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Stereochemistry of Some Aminoboranes Containing *N*-Trimethylsilyl, -germyl, or -stannyl Substituents[1]

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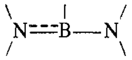
Rotational barriers ($\Delta G_c^\ddagger$) about the B–NMe_2 bond in the compounds RR′NB(Ph)NMe_2 were determined from variable-temperature proton NMR data. The $\Delta G_c^\ddagger$ values vary from approximately 9 to 20 kcal/mol depending on the nature of the RR′N substituent. Compounds containing bis(trimethylsilyl)amino or *tert*-butyltrimethylsilylamino groups were found to have the highest B–NMe_2 barriers while significantly lower $\Delta G_c^\ddagger$ values were obtained for those compounds with other alkyltrimethylsilylamino, Me_3SiNR (R = H, Me, Et, *i*-Pr), *N*-trimethylgermyl, Me_3GeNR (R = Me_3Ge, *t*-Bu), or *N*-trimethylstannyl, Me_3SnNR (R = Me_3Sn, Me), substituents. The results, which are discussed primarily in terms of the steric interactions between the RR′N and Me_2N amino groups, lead to the main conclusion that in compounds such as $(Me_3Si)_2NB(Ph)NMe_2$ the bulky bis(trimethylsilyl)amino substituent is rotated out of the plane of the B–NMe_2 moiety and thus is not an effective π donor to boron.

Introduction

The existence of (p–p)π bonding in aminoboranes and the resultant possibility of cis–trans isomerization was first postulated in 1948 by Wiberg.[2] The concept was formulated primarily on the basis of the isoelectronic nature of the >B=N< and >C=C< linkages. A large number of studies have since been conducted in an effort to better define the extent of π interaction in the boron–nitrogen bond. Molecular orbital calculations[3] and detailed vibrational spectra analysis[4] both indicate a boron–nitrogen π-bond order of at least 0.4 in simple aminoboranes. In a report of the electron diffraction study of dichloro(dimethylamino)borane Clippard and Bartell[5] have characterized the boron–nitrogen linkage as a "double bond" based on the observed planarity of the C_2NBCl_2 skeleton, the very short B–N bond length (1.379 Å), and the spontaneous dimerization of the molecule.

One of the most commonly used methods for estimating the extent of π bonding in aminoboranes has been the measurement of boron–nitrogen rotational barriers by the dynamic nuclear magnetic resonance technique.[6] Such studies have demonstrated that boron–nitrogen rotational barriers are quite sensitive to both the electronic and steric characteristics of the substituents about the B–N moiety. A survey of the published data[7–12] reveals that barriers to rotation, as expressed by $\Delta G^{\ddagger}$, for all types of aminoboranes span a range of about 10–24 kcal/mol. In general, mono(amino)boranes all have rather high rotational barriers (17–24 kcal/mol) while the values for bis(amino)boranes are much lower (usually 10–11 kcal/mol). Dewar and Rona[10] and Friebolin et al.[11] have rationalized this difference in terms of an electronic effect. That is, the introduction of a second nitrogen substituent onto boron results in a decrease in the π-bond order of the first B–N bond since now there are two nitrogen electron pairs competing for overlap with the empty boron orbital. In terms of a resonance formulation, **2** is probably an important contributing structure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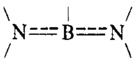
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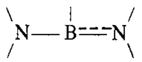
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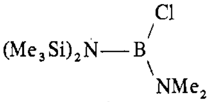
relative to **1** and **3**.

Studies in this laboratory concerning the preparation, properties, and reactions of compounds containing the silicon–nitrogen–boron linkage gave rise to our interest in boron–nitrogen rotational barriers when Paige[13] observed a doublet for the NMe_2 protons in the room-temperature NMR spectrum of (bis(trimethylsilyl)amino)chloro(dimethylamino)borane (**4**). A subsequent quantitative determination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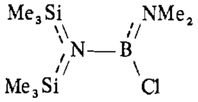
of the rotational barrier about the B–NMe_2 bond in compound **4** gave an energy of activation (E_a) of 18–21 kcal/mol depending on the solvent.[14] The magnitude of this barrier is unexpectedly high considering the fact that **4** is a bis(amino)borane. We speculated[14] that the electrons from the nitrogen of the dimethylamino group are readily available for dative bonding with the boron, whereas the lone pair of the other nitrogen is involved in dative bonding with the silicon atoms and thus less available to the boron. Such a description



of the electron distribution in compounds of this type had been previously proposed by Geymayer and Rochow.[15]

In this paper we wish to report the determination of the rotational barriers about the B–NMe_2 bonds of a number of aminoboranes $RR'NB(Ph)NMe_2$ containing N-trimethylsilyl, -germyl, or -stannyl substituents. Such a study would hopefully allow more definitive conclusions concerning the nature of the bonding in silicon–nitrogen–boron compounds such as **4**.

Experimental Section

Materials. Trimethylsilylamino(dimethylamino)phenylborane (**10**) was prepared according to the procedure reported by Jenne and Niedenzu.[16] With the exception of **14** whose preparation is described below, the syntheses of the remaining compounds used in this study have been previously reported.[17–19] In all cases samples of sufficient purity were obtained by fractional distillation with the center fraction being used in the proton NMR measurements. Samples were prepared as 20% (v/v) solutions in various solvents depending on the temperature range over which the NMR spectra were to be recorded. Di-*n*-butyl ether was used for the high-temperature studies while dichloromethane and chloroethylene were used for the low-temperature work. A few compounds were studied in two different solvents to determine if the nature of the solvent had any significant effect on the $\Delta G^{\ddagger}$ values.

(Methyltrimethylstannylamino)(dimethylamino)phenylborane (14). Under an atmosphere of dry nitrogen chloro(dimethylamino)phenylborane[20] (2.56 ml, 0.016 mol) was added to methylbis(trimethylstannyl)amine[21] (5.65 g, 0.0157 mol) at −80 °C. The mixture was allowed to warm to room temperature and stirred for 30 min. Chlorotrimethylstannane (2.02 g, 65% yield) was removed under vacuum and identified by comparison of its infrared spectrum to that of an authentic sample. The residual yellow liquid was distilled under reduced pressure giving **14** as a colorless viscous liquid (3.57 g, 70% yield; bp 64–65 °C (0.01 Torr)). The mass spectrum contained an intense molecular ion minus methyl peak at *m/e* 311.0745 (calcd for $^{12}C_{11}{}^{1}H_{20}{}^{11}B^{14}N_2{}^{120}Sn$ 311.0742). Anal.[22] Calcd for $C_{12}H_{23}BN_2Sn$: C, 44.37; H, 7.13; N, 8.62; mol wt 324.8. Found: C, 45.01; H, 7.26; N, 8.23; mol wt 325 (mass spectrum).

Spectra. All spectra were recorded on a Varian A-60 spectrometer. Temperatures were controlled to an estimated ±2 °C with a Varian 6040 variable-temperature controller. In a typical experiment the value of $\Delta\nu$, the no-exchange chemical shift difference, was measured at a temperature where the NMe_2 resonance appeared as a pair of sharp lines. Typically this was 30 °C or more below the coalescence temperature (T_c). As the temperature was raised, the lines broadened and began to merge until the coalescence temperature was reached at which point a single, broad, flat-topped peak was observed. At each temperature the sample was allowed to thermally equilibrate for at least 15 min. For each sample a second set of measurements was obtained by cooling the sample from above its coalescence temperature. Thus the values of T_c and $\Delta G_c^{\ddagger}$ reported here represent the average of two independent experiments. For a given sample the two $\Delta G_c^{\ddagger}$ values agreed to within 0.2 kcal/mol except for one case (**8**) where the difference was 0.5 kcal/mol. Values measured for the same compound in different solvents never differed by more than 0.2 kcal/mol.

Results

The dynamic NMR method[6] has been used to determine the free energy of activation at the coalescence temperature ($\Delta G_c^{\ddagger}$) for the hindered rotation about the B–NMe_2 bond in a number of (dimethylamino)phenylboranes, $RR'NB(Ph)NMe_2$. The no-exchange chemical shift difference $\Delta\nu$ and the coalescence temperature T_c for the NMe_2 proton resonance were evaluated from the spectra and then eq 1 was used to

$$\Delta G_c^{\ddagger} = T_c[45.67 + 4.58 \log (T_c/\Delta\nu)] \qquad (1)$$

calculate the $\Delta G_c^{\ddagger}$ values. Equation 1 results from substituting the expression for determining the rate constant at the coalescence temperature,[23] $k_c = \pi\Delta\nu/2^{1/2}$, into the Eyring equation.[24] The accuracy of this so-called "approximate method" for obtaining $\Delta G_c^{\ddagger}$, especially when applied to the simple two-site exchange processes studied here, has been verified.[25,26]

The measured values of T_c and $\Delta\nu$ along with the calculated $\Delta G_c^{\ddagger}$ values for the compounds studied are reported in Table I. For each compound the $\Delta G_c^{\ddagger}$ values represent an average of two independent results. The quoted uncertainties represent mainly the random errors involved in the determination of the coalescence temperature.

The low-temperature spectrum of compound **7** also revealed a measurable barrier to rotation about the B–N(*i*-Pr)$SiMe_3$ boron–nitrogen bond. The methyl resonance of the isopropyl group, which is a sharp doublet at room temperature, broadened and finally coalesced at −65 ± 5 °C. At still lower temperatures two broad peaks separated by 25–30 Hz were observed and at ca. −90 °C four distinct lines were obtained with $\Delta\nu$ = 28.0 Hz. Using eq 1, this leads to a calculated $\Delta G_c^{\ddagger}$ of 10.4 ± 0.3 kcal/mol. For compounds **8** and **9** similar broadening was observed for the NMe and NEt protons at low temperatures but clear coalescence points above −100 °C (the

Table I. Free Energies of Activation ($\Delta G_c^{\ddagger}$) for Rotation about the B–NMe_2 Bond in the Aminoboranes $RR'NB(Ph)NMe_2$

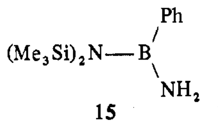
No.	R	R′	Solvent[a]	T_c, °C	$\Delta\nu$, Hz	$\Delta G_c^{\ddagger}$,[b] kcal/mol
5	Me_3Si	Me_3Si	BE	102	9.1	19.8
6	Me_3Si	*t*-Bu	BE	93	18.7	18.8
7	Me_3Si	*i*-Pr	DCM, VC	−47	18.3	11.5
8	Me_3Si	Et	VC	−60	14.8	10.8
9	Me_3Si	Me	VC	−55	15.3	11.1
10	Me_3Si	H	DCM	−16	13.0	13.2
11	Me_3Ge	Me_3Ge	BE, DCM	8	12.6	14.5
12	Me_3Ge	*t*-Bu	BE, DCM	19	21.6	14.8
13	Me_3Sn	Me_3Sn	DCM	−62	12.4	10.8
14[c]	Me_3Sn	Me	VC	(−95)	(10)	(~9)

[a] BE, dibutyl ether, $(n\text{-}C_4H_9)_2O$; DCM, dichloromethane, CH_2Cl_2; VC, vinyl chloride, C_2H_3Cl; concentrations were 20% (v/v). [b] Experimental uncertainties in $\Delta G_c^{\ddagger}$ are ±0.3 kcal/mol or less. [c] Values in parentheses are estimates, not measured quantities (see text).

lower temperature limit of these experiments) were not obtained.

No distinct coalescence point could be observed for the NMe_2 protons of compound **14**. Part of the difficulty was due to overlap of the NMe_2 signal with the other NMe (i.e., Me_3SnNMe) resonance which was also exchange broadened at low temperature. Coalescence of the NMe_2 signal probably occurred at ca. −90 °C but below that two distinct peaks could not be observed because of the overlap problem. Hence the $\Delta G_c^{\ddagger}$ value for **14** is a rather crude estimate using $T_c = -95 \pm 10$ °C and $\Delta\nu \simeq 10$ Hz.

Three additional compounds, not listed in Table I, were studied, i.e.



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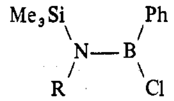
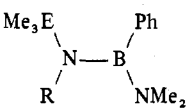


16, R = Me_3Si
17, R = *t*-Bu

Amino(bis(trimethylsilyl)amino)phenylborane (**15**) had a measurable barrier about the B–NH_2 bond. For the NH_2 resonance a coalescence temperature of 43 ± 2 °C and a no-exchange separation of 22.4 Hz were observed leading to a calculated $\Delta G_c^{\ddagger}$ value of 16.1 ± 0.2 kcal/mol. The spectra of the mono(amino)boranes **16** and **17** contained sharp singlets for the Me_3Si and/or *t*-Bu protons at room temperature. At lower temperatures (<−60 °C) some broadening of the signals was observed but even at −100 °C the lines were relatively sharp and did not appear to be approaching coalescence.

Discussion

The present study was begun in an effort to better define the nature of the bonding in Si–N–B compounds of the type studied by Wells et al.[14] Among the first compounds of interest was the following series of analogous *N*-trimethylsilyl, -germyl-, and -stannyl-substituted aminoboranes

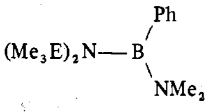


R = Me_3E, *t*-Bu
E = Si, Ge, Sn

Studies of the B–NMe_2 rotational barriers in these compounds should indicate the relative degree of π bonding between boron and an *N*-trimethylsilyl, -germyl, or -stannyl substituent.

A *B*-phenyl substituent is a common feature in all of the compounds used in this study, as well as in a number of earlier studies.[7-12] The reason for this is twofold: (1) dichloro(phenyl)borane is a very convenient starting material for the synthesis of a large number of mono- and bis(amino)boranes; (2) the extreme magnetic anisotropy of the phenyl group provides nonequivalent magnetic environments for the two methyl sites in aminoboranes $Me_2NB(Ph)R$ containing a wide variety of substituents (R). This is especially true for relatively bulky R groups where the phenyl ring is tilted out of the molecular plane.[9]

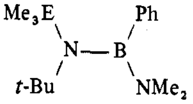
The $\Delta G_c^{\ddagger}$ values measured for rotation about the B–NMe_2 bond in the analogous silicon, germanium, and tin compounds (**5, 11, 13**) show a marked decrease in the series Si > Ge > Sn.



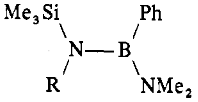
5, E = Si; $\Delta G_c^{\ddagger} = 19.8$ kcal/mol
11, E = Ge; $\Delta G_c^{\ddagger} = 14.5$ kcal/mol
13, E = Sn; $\Delta G_c^{\ddagger} = 10.8$ kcal/mol

It is possible that the $(Me_3E)_2N$ group in these compounds lies in the molecular plane (defined by the three sp^2 orbitals of boron) and that the increased π overlap between boron and the $(Me_3E)_2N$ nitrogen in the germanium and tin compounds is due to a decrease in the amount of (p → d)π interaction in the N–E bonds. A more likely explanation, and one that is consistent with the results of the earlier work,[26] is that the high B–NMe_2 barrier for the silicon compound (**5**) is due to the fact that the $(Me_3Si)_2N$ group is rotated out of the molecular plane thus preventing π overlap between boron and the silyl-substituted nitrogen. Furthermore, it seems reasonable to postulate that the progressively longer E–N bonds for the germanium and tin compounds help to reduce the steric interactions between the $(Me_3E)_2N$ and NMe_2 amino groups, thus allowing the $(Me_3E)_2N$ grouping to approach coplanarity with the $BNMe_2$ moiety resulting in increased π interaction between boron and the Me_3E-substituted nitrogen. Hence the bis(trimethylstannyl)amino compound has a B–NMe_2 barrier whose magnitude is comparable to those expected for normal bis(amino)boranes.

If one of the trimethylsilyl or trimethylgermyl groups of compounds **5** and **11** is replaced by a *tert*-butyl group, the resultant compounds (**6** and **12**) have B–NMe_2 barriers which are essentially unchanged. It has not been possible to prepare the analogous tin compound although it seems likely that the B–NMe_2 barrier for such a compound would be comparable to that observed for the bis(trimethylstannyl)aminoborane (**13**).



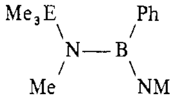
6, E = Si; $\Delta G_c^{\ddagger} = 18.8$ kcal/mol
12, E = Ge; $\Delta G_c^{\ddagger} = 14.8$ kcal/mol



6, R = *t*-Bu; $\Delta G_c^{\ddagger} = 18.8$ kcal/mol
7, R = *i*-Pr; $\Delta G_c^{\ddagger} = 11.5$ kcal/mol
8, R = Et; $\Delta G_c^{\ddagger} = 10.8$ kcal/mol
9, R = Me; $\Delta G_c^{\ddagger} = 11.1$ kcal/mol
10, R = H; $\Delta G_c^{\ddagger} = 13.2$ kcal/mol

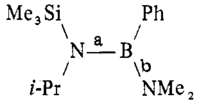
Except for that of the *tert*-butyl-substituted compound (**6**), the B–NMe_2 barriers measured for the series of trimethylsilylamino(dimethylamino)phenylboranes (**6–10**) are in the range normally observed for bis(amino)boranes. Thus considerable π bonding between boron and the Me_3SiNR nitrogen is indicated for compounds **7–10**. Coplanarity of the two amino groups would seem to be more likely for the compounds containing the smaller alkyl groups. The fact that the methyl- and *tert*-butyl-substituted compounds have very different $\Delta G_c^{\ddagger}$ values indicates that *steric interaction between the boron substituents rather than N–Si (p → d)π bonding, as was first postulated,*[14] *is the predominant factor influencing the magnitude of the B–NMe₂ rotational barriers in such compounds.* The large difference in the $\Delta G_c^{\ddagger}$ values obtained for the *tert*-butyl compound (**6**) and those of the other members of the series is not easily explained, but the apparent similarity of the steric effect of the methyl, ethyl, and isopropyl groups is consistent with the results reported by others.[11,26]

In order to further distinguish between steric and (p → d)π bonding effects it would be advantageous to have a series of analogous *N*-trimethylsilyl-, -germyl-, and -stannyl-substituted aminoboranes in which steric interactions between the various boron substituents are minimized. One such series is shown by **9** and **14**. An attempt to prepare the germanium analogue of these compounds was not successful; nevertheless the similarity of the B–NMe₂ barrier for the silicon compound (**9**), for which N–Si (p → d)π bonding is possible, to that of the tin compound (**14**), for which N–Sn (p → d)π bonding is very unlikely, would seem to indicate that π bonding between boron and the silyl-substituted nitrogen will occur so long as steric effects do not prevent it.



9, E = Si; $\Delta G_c^{\ddagger} = 11.1$ kcal/mol
14, E = Sn; $\Delta G_c^{\ddagger} = 9$ kcal/mol

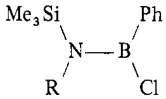
Up to now this discussion has dealt with the interpretation of steric and/or electronic effects in one area of a molecule based on a measurement of a barrier to rotation about a B–NMe₂ bond in another region. One would like to be able to obtain rotational barriers about the bond between boron and the silyl-substituted nitrogen. This has proven to be possible for one compound in this study. For the bis(amino)borane **7** the rotational barriers of the two B–N bonds are quite similar indicating that the boron is π bonded to each nitrogen to an approximately equal extent.



7

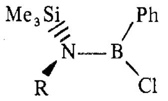
a: $\Delta G_c^{\ddagger} = 10.4$ kcal/mol
b: $\Delta G_c^{\ddagger} = 11.5$ kcal/mol

Variable-temperature proton NMR studies were conducted on two mono(amino)boranes (**16** and **17**) containing the Si–N–B linkage, but no splitting of the Me_3Si and/or *t*-Bu proton resonance was observed at temperatures as low as −100 °C. This is somewhat surprising since the dialkylamino compounds $R_2NB(Ph)Cl$ (R = Me, Et, *i*-Pr, *s*-Bu), all have rather high B–N rotational barriers ($\Delta G_c^{\ddagger} = 17$–$20$ kcal/mol).[11] Furthermore, the chemical shift difference $\Delta\nu$ for the methyl protons of the R groups is quite large ($\Delta\nu = 20$–46 Hz) indicating that the anisotropy of the phenyl ring imparts considerable magnetic nonequivalence to the two alkyl sites. Thus it seems unlikely that the failure to observe two *tert*-butyl signals in the low-temperature spectrum of **17** can be attributed to a coincidental equivalence of the chemical shifts of the *tert*-butyl group in its two possible environments.



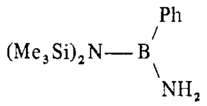
16, R = Me_3Si
17, R = *t*-Bu

Another possible explanation for the lack of splitting of the *tert*-butyl resonance of **17** or the Me_3Si resonance of **16** is that rotation about the B–N bond is very rapid even at −100 °C indicating that the $\Delta G_c^{\ddagger}$ value is very low. A third explanation and one which seems to be consistent with the other results reported here is that the preferred configuration of these molecules is that in which the Me_3SiNR group is approximately perpendicular to the molecular plane, as was concluded for the other compounds containing the Me_3SiNR (R = *t*-Bu, Me_3Si) substituents. More extensive investigations for the structures of such *N*-silylated mono(amino)boranes, however, are clearly indicated.



R = *t*-Bu, Me_3Si

When the chlorine substituent of compound **16** is replaced by an amino group, compound **15** is obtained. The $\Delta G_c^{\ddagger}$ value for rotation about the B–NH₂ bond is quite substantial, again implying that little π overlap occurs between boron and the silyl-substituted nitrogen.



15

$\Delta G_c^{\ddagger} = 16.1$ kcal/mol

Registry No. Chloro(dimethylamino)phenylborane, 1196-44-7; methylbis(trimethylstannyl)amine, 1068-67-3; **5**, 41990-67-4; **6**, 41990-66-3; **7**, 42561-78-4; **8**, 42423-14-3; **9**, 42423-15-4; **10**, 17995-03-8; **11**, 41990-68-5; **12**, 41990-64-1; **13**, 42077-22-5; **14**, 60661-62-3; **15**, 41990-69-6; **16**, 41990-65-2; **17**, 42423-16-5.

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Free-Radical Intermediates in the Photochemistry of Alkylborazines. Synthetic Applications

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Mercury photosensitization of alkylborazine–H$_2$ mixtures at 2537 Å leads to products identified as dimers of an intermediate radical formed by H abstraction from the alkyl group. Reactions of *N*-mono-, -di-, and -trimethylborazine yield exclusively C–C bonded diborazinyl derivatives; B–B bonded products are not observed. The dimer formed by photolysis of *N*-triethylborazine, a 2,3-disubstituted butane, indicates that the intermediate radical is formed at the carbon atom α to the borazine ring. Reactions of *B*-trimethylborazine involve formation of an intermediate radical at a carbon and H–CH$_3$ exchange at a boron site. Hexamethylborazine reacts with H atoms by H–CH$_3$ exchange at the boron sites.

Introduction

It has previously been demonstrated that mercury photosensitization of gaseous mixtures of *N*-trimethylborazine and H$_2$ with radiation at 2537 Å yields a well-defined crystalline product, 1,2-bis[*N*-(3′,5′-dimethylborazinyl)]ethane (DMBE).[1] It is believed that the mechanism of the reaction involves abstraction of a methyl hydrogen by an H atom to form the intermediate radical $H_3B_3N_3(CH_3)_2CH_2\cdot$ which then dimerizes to form a stable product. We have now tested the generality of this radical mechanism for a number of alkyl-substituted borazines, including the *N*-methylborazines, *N*-triethylborazine, and *B*-trimethylborazine. For all of the *N*-methylborazines studied the reaction product obtained is an *N*-diborazinylethane. The product of the *N*-triethylborazine reaction is an *N*-diborazinylbutane. The product with *B*-trimethylborazine is predominantly a *B*-diborazinylethane. The photochemical mechanism for hexamethylborazine is somewhat complicated by competing processes. Throughout this paper we will use the following abbreviations: *N*-trimethylborazine, *N*-TMB; *N*-dimethylborazine, *N*-DMB; *N*-methylborazine, *N*-MB; *N*-triethylborazine, *N*-TEB; *B*-trimethylborazine, *B*-TMB; $(CD_3)_3B_3N_3H_3$, *B*-TMB-d_9; hexamethylborazine, HMB.

Experimental Section

The unsymmetrically substituted *N*-methylborazines were prepared by the method of Beachley,[2] using dimethoxyethane solvent dried over NaBH$_4$, CH$_3$NH$_3$Cl, and NH$_4$Cl under a helium atmosphere. *N*-MB and *N*-DMB were separated by vacuum distillation through U-tube traps. Product purities were checked by mass spectrometry. *N*-TMB was similarly prepared using CH$_3$NH$_3$Cl and NaBH$_4$. Purification by vacuum distillation was checked by mass and infrared[3] spectra. *N*-TEB was prepared from C$_2$H$_5$NH$_3$Cl and NaBH$_4$. Purity of the product, separated by vacuum distillation, was checked by mass spectrometry,[4] proton NMR,[5] and vapor pressure measurements.[6]

Hexamethylborazine was prepared by the method of Haworth and Hohnstedt[7] using CH$_3$I, Mg, and Cl$_3$B$_3$N$_3$(CH$_3$)$_3$ in diethyl ether solvent under dry N$_2$. Purity of the product collected by vacuum distillation was checked by mass spectrometry[8] and its melting point, 98–99 °C (lit.[7,9] mp 97.1 °C). *B*-TMB was similarly prepared from Cl$_3$B$_3$N$_3$H$_3$. Its purity was checked by mass spectrometry,[10] infrared spectroscopy,[11,12] and vapor pressure measurements.[13] The partially deuterated compound, *B*-TMB d_9, was prepared by the same procedure, starting with CD$_3$I. These Grignard reactions were performed by slowly adding the CH$_3$I (CD$_3$I) to a stirred reaction mixture containing Mg in diethyl ether under dry N$_2$.

Table I. Partial Mass Spectra of the Dimers of the *N*-Methylborazine Radicals

$[H_3B_3N_3\text{-}H_2CH_2]_2$		$[H_3B_3N_3\text{-}HCH_3CH_2]_2$		$[H_3B_3N_3\text{-}(CH_3)_2CH_2]_2$	
m/e	Rel ion intens	*m/e*	Rel ion intens	*m/e*	Rel ion intens
187	8	215	8.5	244	3
186	12.5	214	12.5	243	26.5
185	10	213	9.5	242	36
184	4	212	4.5	241	22
183	3	109	7	240	8
182	1.5	108	100	239	2
95	4.5	107	74.5	123	4.5
94	100	106	21.5	122	100
93	73	105	4	121	75
92	19			120	19
91	3			119	2

Mass spectra were obtained on a Consolidated Electrodynamics Corp. Model 21-103A spectrometer with gas inlet. An AEI-MS902/CIS-2 mass spectrometer was used for high-resolution spectra, chemical ionization spectra, and spectra of samples of low volatility. The sample inlet probe temperature was approximately 30 °C. Electron impact mass spectra were run at 70 eV.

Proton NMR spectra were obtained with a Varian A-60A spectrometer or with a Bruker HX-90 high-resolution spectrometer with a Digilab NMR-3 Fourier transform system with Alpha Data Disc memory storage of 128K and a Fourier transform radiofrequency probe amplifier, Model 400-2. Proton chemical shifts were obtained relative to the residual protons in deuterated solvents. Using downfield shifts from TMS as positive δ (ppm), the following relationships were used: $\delta_{TMS} = 7.28 + \delta_{CHCl_3}$, $\delta_{TMS} = 7.20 + \delta_{C_6D_5H}$, $\delta_{TMS} = 2.05 + \delta_{CD_3COCD_2H}$. Resonances for protons bound to nitrogen or boron atoms were too broad and weak for accurate measurement.

Infrared spectra were recorded on either a Perkin-Elmer Model 337 or Model 521 grating spectrophotometer.

The photolysis cell was a 2-l. Pyrex vessel equipped with a quartz immersion well. The light source was a medium-pressure Hanovia mercury arc lamp surrounded by a Vycor sleeve. The lamp and surroundings were purged with cool dry N$_2$. A pool of triply distilled Hg at the bottom of the photolysis vessel was agitated with a Teflon-clad stir bar during the photolysis. Fisher High-Purity grade H$_2$