reactions also produce small amounts of other monohalogenated and dihalogenated products.

Shift Assignments. Boron-11 nuclear magnetic resonance shift assignments have been made for decaborane(14) through a series of iodination¹⁹ and deuteration²⁰ studies. Tentative shift assignments have also been made for some of the monohalogenated decaboranes.²¹⁻²⁴ Recently, ¹¹B double resonance experiments were used to obtain chemical shift assignments for 6-methyldecaborane(14).¹² We have used the same technique to obtain complete ¹¹B shift assignments for the 12 possible chlorinated, brominated, and iodinated decaboranes.

The ¹¹B-¹¹B double resonance experiment is similar to the transitory selective irradiation experiment described by Hoffman and Forsén,²⁵ except that the observing field (H_1) is not swept through the transition under examination but rather remains on that transition throughout the experiment. The perturbing field (H_2) is swept through the remainder of the spectrum repeatedly and the response to H_1 is accumulated as a function of the frequency of H_2 . We follow Hoffman and Forsén in the analysis of the intensity perturbations to be expected in the experiment.

For simplicity we will consider two coupled spin $3/2$ nuclei in the limit of $\delta \gg J$. The product functions are then the eigenfunctions and the energy level diagram is that given by Sprecher and Carter¹² and is reproduced in Figure 4. The spectrum is seen to be composed of two sets of four triply degenerate lines. In the high-temperature limit the equilibrium population of a state is given by

$$p = N_0(1 - (F_2 h\nu_0/kT))$$

where N_0 is the average population, F_2 is the total spin in units of $h/2\pi$, and ν_0 is the mean precession frequency. If we let $N_0 h\nu_0/kT$ be represented by K and discuss populations relative to N_0 , then the equilibrium population of state $\delta\delta$ is $3K$, that of states $\delta\gamma$ and $\gamma\delta$ is $2K$, and so on. To first order the sum of the equilibrium intensities of transitions 1, 3, and 7 is $3K$. After an adiabatic fast passage of H_2 through the degenerate transitions 2, 6, and 12, the populations of states $\delta\delta$ and $\alpha\delta$ will be interchanged, as will those of states $\gamma\delta$ and $\beta\delta$. The sum of intensities of transitions 1, 3, and 7 will be $0K$ after the passage and the change will be $-3K$. Similar reasoning leads to a change of $0K$ on passage through 4, 10, 14 and 8, 16, 20 and a change of $3K$ on passage through 18, 22, 24. The same considerations lead to changes in the intensity of 5, 9, 17 of $-K$, 0, 0, and K on passage through 2, 6, 12; 4, 10, 14; 8, 16, 20; and 18, 22, 24. Thus, we expect H_2 to have the largest effect on the outermost lines of the monitored multiplet and then only when H_2 passes through the

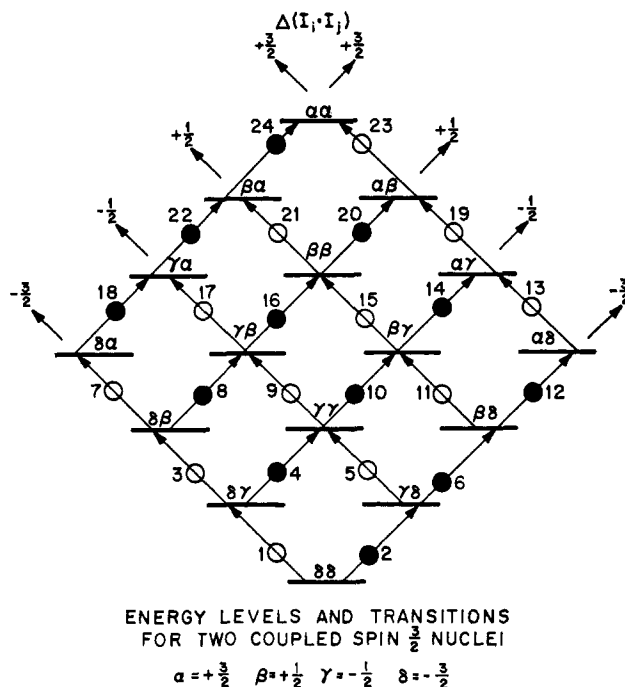


Figure 4. Energy levels and transitions for two coupled spin $3/2$ nuclei.

outermost lines of the connected multiplet. The directions of the intensity changes will reverse if the high-field side rather than the low-field side of the resonance is monitored.

In order to attain an adiabatic fast passage of H_2 , the sweep rate and H_2 must satisfy the relationship

$$T_1^{-1} \ll H_2^{-1} dH_0/dt \ll \gamma H_2$$

In a typical experiment, the frequency of H_2 is swept at a rate equivalent to 1.8 G sec^{-1} and Allerhand²⁶ gives a value of 0.1 sec for T_1 in decaborane(14). Thus a value of H_2 between 0.01 and 0.2 G is required and is readily obtained with most spectrometers.

The above discussion assumes the equilibrium populations would be reestablished in the time required to sweep H_2 from one line to the next. If $J = 20 \text{ Hz}$ the above conditions result in passage of H_2 through all transitions in 0.025 sec, which is about $T_1/4$, and the assumption is not valid. An analysis along the same lines, but assuming no reequilibration, shows that the change in the sum of the intensities of transitions 1, 3, and 7 on passage through 2, 6, 12; 4, 10, 14; 8, 16, 20; and 18, 22, 24 will be $-3K$, $-3K$, $-3K$, and $0K$. On passage through the same set of transitions, the change in the sum of intensities of transitions 13, 19, and 23 will be $3K$, $3K$, $3K$, and $0K$. We have observed both line shapes under identical conditions and attribute the observation to variations of T_1 with the position of the boron atom in the cage. The intensity changes we observe are much smaller than the maximum theoretical effects, which we attribute to the conflicting requirements of adiabaticity and T_1 processes.²⁵

1-Bromodecaborane(14) has a symmetry plane containing B_1 and B_3 . Both are unique borons, B_1 appearing as a one-boron singlet and B_3 as a one-boron

(19) R. Schaeffer, J. N. Shoolery, and R. Jones, *J. Amer. Chem. Soc.*, **79**, 4606 (1957).

(20) R. E. Williams and I. Shapiro, *J. Chem. Phys.*, **29**, 677 (1958).

(21) R. Schaeffer, J. N. Shoolery, and R. Jones, *J. Amer. Chem. Soc.*, **80**, 2670 (1958).

(22) R. E. Williams and T. P. Onak, *J. Amer. Chem. Soc.*, **86**, 3159 (1964).

(23) R. E. Williams and E. Pier, *Inorg. Chem.*, **4**, 1357 (1965).

(24) P. Sedmera, F. Hanousek, and Z. Samek, *Collect. Czech. Chem. Commun.*, **33**, 2169 (1968).

(25) R. A. Hoffman and S. Forsén, "Progress in Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press, Oxford, 1966.

(26) A. Allerhand, J. D. Odom, and R. E. Moll, *J. Chem. Phys.*, **50**, 5037 (1969).

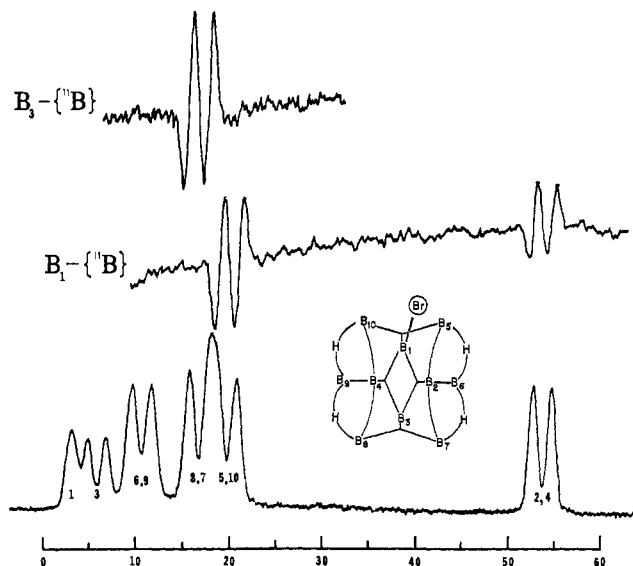


Figure 5. Boron-11 nmr assignments and double resonance spectra of 1-bromodecaborane(14). The scale is in terms of ppm upfield from trimethyl borate.²⁷

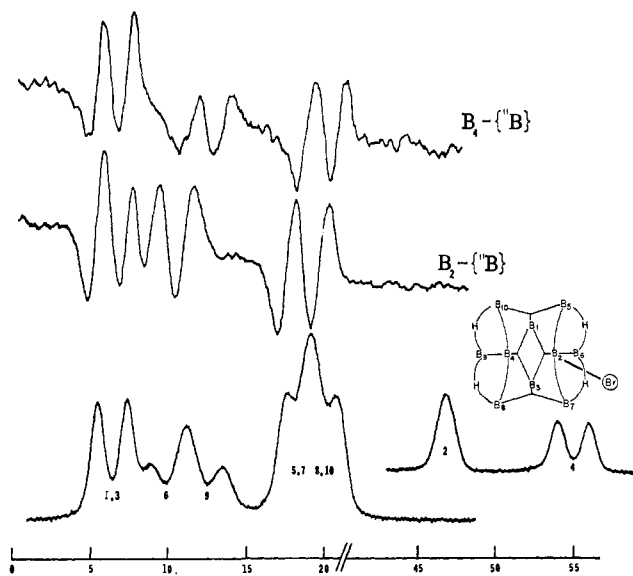


Figure 6. Boron-11 nmr assignments and double resonance spectra of 2-bromodecaborane(14). The scale is in terms of ppm upfield from trimethyl borate.²⁷

doublet (Figure 5).²⁷ They can be assigned on this basis. There are also four, two-boron doublets, which arise from four different symmetry equivalent pairs: $B_{2,4}$, $B_{5,10}$, $B_{6,9}$, and $B_{7,8}$. B_1 should be coupled to B_3 , $B_{2,4}$, and $B_{5,10}$. When the B_1 resonance is monitored with H_1 , and the rest of the spectrum is swept with H_2 , we note that H_2 perturbs the intensity of the B_1 resonance when at 18.4 and 52.2 ppm, the positions of the two low-frequency two-boron doublets. Coupling to the one-boron doublet, B_3 , is not seen because of interference between H_1 and H_2 . B_3 should be coupled to B_1 , $B_{2,4}$, and $B_{7,8}$. While monitoring B_3 , coupling is observed with the two-boron doublet at 52.2 ppm and with the two-boron doublet at 15.6 ppm. The only two equivalent borons coupled to both B_1 and B_3 are

(27) $B_n - \{^{11}B\}$ indicates that the intensity of B_n was observed while the rest of the spectrum was swept with H_2 .²⁶

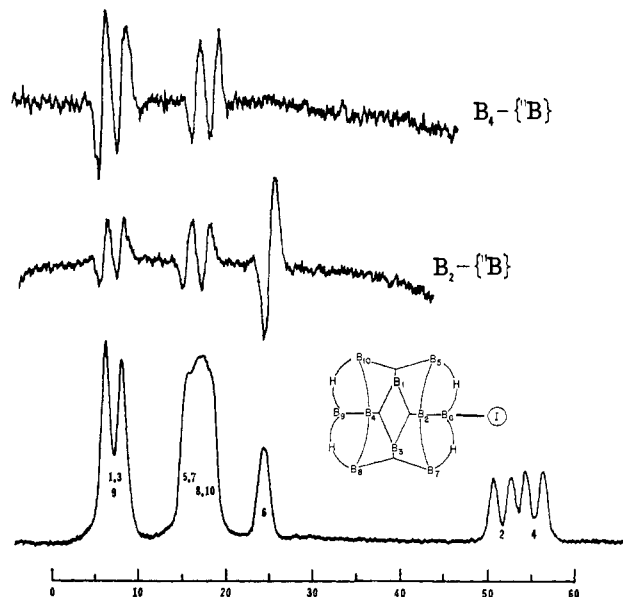


Figure 7. Boron-11 nmr assignments and double resonance spectra of 6-iododecaborane(14). The scale is in terms of ppm upfield from trimethyl borate.²⁷

B_2 and B_4 . Therefore, the two-boron doublet at 52.2 ppm is assigned to $B_{2,4}$. The doublet at 15.6 ppm must be due to $B_{7,8}$. The resonance at 18.4 ppm can be assigned to $B_{5,10}$ as it shows coupling with B_1 and is not coupled to B_3 . The two-boron doublet at 9.4 ppm which is coupled to neither B_1 nor B_3 is then $B_{6,9}$.

2-Bromodecaborane(14) has a symmetry plane defined by B_2 , B_4 , B_6 , and B_9 . B_2 appears as a one-boron singlet (Figure 6) while B_1 , B_6 , and B_9 appear as one-boron doublets. There are also three different symmetry equivalent pairs: $B_{1,3}$, $B_{5,7}$, and $B_{8,10}$. B_2 is assigned to the one-boron singlet and should be coupled to $B_{1,3}$, $B_{5,7}$, and B_6 . Monitoring the B_2 resonance, we note coupling with a one-boron doublet and a pair of two-boron doublets. The one-boron doublet at 7.9 ppm is assigned to B_6 . Two, one-boron doublets remain to be assigned, B_4 and B_9 . B_9 should be coupled to only B_1 .¹² Observing the unassigned one-boron doublet at 53.8 ppm, we see coupling with a pair of two-boron doublets and the other unassigned one-boron doublet. The one-boron doublet at 53.8 ppm is necessarily B_4 . The two-boron doublet at 4.8 ppm is coupled to B_4 and as we noted previously B_2 . It is, therefore, assigned to $B_{1,3}$. The one-boron doublet coupled to only B_4 is B_9 . This leaves a pair of two-boron doublets, that coupled to B_2 is $B_{5,7}$ and that coupled to B_4 is $B_{8,10}$.

6-Iododecaborane(14) has a symmetry plane containing B_2 , B_4 , B_9 , and B_6 . The first three should appear as one-boron doublets and B_6 as a one-boron singlet. The three symmetry equivalent pairs are $B_{1,3}$, $B_{5,7}$, and $B_{8,10}$. The one-boron singlet is assigned to B_6 (Figure 7). Monitoring the one-boron doublet at 51.4 ppm, we observe coupling with B_6 , a two-boron doublet at 6.9 ppm, and a two-boron doublet at 16.1 ppm. The only boron coupled to B_6 is B_2 and, therefore, the one-boron doublet at 51.4 ppm can be assigned to B_2 . Two, one-boron doublets remain to be assigned, B_1 and B_9 . B_9 is coupled to only B_4 , while B_4 is coupled to $B_{1,3}$, B_9 , and $B_{8,10}$. The one-boron doublet at 55.1 ppm

shows coupling to the two-boron doublet at 6.9 ppm and the one-boron doublet at 7.0 ppm with which it overlaps as well as the two-boron doublet at 17.8 ppm. The resonance at 55.1 ppm cannot be B₉ because it is coupled to five other borons, thus it must be B₄. The two-boron doublet at 6.9 ppm which is coupled to both B₂ and B₄ can then be assigned to B_{1,3}. The remaining one-boron doublet at approximately 7.0 ppm which overlaps with B_{1,3} and is coupled to B₄ is then assigned to B₉. The only coupling to B₂ yet to be assigned is to the two-boron doublet at 16.1 ppm which must be due to B_{5,7}. The other two-boron doublet which overlaps with B_{5,7} and is coupled to B₄ is necessarily B_{8,10}.

Decaborane(14) substituted in the 5 position is totally asymmetric leading to a resonance spectrum due to ten nonequivalent borons. The spectrum of 5-bromodecaborane(14) is shown in Figure 8 and the double resonance experiments are summarized in Table III. The

Table III. ¹¹B-¹¹B Double Resonance Experiments Needed to Assign Shifts for 5-Bromodecaborane(14)^a

	B _{1,3}	B ₉	B ₆	B ₁₀	B ₅	B ₈	B ₇	B ₂	B ₄
Monitoring B ₂	X ^b		X		X		X	--	
Monitoring B ₄	X ^b	X		X		X		--	--
Monitoring B ₇	X				X	--	--	X	
Monitoring B ₈	X			--		--	--		X
Monitoring B ₁₀	X			--	--	X			X

^a X indicates coupling was observed to the monitor d boron. The symbol -- refers to a position at which interference of H₁ and H₂ precludes observation of coupling. ^b The amplitude of this perturbation was twice as intense as usual.

one-boron singlet at 15.0 ppm is assigned to B₅. We note that only four borons B₁, B₂, B₃, and B₄ should be coupled to five other boron atoms as are the doublets at 52.4 and 54.4 ppm. An effect of double intensity at 5.1 ppm is repeated in both experiments. This indicates that both of the accidentally degenerate borons at 5.1 ppm are coupled to the doublets at 52.4 and 54.4 ppm. These two, one-boron doublets must be either B₂ and B₄ or B₁ and B₃ and the degenerate pair to which they are coupled is necessarily the remaining pair. B₆ and B₉ must be determined to make a more definitive assignment of B₁, B₂, B₃, and B₄. Three experiments, in which the one-boron doublets at 14.3, 18.8, and 21.0 ppm were monitored, showed that each doublet was coupled to more than one boron. These three cannot include B₆ or B₉ since B₆ should be coupled to only B₂ and B₉ should be coupled to only B₄. This leaves the two remaining doublets at 8.6 and 7.3 ppm to be assigned as B₈ and B₉. The doublet at 52.4 ppm, formerly assigned as a member of the B₁, B₂, B₃, and B₄ set, is coupled to B₅ and to the doublet at 8.6 ppm. The doublet at 52.4 ppm is, therefore, B₂ and that resonance (at 8.6 ppm) to which it is coupled is B₆. The resonance at 7.3 ppm can then be assigned to B₉ and the doublet at 54.4 ppm to which it is coupled is due to B₄. The two accidentally degenerate doublets at 5.1 ppm which are coupled to both B₂ and B₄ are assigned to B₁ and B₃. Of the five borons coupled to B₂, the only one yet to be assigned is that at 21.0 ppm which must be B₇. Only B₈ and B₁₀ remain. Observing the doublet at 14.3 ppm, we see that it is coupled to B₁ or B₃ and B₄, as expected for either B₈ or B₁₀, but it is not coupled to B₇ and thus must be B₁₀. The reverse experiment was performed to

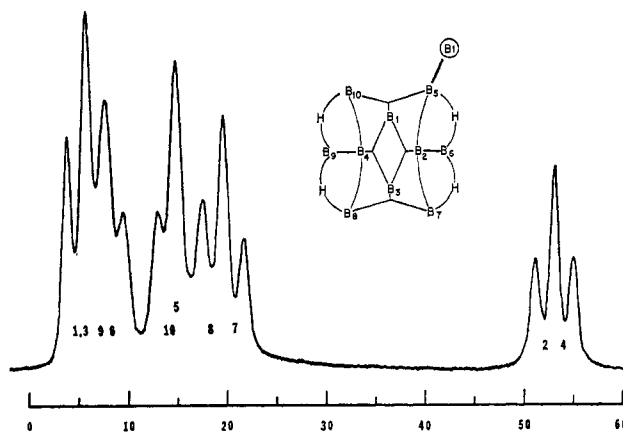


Figure 8. Boron-11 nmr assignments of 5-bromodecaborane(14). The scale is in terms of ppm upfield from trimethyl borate.

confirm the assignment, and while observing B₇ coupling is seen to B₅, none is seen to the underlying doublet B₁₀.

Shift assignments for the remaining eight chlorinated, brominated, and iodinated decaboranes were accomplished in a similar manner. The chemical shifts determined in this study are presented in Table I.

III. Experimental Section

The halodecaboranes reported in this paper are all white crystalline solids and are air sensitive; the 5 and 6 isomers are generally much more sensitive than the 1 and 2 isomers. Most work was performed either *in vacuo* or under dry nitrogen. Melting points of all 1- and 2-halodecaboranes were taken in sealed capillaries while those of the 5- and 6-halodecaboranes were taken on the cold finger onto which the material had been sublimed. All melting points were corrected and except for 5-iododecaborane(14) compared well with those recently reported by Hanousek, *et al.*²⁸ Tlc, high resolution mass spectral data reported in Table IV, and

Table IV. High Resolution Mass Spectral Data

	Ion	Obsd m/e	Calcd m/e	Error
5-Chlorodecaborane(14)	¹⁰ B ¹¹ B ₉ ¹ H ₇ ³⁵ Cl	151.1214	151.1203	-0.0011
	¹⁰ B ¹¹ B ₉ ¹ H ₉ ³⁶ Cl	153.1374	153.1360	-0.0014
	¹⁰ B ₂ ¹¹ B ₈ ¹ H ₉ ³⁶ Cl	152.1396	152.1396	0.0000
5-Iododecaborane(14)	¹¹ B ₁₀ ¹ H ₇ ¹²⁷ I	152.1184	152.1167	-0.0017
	¹⁰ B ₈ ¹¹ B ₇ ¹ H ₉ ¹²⁷ I	243.0784	243.0788	0.0004
	¹⁰ B ¹¹ B ₉ ¹ H ₇ ¹²⁷ I	243.0551	243.0559	0.0008
	¹⁰ B ¹¹ B ₆ ¹ H ₉ ¹²⁷ I	242.0822	242.0825	0.0003
6-Iododecaborane(14)	¹⁰ B ₂ ¹¹ B ₈ ¹ H ₇ ¹²⁷ I	242.0598	242.0596	-0.0002
	¹¹ B ₁₀ H ₁₃ ¹²⁷ I	250.0960	250.0992	0.0032
	¹⁰ B ₂ ¹¹ B ₈ ¹ H ₁₃ ¹²⁷ I	248.1046	248.1065	0.0019
	¹⁰ B ¹¹ B ₉ ¹ H ₇ ¹²⁷ I	243.0545	243.0559	0.0014
	¹⁰ B ₃ ¹¹ B ₇ ¹ H ₉ ¹²⁷ I	243.0767	243.0788	0.0021
	¹⁰ B ¹¹ B ₉ ¹ H ₇ ¹²⁷ I	245.0699	245.0716	0.0017

¹H and ¹¹B nmr data lead us to believe the sample of 5-iododecaborane(14) to be pure. The properties of 5-chlorodecaborane(14) and 6-iododecaborane(14) have not been previously reported and their mass spectral data are included in Table IV.

The data were taken on an AEI MS-9 mass spectrometer. Each isomer displayed the large number of fragments with intensity ratios expected for a molecule having ten boron atoms (¹¹B = 81.3%; ¹⁰B = 18.7%), possibly two halogen isotopes and large proton losses. In each case, the peak of highest m/e ratio agreed with that expected. The preparative thin layer chromatography (tlc) plates used in the purification of the halodecaborane isomers

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reported in this paper were 20 × 20 cm and coated with a 1-mm layer of Mallinckrodt Silic AR TLC-7GF silica gel. The plates were activated at 100–105° for over 2 hr and used immediately after removal from the oven. A 3:1 mixture of hexane:benzene produced R_f values of approximately 0.7 for 6-halodecaboranes, 0.6 for 5-halodecaboranes, 0.4 for 1-halodecaboranes, and 0.3 for 2-halodecaboranes with the exact value varying slightly with each compound, activation time, and amount of material used.

Linde 5 Å molecular sieves were used in the preparation of 5- and 6-bromodecaborane(14) and 5- and 6-iododecaborane(14) to adsorb the dimethyl sulfide liberated by the reaction. They were found to have a slight effect on the relative yields of the two isomers in both reactions. The sieves also act as a buffer and tend to regulate the halogen acid concentration. Removal of dimethyl sulfide by distillation²⁹ or by use of molecular sieves gave comparable overall yields of products in the reaction with HBr.

Boron-11 spectra were recorded at 80.2 MHz on the time-sharing nmr spectrometer at the NIH Facility for Biomedical Research in Pittsburgh, Pa. For ¹¹B–¹¹B double resonance experiments, the spectrometer was operated in the linear frequency sweep mode under program control using a Xerox Data Systems (XDS) Sigma 5 computer with a 15 bit digital to analog converter. The data were collected at the output of a Princeton Applied Research Model 121 synchronous detector using an XDS Model MD 51 analog to digital converter. A total of 4096 sample points were collected on each sweep, accumulated in memory, and then plotted on a Hewlett-Packard recorder. All chemical shifts were derived from single sweep slow passage spectra run in that mode under standard conditions. Spectra were calibrated by counting the swept radiofrequency. Each sample was run at a concentration of 0.1 M in CH₂Cl₂ and referenced by replacement to a sample of 0.1 M TMB in CH₂Cl₂. The susceptibility correction under these conditions is negligible. Concentrations of >0.1 M were necessary for the ¹¹B–¹¹B double resonance experiments, but the appearance of the spectrum did not change with increasing concentration, and, therefore, assignments made at higher concentrations were carried over to the 0.1 M standard spectra. Nuclear magnetic resonance data are collected in Table I and high resolution mass spectral data are collected in Table IV.

1-Chlorodecaborane(14) (1) and 2-Chlorodecaborane(14) (2). Under a nitrogen atmosphere, 30 ml of dry methylene chloride was distilled into a 50-ml three-necked round-bottom flask containing 2.0 g (0.016 mol) of decaborane(14). A Teflon magnetic stirring bar and 0.1 g of AlCl₃ were then added. Using dry nitrogen as a carrier gas, 350 ml (0.016 mol) of chlorine gas was bubbled through the decaborane solution at 10° over a period of 1 hr. The methylene chloride was then evaporated *in vacuo* and the residue of 2.4 g (81% yield of monochlorodecaboranes) was shown by ¹¹B nmr to be approximately 70% **2**, 15% **1**, and 15% unreacted starting material. The residue was extracted three times with 25-ml portions of boiling hexane. The solution was then cooled to –10° for 10 hr to allow much of **2** to precipitate. The crystals were filtered, recrystallized from hexane, and sublimed *in vacuo* to give pure **2**, mp 94.5–95° (lit.²⁸ mp 86.5–88°), *m/e* obsd 160 (calcd for ¹¹B₁₀H₁₃³⁷Cl, 160). A second crop of **2** was obtained upon evaporation of the mother liquor to half the original volume and subsequent cooling. From the solution remaining, **1** was isolated by preparative tlc over silica gel. It was then recrystallized from hexane and sublimed *in vacuo* to give **1**, mp 71–72° (lit.²⁸ 74–75°), *m/e* obsd 160 (calcd for ¹¹B₁₀H₁₃³⁷Cl, 160).

1-Bromodecaborane(14) (3) and 2-Bromodecaborane(14) (4). A 50-ml three necked round-bottom flask was equipped with a nitrogen inlet and outlet and a pressure equalized dropping funnel containing 2.5 g (0.031 mol) of bromine and 5 ml of dry carbon disulfide. Another 25 ml of dry carbon disulfide was distilled into the round-bottom flask under nitrogen and then 2.0 g (0.016 mol) of decaborane, 0.1 g of AlCl₃, and a stirring bar were added. The bromine solution was added at 10° over a period of 30 min and the reaction mixture was then allowed to warm to room temperature. The carbon disulfide was evaporated *in vacuo* and the residue of 3 g (94% yield of monobromodecaboranes) was shown by ¹¹B nmr to be 80% **4** and 20% **3**. The residue was extracted three times with 25-ml portions of refluxing hexane. The combined extracts were cooled to –10° to allow **4** to precipitate. The crystals were filtered, recrystallized from hexane, and sublimed *in vacuo* to give

pure **4**, mp 107–108° (lit.²⁸ 108–109.5°), *m/e* obsd 204 (calcd for ¹¹B₁₀H₁₃⁸¹Br, 204). The mother liquors were enriched in **3** by fractional crystallization of most of the remaining **4**. Preparative tlc, recrystallization from hexane, and sublimation *in vacuo* produced pure **3**, mp 90.5–91° (lit.²⁸ 92–93°), *m/e* obsd 204 (calcd for ¹¹B₁₀H₁₃⁸¹Br, 204).

1-Iododecaborane(14) (5) and 2-Iododecaborane(14) (6). Into a dried, thick-walled glass tube, which had been sealed at one end, was placed 2.0 g (0.016 mol) of decaborane(14) and 4.0 g (0.031 mol) of iodine. The tube was evacuated, sealed off, heated at 115° for 24 hr, cooled, and opened. The product was extracted three times with 25-ml portions of refluxing hexane and shown to be approximately 60% **6**, 35% **5**, and 5% unreacted starting material. The solution was cooled to –10° upon which **6** precipitated. The solid was recrystallized from hexane and sublimed *in vacuo* to produce pure **6**, mp 117.5–118° (lit.²⁸ 117.5–119°), *m/e* obsd 250 (calcd for ¹¹B₁₀H₁₃¹²⁷I, 250). **5** was concentrated in the mother liquor by further fractional crystallization of **6** and then finally purified by preparative tlc, recrystallization from hexane, and sublimation *in vacuo* to give pure **5**, mp 99.5–100° (lit.²⁸ 98.5–100°), *m/e* obsd 250 (calcd for ¹¹B₁₀H₁₃¹²⁷I, 250).

General Procedure for 5- and 6-Halodecaboranes. A 100-ml three-neck round-bottom flask was equipped with a gas inlet, mechanical stirrer, and gas outlet to a liquid nitrogen trap. Dry benzene was distilled under nitrogen into the flask to which had been added 4.0 g (0.016 mol) of B₁₀H₁₂[S(CH₃)₂]³⁰ and 12 g of Linde 5 Å molecular sieves. Approximately 2 equiv (0.032 mol) of dry hydrogen halide was then bubbled through the stirred solution over a period of 1 to 2 hr. The solution was allowed to stand for one more hour under a positive hydrogen halide pressure and then the benzene was evaporated *in vacuo* and the residue extracted three times with 30-ml portions of boiling hexane. The extract was evaporated to one-third the original volume and cooled to –10°. After sufficient time, the small amount of unreacted decaborane(14) and dihalogenated and other monohalogenated products present precipitated, leaving a mixture of 5- and 6-halodecaboranes.

5-Chlorodecaborane(14) (7) and 6-Chlorodecaborane(14) (8). Approximately 1.2 g (0.032 mol) of dry HCl was bubbled through the B₁₀H₁₂[S(CH₃)₂]₂ solution. Molecular sieves were not used. The 1.5 g (60% yield of monochlorodecaboranes) of viscous residue was shown by ¹¹B nmr to be approximately 95% **8** and less than 5% **7**. The mixture was separated by preparative tlc, recrystallized from hexane at –70°, and sublimed *in vacuo* to give pure **8**, mp 28–29° (lit.²⁸ 31–32°) and *m/e* obsd 160 (calcd for ¹¹B₁₀H₁₃³⁷Cl, 160), and **7**, mp 17–19.5° and *m/e* obsd 160 (calcd for ¹¹B₁₀H₁₃³⁷Cl, 160).³¹

5-Bromodecaborane(14) (9) and 6-Bromodecaborane(14) (10). The reaction of 2.5 g (0.032 mol) of dry HBr with B₁₀H₁₂[S(CH₃)₂]₂ produced 3.1 g (96% yield of monobromodecaborane) of a viscous mixture shown by ¹¹B nmr to be approximately 80% **10** and 20% **9**. The mixture was separated by preparative tlc, recrystallized from hexane at –70°, and sublimed *in vacuo* to give pure **10**, mp 28.5–30° (lit.²⁸ 32–34°) and *m/e* obsd 204 (calcd for ¹¹B₁₀H₁₃⁸¹Br, 204), and pure **9**, mp 46–48° (lit.²⁸ 48–49°) and *m/e* obsd 204 (calcd for ¹¹B₁₀H₁₃⁸¹Br, 204).

5-Iododecaborane(14) (11) and 6-Iododecaborane(14) (12). Gaseous hydrogen iodide was generated by slowly dropping 8.5 g of a 47% solution of hydrogen iodide (0.032 mol) in water onto phosphorus pentoxide and then flushing through the solution of B₁₀H₁₂[S(CH₃)₂]₂ with dry nitrogen. A product of 0.62 g (16% yield of monoiododecaboranes) was shown by ¹¹B nmr to be 60% **11**, 35% **12**, and a small amount of starting material and dihalogenated decaboranes. The compounds were purified by preparative tlc, recrystallized from hexane at –70°, and sublimed *in vacuo* to give pure **11**, mp 56.5–57.5° (lit.²⁸ 70–72.5°) and *m/e* obsd 250 (calcd for ¹¹B₁₀H₁₃¹²⁷I, 250),³¹ and pure **12**, mp 75–76° and *m/e* obsd 250 (calcd for ¹¹B₁₀H₁₃¹²⁷I, 250).³¹

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(31) High-resolution mass spectral data for this compound will be found in Table IV.

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