

Summary

The CNDO calculations of XCO and XCN indicate that the currently observed CN force constant increase on CN⁻ coordination is primarily a result of reduced C-N repulsion *via* charge withdrawal from carbon. For the comparison CO → XCO, however, the covalent binding energy change is primarily responsible for the change in CO force constant. For moderately back-bonding substituents, the parent σ and π binding changes, as measured by bond orders and diatom binding energies, are of comparable importance. Generally speaking, *within* either series of "adducts," variation in CN and CO binding energy seems to be primarily a result of changes in C-N and C-O π binding, although

the CNDO method appears to overestimate the importance of π changes, and this prevents us from placing the importance of σ changes in a completely subjugated position relative to the π changes. That both CN and CO do tend to have increased σ bond orders as a result of coordination has been traced to polarization of the nitrogen and oxygen lone-pair electrons.

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Diboranes Derived from the Hydroboration of 1,3-Butadiene. Structures, Hydrogen-Bridge Cleavage Reactions, and Factors Which Affect the Course of Bridge Cleavage

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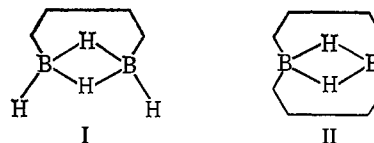
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Abstract: Convenient syntheses of 1,2-tetramethylenediborane(6) (I) and 1,2-bis(tetramethylene)diborane(6) (II) have been developed. It has been possible to distinguish between II and 1,1-tetramethylene-2,2-tetramethylenediborane(6) (III) and show that II is the product prepared in the synthetic procedures employed. Ammonia and methylamines react with I and II to produce either symmetrical or unsymmetrical cleavage of the hydrogen-bridge system, with the unsymmetrical cleavage products being zwitterions. The type of cleavage product formed (identified by boron-11 nmr) depends upon the reactants. Factors which affect the course of cleavage are considered and discussed.

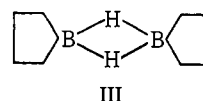
In recent years studies of cleavage reactions of the hydrogen-bridge system of diborane(6) by Lewis bases have suggested that unsymmetrical cleavage occurs more frequently than was previously thought.¹⁻⁵ These studies have also suggested that steric requirements of the base can influence the course of bridge cleavage reactions. With increasing methyl substitution in the methylamine series, the tendency for the base to produce symmetrical cleavage increases.^{2,5}

In the present study, we have attempted to obtain additional information which could be related to the role of steric factors in determining the course of hydrogen-bridge cleavage. To this end, we have been interested in the type of cleavage product produced by a given base as substitution of the terminal positions of diborane(6) is increased. Since Moews and Parry⁴ have shown that tetramethyldiborane(6) is cleaved unsymmetrically by ammonia, it would have been of interest to have determined the type of cleavage produced by methyl-substituted amines on the series of

methyl-substituted diboranes. However, because of the tendency of methylboranes to rearrange,⁶ it was decided to work with other substituted diboranes. The compounds 1,2-tetramethylenediborane(6) (I) and 1,2-bis(tetramethylene)diborane(6) (II) were chosen.



They have been prepared from the hydroboration of 1,3-butadiene and show no tendency to rearrange. However, their structures have been the subject of some debate. While boron-11 nmr spectroscopy has clearly established structure I,⁷ there is no simple spectroscopic approach which will distinguish between structure II and an alternative structure III, 1,1-tetramethylene-2,2-tetramethylenediborane(6).



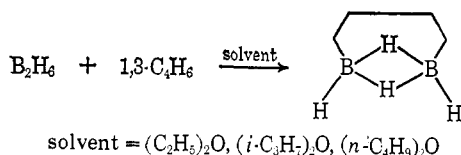
- (1) G. E. McAchran and S. G. Shore, *Inorg. Chem.*, **4**, 125 (1965).
- (2) S. G. Shore, C. W. Hickam, Jr., and D. Cowles, *J. Am. Chem. Soc.*, **87**, 2755 (1965). References to the earlier work of Parry, Schultz, and Shore which established the first example of unsymmetrical cleavage, $\text{BH}_2(\text{NH}_3)_2^+\text{BH}_4^-$, are given here.
- (3) O. T. Beachley, *Inorg. Chem.*, **4**, 1823 (1965).
- (4) P. C. Moews, Jr., and R. W. Parry, *ibid.*, **5**, 1552 (1966).
- (5) M. Inoue and G. Kodama, *ibid.*, **7**, 430 (1968).

- (6) H. I. Schlesinger and A. O. Walker, *J. Am. Chem. Soc.*, **57**, 621 (1935); H. I. Schlesinger, L. Horwitz, and A. B. Burg, *ibid.*, **58**, 407 (1936).
- (7) H. G. Weiss, W. J. Lehmann, and I. Shapiro, *ibid.*, **84**, 3840 (1962); H. H. Lindner and T. Onak, *ibid.*, **88**, 1886 (1966).

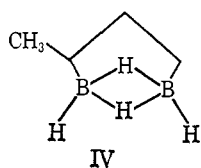
Brown, Zwiefel, and Nagase⁸ favor structure II, while Köster and Iwasaki⁹ favor structure III. In the present investigation we have been able to distinguish between these two structures and have shown that structure II is the one obtained from the preparative procedures which were employed. Convenient syntheses of I and II were developed, and the reactions of I and II with amine bases to produce symmetrical and unsymmetrical cleavage products were studied.

Results

Syntheses. 1,2-Tetramethylenediborane(6). Synthetic procedures have been developed for preparing I on a relatively large scale (25 mmoles). Previous reported syntheses⁷ were based on gas-phase reactions of diborane(6) with 1,3-butadiene, yielding only 1–2-mmole quantities of product. In the present study, the reaction of 1,3-butadiene with a slight excess of diborane(6) was allowed to proceed in an ether solvent for a period of 3 to 7 days at temperatures ranging from 25 to 45°.



Good yields were obtained from reactions carried out in each of the solvents listed above, but dibutyl ether proved to be the best solvent with respect to separation of pure product from the reaction mixture by vacuum line fractionation. Yields of over 60% were obtained in addition to a small amount of the isomer, 1,2-(1'-methyltrimethylene)diborane(6) (IV) which was re-

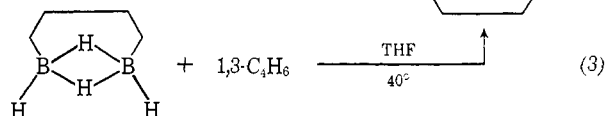
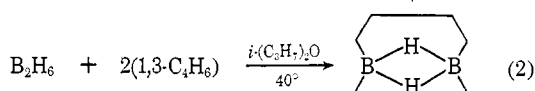
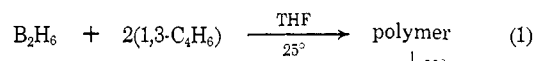


ported in the earlier gas-phase studies.⁷

The key to obtaining good yields of product from reactions in solution appears to rest in the choice of a solvent which does not cleave the bridge system of diborane(6). By contrast, when 1,3-butadiene and diborane(6) were allowed to react in tetrahydrofuran, a solvent which reacts with B_2H_6 to form THFBH_3 , the yield of I in the volatile portion of the reaction mixture was small. The product was principally a polymer of low volatility which upon heating to 125° rearranged to produce I and II in comparable amounts.

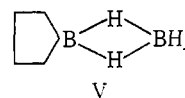
1,2-Bis(tetramethylene)diborane(6). This compound was prepared by three different methods which are outlined in reactions 1–3. Reaction 1 has been described earlier.⁸ Reaction 2 is analogous to the synthesis of

I and minimizes the formation of polymer. Polymeric material was not formed in reaction 3 since unlike B_2H_6 , the hydrogen-bridge system of I is not cleaved by THF.



All of the products obtained from the three reactions had vapor pressures of approximately 1 mm at 25°. Their mass spectra were identical: the parent mass was 136 in each case which supports the molecular formula $\text{B}_2\text{H}_2(\text{C}_4\text{H}_8)_2$. All materials had identical boron-11 nmr and proton nmr spectra. The proton nmr spectra of samples of II showed no evidence for isomeric species such as might be derived from structure IV. The nmr spectra of the C–H protons of II showed two types of methylene hydrogen in a 1:1 area ratio with chemical shifts in good agreement with those assigned to $\alpha\text{-CH}_2$ and $\beta\text{-CH}_2$ in structure I by Lindner and Onak.⁷

Structures. 1,2-Tetramethylenediborane(6). The assignment of structure I is based upon earlier reports⁷ of boron-11 nmr spectra, which have been fully confirmed in this laboratory. Furthermore, the products obtained from reactions with amines also confirm this structure. Koster and Iwasaki⁹ assign structure V to a material of



identical composition. However, its published infrared spectrum is identical with that observed for I. The principal point of interest in this spectrum is that a sharp singlet is observed in the terminal B–H stretching region. It is well known that “In diboranes having two terminal hydrogens bound to boron, one observes a doublet due to in-phase asymmetrical and out-of-phase symmetrical stretches.”¹⁰ Thus, for the structure Koster and Iwasaki⁹ report (V), the terminal boron–hydrogen stretching region would most likely be a doublet. The existence of the sharp singlet observed for the terminal B–H stretching frequency suggests the presence of only one terminal hydrogen per boron as in structure I. Although no attempt was made to duplicate the work of Köster and Iwasaki⁹ since experimental details were scant, we believe that the available evidence indicates that they prepared I rather than V.

1,2-Bis(tetramethylene)diborane(6). In the case of the principal product obtained from the reaction of diborane(6) with 1,3-butadiene in a 1:2 molar ratio, neither nmr spectroscopy nor vibrational spectroscopy can be readily employed to distinguish between the two possible structures which have been proposed, II and III. For the compounds prepared in this study, we

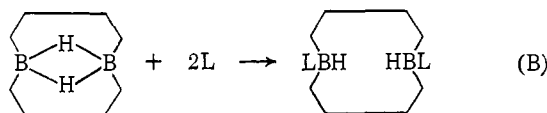
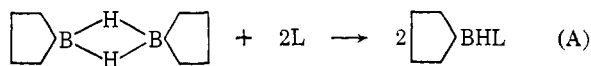
(8) H. C. Brown, “Hydroboration,” W. A. Benjamin, Inc., New York, N. Y., 1962, pp 209–212; G. Zweifel, K. Nagase, and H. C. Brown, *J. Am. Chem. Soc.*, **84**, 183 (1962).

(9) R. Koster, *Angew. Chem.*, **71**, 520 (1959); R. Koster, *ibid.*, **72**, 726 (1960); R. Koster and K. Iwasaki, “Boron-Nitrogen Chemistry,” *Advances in Chemistry Series*, No. 42, American Chemical Society, Washington, D. C., 1964, pp 148–165; R. Koster, “Progress in Boron Chemistry,” Vol. 1, H. Steinberg and A. L. McClosky, Ed., The Macmillan Co., New York, N. Y., 1964, Chapter 7; R. Koster, *Advan. Organometal. Chem.*, **2**, 257 (1964).

(10) W. J. Lehmann, C. O. Wilson, Jr., J. F. Di Her, and I. Shapiro, “Borax to Boranes,” *Advances in Chemistry Series*, No. 32, American Chemical Society, Washington, D. C., 1961, p 139.

have found that the molecular weights of amine addition compounds clearly support structure II, the structure favored by Brown and coworkers⁸ on the basis of chemical arguments.

Consider symmetrical cleavage reactions of amine bases with the structures in question.



L = amine

The molecular weights of the resulting products would be one-half as large from reaction A as from reaction B. Results of molecular weight studies are given in Table I below. They clearly support reaction B, thereby providing evidence for structure II, 1,2-bis(tetramethylene)diborane(6).

Table I. Molecular Weight Data from Dioxane Solutions

Amine reactant	Theoret mol wt of product		Exptl mol wt
	Reaction A	Reaction B	
N(CH ₃) ₃	127	254	233 ^a
NH(CH ₃) ₂	113	226	218, 222
NH ₂ CH ₃	99	198	208

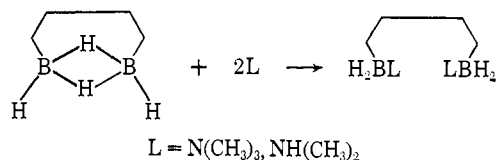
^a The N(CH₃)₃ adduct is noticeably dissociated in solution at room temperature (free amine is observed), accounting for the low molecular weight.

It is of interest to note that the infrared spectrum of II is identical with the spectrum assigned to III by Köster.⁹ Little experimental detail was reported, yet it appears as if his product was prepared under conditions which were roughly equivalent to those used to degrade the polymer derived from reaction 1 above. Although no effort was made to duplicate his work, our results imply that Köster⁹ in point of fact prepared II rather than III.

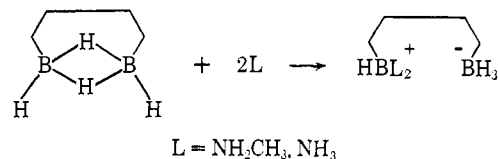
Reactions. Ether bases such as tetrahydrofuran do not react with I and II. On the other hand, methylamines and ammonia form identifiable adducts with these organodiboranes. In general, reactions occur more slowly in systems in which II is employed. Furthermore, the N(CH₃)₃ adduct of II is partially dissociated at room temperature while the analogous adduct with I is not. These observations are consistent with increasing steric hindrance as methylene substitution on boron is increased. Products of reactions were examined by boron-11 nmr spectroscopy, a method which has proved to be successful for distinguishing between so-called "symmetrical" and "unsymmetrical cleavage" in the reactions of Lewis bases with diborane(6).^{1,2}

1,2-Tetramethylenediborane(6). Reactions with N(CH₃)₃ and with NH(CH₃)₂ produce symmetrical cleavage of the hydrogen-bridge system of I. Unsymmetrical cleavage products were not detected in these reactions. The adducts are stable solids which show no tendency to dissociate even at elevated temperature.

The N(CH₃)₃ adduct can be sublimed, quantitatively, at 100°, while the NH(CH₃)₂ adduct shows no tendency to split out hydrogen at temperatures up to 70°.

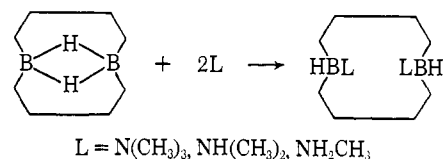


Unsymmetrical cleavage products were obtained in the reactions of NH₂CH₃ and NH₃ with I, resulting in the formation of zwitterions.



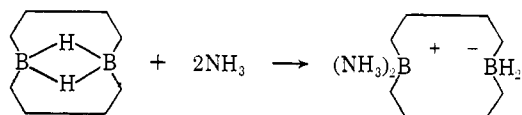
Symmetrical cleavage products were not detected. The unsymmetrical cleavage products decompose, giving off hydrogen at temperatures above -20°.

1,2-Bis(tetramethylene)diborane(6). Symmetrical cleavage was produced by N(CH₃)₃, NH(CH₃)₂, and NH₂CH₃. No evidence for an unsymmetrical cleavage product was detected in the reactions with these amine



bases. These addition compounds do not sublime quantitatively. Trimethylamine can be pumped away from the adduct at room temperature.

Reaction of II with NH₃ produces unsymmetrical cleavage, giving a ten-membered zwitterion ring. Unlike the thermally unstable unsymmetrical cleavage products of I, this product was found to be stable at



room temperature, with no apparent evolution of hydrogen. Evidence for symmetrical cleavage by NH₃ was not detected.

Nmr Spectra. 1,2-Tetramethylenediborane(6). The proton and boron-11 nmr spectra of I were in complete accord with earlier reports.⁷ Boron-11 nmr spectra of products of symmetrical cleavage of I were obtained at ambient temperature (30°), although in the case of the NH(CH₃)₂ adduct, the spectrum was taken at 30-100° in order to observe improved resolution. The spectrum of each of the symmetrical cleavage products consisted of a 1:2:1 triplet which resulted from spin coupling of BH₂ hydrogen with boron. A typical spectrum is shown in Figure 1.

Because of the thermal instability of the unsymmetrical cleavage products of I, best boron-11 nmr spectra were obtained below -15°. Each spectrum displayed a 1:3:3:1 quartet which arose from spin coupling of BH₃ hydrogen with boron in the anionic end of the zwitterion. No signal was observed for the

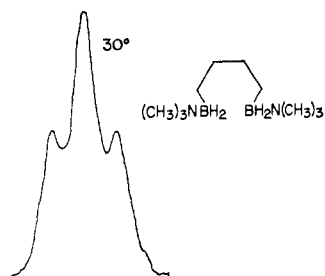


Figure 1. Boron-11 nmr spectrum: product of reaction between 1,2-tetramethylenediborane(6) and trimethylamine.

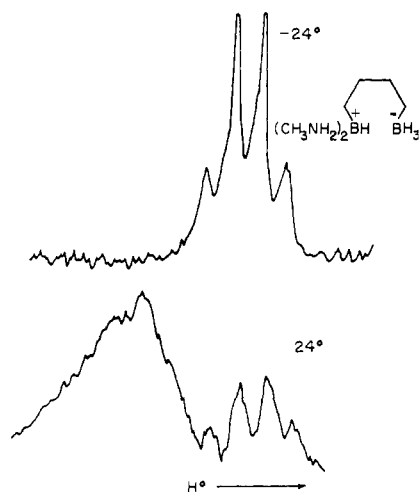


Figure 2. Boron-11 nmr spectrum: product of reaction between 1,2-tetramethylenediborane (6) and methylamine.

cationic boron at low temperature; however, by raising the temperature to ambient, a broad downfield signal appeared which probably arose from the cationic boron of the zwitterion. Rapid decomposition precluded obtaining detailed spectra at ambient temperature. Typical spectra of an unsymmetrical cleavage product of I are shown in Figure 2. The absence of the cation spectrum at low temperature is not unexpected since it has been shown that temperatures near 30° are required in order to observe a well-resolved spectrum of the $\text{BH}_2(\text{NH}_2\text{CH}_3)_2^+$ ion.² Other examples^{1,11} are known of unobserved boron-11 nmr spectra of the cations of unsymmetrical cleavage products at low temperature. In the case of the $\text{BH}_2(\text{NH}_2\text{CH}_3)_2^+$ ion,² it has been suggested that the temperature dependence of the spectrum arises from nuclear quadrupole spin-lattice relaxation which is responsible for line broadening and the absence of a detectable triplet at low temperature. Such a suggestion is also applicable to the temperature-dependent spectra described herein.

1,2-Bis(tetramethylene)diborane(6). The proton nmr spectrum of II in CDCl_3 consisted of two singlets in a 1:1 area ratio at τ 9.13 and 8.48 (τ is given with respect to TMS). These peaks are in close agreement with those observed by Lindner and Onak⁷ for 1,2-tetramethylenediborane(6) and are assigned to the α - and β -hydrogens of the methylene groups on the basis of this earlier work. Bridge hydrogens or the influence of

(11) R. Schaeffer, F. Tebbe, and C. Phillips, *Inorg. Chem.*, **3**, 1475 (1964).

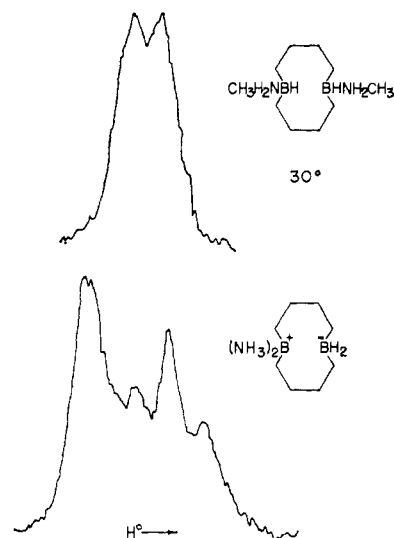


Figure 3. Boron-11 nmr spectrum: product of reactions between bis-1,2-tetramethylenediborane(6) and methylamine and bis-1,2-tetramethylenediborane(6) and ammonia.

bridge hydrogens were not observed in either the proton or boron-11 nmr spectrum of II. The latter spectrum consisted of a single broad peak. Boron-11 nmr spectra of symmetrical and unsymmetrical cleavage products of amine adducts of II are shown in Figure 3. The spectrum of a symmetrical cleavage product is characterized by a 1:1 doublet which arises from spin coupling of the B-H hydrogen with boron. The spectrum of an unsymmetrical cleavage product shows a triplet for the anion and a singlet for the cation. The cation spectrum is temperature dependent; it is markedly attenuated at low temperature. Data gathered from nmr studies in this investigation are presented in Table II.

Table II. Nuclear Magnetic Resonance Data

Compound	δ , ppm ^a	J_{BH_1} , Hz	J_{BH_2} , Hz	Solvent
I	-22.6	129	40	THF
Adducts of I				
2N(CH ₃) ₃	+1.4	92		THF
2NH(CH ₃) ₂	+6.7	89		CH ₂ Cl ₂ , ^b dioxane
2NH ₂ CH ₃	+26.4 (anion) ^c	76		NH ₂ CH ₃
2NH ₃	+26.4 (anion) ^c	76		NH ₃
II	-28.5		<i>d</i>	THF
Adducts of II				
2N(CH ₃) ₃	-2.0	88		Dioxane
2NH(CH ₃) ₂	+1.8	84		NH(CH ₃) ₂
2NH ₂ CH ₃	+5.2	81		NH ₂ CH ₃
2NH ₃	+13.1 (anion)	74		CH ₃ CN
	+1.6 (cation)			

^a $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ standard. ^b 60° . ^c -15° cation spectrum unobserved. ^d Unresolved in boron-11 spectrum.

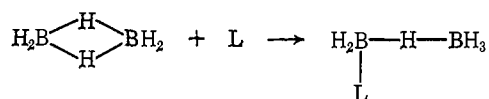
Discussion

In the preceding section it was shown that reactions of the organodiboranes I and II with ammonia and methylamines result in either symmetrical or unsymmetrical bridge cleavage.

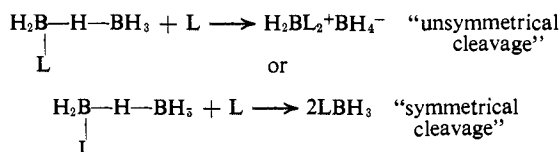
Possible factors which influence the type of bridge cleavage have been stated in conjunction with the results

of earlier work.^{2,5} At this point it is of interest to restate some of the earlier suggestions and to consider them with respect to the results of the present study.

It has been proposed that the reaction of diborane with a Lewis base, L, can occur in a stepwise process, with the first step involving displacement of hydrogen from the bridge position.^{12,13}



The second step involves displacement of hydrogen from the remaining bridge and determines the type of product produced.



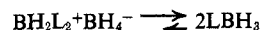
The existence of singly bridged structures such as that shown above has since been questioned and an alternative structure has been proposed.¹⁴ While the available experimental facts do not lend credence to this alternative structure, a number of types of independent results establish the singly bridged species on a much firmer footing.¹⁵ Therefore we continue to consider the path of bridge cleavage in terms of a singly bridged intermediate.

In the sequence of steps given above, three principal factors could determine the course of the reaction. They are an inductive effect, the inherent donor character of the ligand, and a steric effect.

In the singly hydrogen-bridged intermediate depicted above, the two boron atoms differ in that a hydride ligand on one of the boron atoms has been replaced by a ligand of another type (an amine base for the cases discussed herein). Since the electron-withdrawing ability of nitrogen is greater than that of hydrogen, it is to be expected that the boron to which the amine is attached is the more positive of the two, with respect to net charge, and is therefore more susceptible to nucleophilic attack by the amine base in the second step of the reaction sequence. Thus, if an inductive effect is operative, and in the absence of other factors, unsymmetrical cleavage is to be expected in reactions involving amine bases.

By the same token, unsymmetrical cleavage is to be expected in reactions involving oxygen bases. However, with the exception of dimethyl sulfoxide which produces $\text{BH}_2[\text{OS}(\text{CH}_3)_2]^+ \text{BH}_4^-$,¹ those oxygen bases which react with diborane appear to produce symmetrical cleavage products LBH_3 . The apparent tendency of oxygen bases such as dimethyl ether, tetrahydrofuran, and tetrahydropyran to produce symmetrical cleavage products in their reactions with diborane can be attributed to the fact that they are inherently weak bases. Thus while the inductive effect would favor unsymmetrical cleavage, the fact that the oxygen base is a weak donor compared to hydride

could favor the following reaction.



Such a suggestion concerning weak oxygen bases was first proposed by Schaeffer, Tebbe, and Phillips.^{11,16}

On the other hand, for amine bases, the base strength is sufficient to preclude hydride transfer. Thus, for example, $\text{H}_2\text{B}(\text{NH}_3)_2 + \text{BH}_4^-$ and $\text{H}_2\text{B}(\text{NH}_2\text{CH}_3)_2 + \text{BH}_4^-$ show no evidence for conversion to H_3NBH_3 and $\text{H}_2\text{CH}_3\text{NBH}_3$, respectively.^{2,5} Although phosphine and sulfide bases are stronger donors to boron hydrides than their nitrogen and oxygen counterparts, they appear to produce symmetrical cleavage exclusively.¹⁷ Perhaps this can be related to the fact that the electron-withdrawing character of phosphorus and sulfur is significantly less than that of nitrogen and oxygen and approaches that of hydrogen. In such a circumstance, the inductive effect should be negligible and on the basis of steric grounds symmetrical cleavage would be favored.

With respect to steric factors, a possible steric effect was suggested by the fact that the tendency for symmetrical cleavage of diborane by an amine base increases with increasing methyl substitution from ammonia to trimethylamine.² In terms of the two-step reaction sequence given above, it is to be expected that with increasing bulk or steric requirement of the ligand, the tendency for symmetrical cleavage should increase. Thus in the second step of the sequence, nucleophilic displacement of bridge hydrogen would be expected at the less hindered boron atom, the one from which hydrogen had not been displaced in the first step of the sequence.

If we consider a series of diborane structures in which terminal hydrogens have been progressively substituted by larger groups, the two-step reaction sequence would predict that the tendency for a given base to produce symmetrical cleavage would increase with increasing substitution of the terminal positions of diborane. This statement is supported by the results presented in Table III. Clearly, the tendency for symmetrical cleavage of the hydrogen bridge system by dimethylamine and methylamine increases in the series $\text{B}_2\text{H}_6 < \text{I} < \text{II}$. Thus with increasing substitution of diborane(6) decreasingly hindered bases produce symmetrical cleavage, suggesting that as the steric requirements of either boron or nitrogen increase, symmetrical cleavage products result. Presumably, if the borons were even more hindered, ammonia, which produces unsymmetrical cleavage in all of the examples studied to date, would produce symmetrical cleavage.

(16) Schaeffer, Tebbe, and Phillips¹¹ observed that the low-temperature reaction of B_3H_9 with THF appeared to produce $\text{BH}_2(\text{THF})_2^+ \text{B}_3\text{H}_8^-$, the analog of unsymmetrical cleavage of B_2H_6 . This material was stable at low temperature, but rearranged upon warming to form THFBH_3 plus THFB_3H_7 , the symmetrical cleavage analogs. They suggested that apparent symmetrical cleavage of B_3H_9 occurs through an initial unsymmetrical cleavage reaction followed by transfer of hydride ion from B_3H_8^- to the $\text{BH}_2(\text{THF})_2^+$ ion. It is of further interest to note that although B_2H_6 reacts with THF to form THFBH_3 , apparently exclusively on the basis of boron-11 nmr, it has been found that solutions of B_2H_6 in THF show significantly greater conductivity than that of the pure solvent. This has been attributed to the presence of an ionic species, possibly $\text{BH}_2(\text{THF})_2^+ \text{BH}_4^-$: H. C. Brown and W. J. Wallace, Abstracts, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., 1962, No. 9N; W. J. Wallace, *Dissertation Abstr.*, **22**, 425 (1961).

(17) T. D. Coyle and F. G. A. Stone, *Progr. Boron Chem.*, **1**, 83 (1964); R. W. Rudolph, R. W. Parry, and C. F. Farran, *Inorg. Chem.*, **5**, 723 (1966).

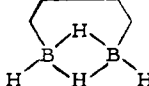
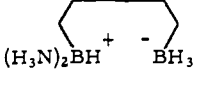
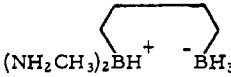
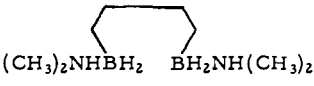
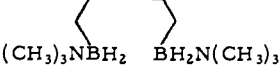
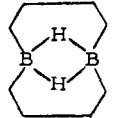
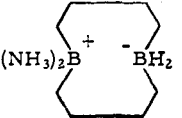
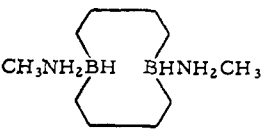


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Table III. Relative Yields of Symmetrical and Unsymmetrical Cleavage Products

Reactants	Unsymmetrical Cleavage Product	Relative Yield	Symmetrical Cleavage Product
$B_2H_6 + 2NH_3$	$[BH_2(NH_3)_2^+][BH_4^-]$		No evidence for product
$+ 2NH_2CH_3$	$[BH_2(NH_2CH_3)_2^+][BH_4^-]$	\gg	$CH_3NH_2BH_3$
$+ 2NH(CH_3)_2$	$[BH_2(NH(CH_3)_2)_2^+][BH_4^-]$	$<$	$(CH_3)_2NHBH_3$
$+ 2N(CH_3)_3$	No evidence for product		$(CH_3)_3NBH_3$
<hr/>			
 + $2NH_3$			No evidence for product
$+ 2NH_2CH_3$			No evidence for product
$+ 2NH(CH_3)_2$	No evidence for product		
$+ 2N(CH_3)_3$	No evidence for product		
<hr/>			
 + $2NH_3$			No evidence for product
$+ 2NH_2CH_3$	No evidence for product		
$+ 2NH(CH_3)_2$	No evidence for product		
$+ 2N(CH_3)_3$	No evidence for product		

Experimental Section

Reagents. All reactants and products were handled in a standard vacuum-line system. Purification of these materials was accomplished by vacuum-line fractionation through a distillation train, and measurement of volatile reactants was accomplished in a calibrated trap system. All solvents were dried over CaH_2 or $LiAlH_4$ and vacuum distilled.

Syntheses. **1,2-Tetramethylenediborane(6).** I was prepared in several ether solvents ($(C_2H_5)_2O$, $(i-C_3H_7)_2O$, $(n-C_4H_9)_2O$). Approximately the same yield of I (60–70%) was obtained from each solvent; however, $(n-C_4H_9)_2O$ proved to be the most suitable solvent with respect to ease of separation of product.

In a typical preparation, about 25 ml of dry solvent was distilled into an evacuated bulb which contained a Teflon-covered magnetic stirring bar and was equipped with a Fischer-Porter Teflon stopcock. The bulb was placed on the vacuum line and evacuated,

and a measured amount of 1,3-butadiene (37 mmole) was then condensed into the bulb which was cooled with liquid N_2 . The bulb was allowed to warm to room temperature and the contents was stirred to obtain a homogeneous solution. The solution was then frozen with liquid N_2 and a measured amount of B_2H_6 (38.5 mmole) in 4% excess of a 1:1 molar ratio of reactants was condensed into the bulb. With the stopcock closed, the bulb was warmed to room temperature. Stirring was started as soon as the solvent had melted. The reaction mixture was allowed to stir at room temperature for about 1 hr, and then a heating bath was placed under the bulb and stirring was continued at 45–50° for periods ranging from 3 to 10 days. The reaction bulb was then cooled to room temperature and the volatile materials in the reaction mixture were fractionated in the vacuum line. Repeated fractionation through a Skellysolve F slush bath (–140°) to liquid N_2 in the distillation train removed unreacted traces of B_2H_6 . Then repeated fractionation through a chlorobenzene slush bath (–45°) removed

the solvent ($n\text{-C}_4\text{H}_9\text{O}$). The remaining crude material was principally I plus a small amount of the isomer IV. Pure I was isolated from the crude product by repeated fractionation through a trap at Dry Ice temperature (-78°). I remained in the Dry Ice trap. In addition to the volatile materials of the reaction, some viscous, nonvolatile liquid was formed which remained in the reaction bulb. Heating this material to approximately 120° yielded additional amounts of I. Total yield from the reaction amounted to about 25 mmoles of I.

A second method which also produced I, but was less suitable as a synthetic procedure, involved the use of THF as a solvent. The procedure was similar to that described above, except that the order of addition of reactants was reversed. A measured amount of B_2H_6 (30 mmoles) was condensed into the reaction tube which contained about 25 ml of THF. The tube was warmed to room temperature in order to permit the formation of the adduct $\text{THF}\cdot\text{BH}_3$. The solution was then frozen in liquid N_2 , and 1,3-butadiene (29 mmoles) was condensed in the tube. With continuous stirring the mixture was allowed to warm to room temperature. Vigorous reaction accompanied by formation of a froth occurred at about 0° . By immersing the tube in liquid N_2 for a few seconds, the reaction was quenched and prevented from getting out of hand. After this quenching procedure, the reaction was allowed to continue to warm to room temperature. After standing at room temperature for a period of about a day, all volatile materials were distilled from the reaction tube. A viscous, nonvolatile, presumably polymeric, material remained in the tube. At this point, dry N_2 was let into the tube and a U-tube trap which contained ground joints at each end was fitted to the reaction tube and the vacuum line by means of these joints. The system was evacuated and the nonvolatile residue was heated to above 125° . Volatile products of thermal breakdown included I and II. These two products were trapped in the U tube which was cooled to -80° and pumped on continuously. After approximately 1 hr of heating the viscous reaction product, detectable formation of I and II ceased. The U-tube trap was immersed in a chlorobenzene slush (-45°) and I was distilled away. Dry N_2 was again let into the apparatus, and the original reaction tube was replaced with a clean tube which was used to collect II. The system was again evacuated and II was distilled slowly at room temperature by immersing the collection tube in a Dry Ice bath. Yields of about 6 and 7 mmoles of I and II were obtained.

The infrared spectra,^{7,9} mass spectra,⁷ and boron-11 nmr spectra of samples of I which were prepared by the above described procedures were in excellent agreement with earlier reports.

1,2-Bis(tetramethylene)diborane(6). Procedures used for preparing II closely paralleled those described above, except that reaction stoichiometries involved 2:1 molar ratios of 1,3-butadiene to B_2H_6 .

The best method for preparing II from the standpoint of simplicity and yield involved the use of ($i\text{-C}_3\text{H}_7\text{O}$) as a solvent. The reaction tube used was of about 250-ml volume; it contained a Teflon stirring bar and was fitted with a side arm which was attached to a smaller tube of about 20-ml volume. The procedure employed was the same as that described above for the preparation of I in which ($n\text{-B}_4\text{H}_9\text{O}$) was used as the solvent. In a typical preparation, 40 mmoles of 1,3-butadiene and 20 mmoles of B_2H_6 were used. After the reaction mixture was maintained at 40° with continuous stirring for 2 days, the solvent was distilled away at 0° . The yield of II was about 15 mmoles. Some nonvolatile material remained behind in the reaction vessel.

Good yields, 75%, of II were also obtained when THF was used as a solvent. However, the initial product of the reaction was a polymer which required heating above 125° in order to generate II. Small amounts of I were formed also. The procedure used was identical with that described for the preparation of I in which THF is used as a solvent. In a typical reaction, 40 mmoles of 1,3-butadiene and 20 mmoles of B_2H_6 were used. To avoid vigorous and potentially hazardous reaction, the system should be quenched as described in the preparation of I.

A third method for the preparation of II employed I as a starting material. It was not intended to be a regular method for preparing II, but was merely intended to show that I will react with 1,3-butadiene to form II. A 2-mmole quantity of I was allowed to react with 2 mmoles of 1,3-butadiene for 2 days in THF at 40° . Both reactants were measured in the vacuum line and distilled into a reaction tube which contained a Teflon-covered magnetic stirring bar. The reaction mixture was allowed to warm, with stirring, to room temperature, and was then placed in a 40° bath for 2 days with continuous stirring. At the end of this period, the solvent

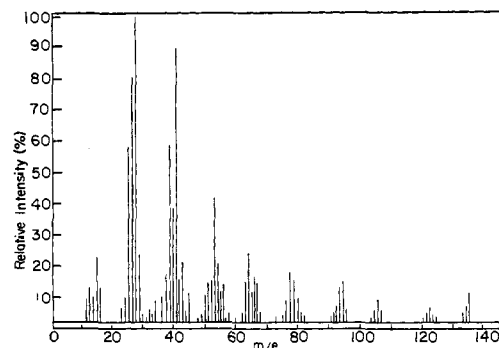


Figure 4. Mass spectral cracking pattern of bis-1,2-tetramethylenediborane(6).

was removed at 0° leaving the product II behind. II was distilled at 40° from the reaction tube. No polymeric product was produced in the reaction.

The infrared spectra of samples of II which were prepared by the above described procedures were in excellent agreement with a spectrum reported by Köster.⁹ The mass spectral cracking pattern of II is shown in Figure 4.

Amine Adducts. Adducts of I and II with NH_3 , NH_2CH_3 , $\text{NH}(\text{CH}_3)_2$, and $\text{N}(\text{CH}_3)_3$ were prepared by the direct reaction of the organodiborane with a measured excess of amine. The stoichiometry of each reaction was shown to be 2 moles of amine per 1 mole of organodiborane by recovering and measuring volumetrically the excess amine. In general, reactions were carried out on a 0.5-1.5-mmole scale with respect to the organodiborane and the amine was in a 3-4 molar ratio excess. In cases where it was desirable to use the amine as a solvent for the adduct, for example for the purpose of obtaining nmr spectra, several milliliters of liquid amine was used.

In a typical reaction a measured amount of organodiborane was distilled into a tube of about 20-mm diameter which was immersed in liquid N_2 and contained a Teflon-covered stirring bar. The tube was connected to a Fischer-Porter Teflon stopcock by means of a Fischer-Porter "Solv Seal" Teflon joint. A side arm on the tube was connected to a 5-mm nmr tube. Excess amine, 2-3 ml, was condensed on top of the organodiborane, and the system was warmed up with continuous stirring to a temperature no higher than -45° . Solutions were stirred for several hours to ensure complete reaction. Samples for nmr spectra were obtained by simply cooling solutions to around -80° , removing the reaction tube, with its stopcock closed, from the vacuum line and tipping the solution into the nmr tube which had been precooled to -80° . In cases in which the amine adduct was to be isolated as a solid, the excess amine was distilled away at about -40° .

In addition to direct reactions with amines, adducts were also formed in solvents, such as dioxane, THF, and CH_3CN , by simply distilling 0.5-1 ml of the solvent into the reaction tube along with the reactants. In such cases the amine was in excess by about 10%. The use of a solvent permitted the formation of the adduct in a homogeneous system at or near room temperature without accompanying pressures greater than 1 atm. The types of cleavage products obtained when these solvents were used were the same as those obtained from the direct reactions of amines with I and II. In the case of the unsymmetrical cleavage product from the reaction of NH_3 with II, its solubility in NH_3 is slight below -30° . Acetonitrile proved to be the best solvent of those listed above, for the purpose of preparing this adduct and obtaining its nmr spectrum.

With the exception of the unsymmetrical cleavage products of I with NH_3 and NH_2CH_3 , all of the adducts of I and II were sufficiently stable to be handled at room temperature either as solids or in solution. It should be noted, however, that the $\text{N}(\text{CH}_3)_3$ adduct of II is slightly dissociated at room temperature as the solid and in solution.

Molecular Weights. Molecular weights were determined cryoscopically in dioxane solution using a Beckmann thermometer in a Beckmann-type freezing point cell. The cell was so constructed that solutions could be syringed into the sealed cell under an atmosphere of dry N_2 . Solutions were stirred by means of a magnetically operated spiral, hopper stirrer.

Samples for molecular weight studies were freshly prepared on the vacuum line, in concentrations of about 0.15 *m*. Dry N_2 gas

was admitted to the solutions and samples for molecular weights were withdrawn by means of a syringe which was inserted into a side arm of the reaction vessel. The side arm was sealed by means of a serum bottle stopper. Molecular weight data are presented in Table I.

Spectra. All boron-11 nmr spectra were obtained using a Varian HR-60 high-resolution spectrometer. Proton nmr data were obtained on an A-60. The basic procedures for preparing nmr

samples are described in the section entitled "Amine Adducts." Boron-11 nmr data are given in Table II.

Mass spectra were obtained on an AEI MS10 mass spectrometer operating at 70 V with a fixed field of 1.8 kG.

Acknowledgment. We wish to acknowledge, gratefully, the support of this work by the National Science Foundation.