

The final step in benzene formation must involve excision of one of the carbons from the π -coordinated C_7H_7 ring. The labeling experiments described herein do not provide insight into this step. Analogous ring contraction has been observed for reaction of 7-exo-substituted cycloheptatriene-Cr(CO)₃ complexes.²⁴ However, a detailed mechanism for this reaction has not been proposed.

Spectroscopic studies are required to characterize the adsorption structure of cycloheptatriene and the proposed C_7H_7 intermediate. Near edge X-ray absorption fine structure measurements in the

(21) Green, M.; Kuc, T. A. *J. Chem. Soc., Dalton Trans.* **1972**, 832.

(22) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, 73, 3089.

(23) Brookes, A.; Knox, S. A. R.; Riera, V.; Soskinsky, B. A.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1975**, 1641.

(24) Wilkinson, G.; Stone, F. G. A. *Comp. Organomet. Chem.* **1982**, 8, 1060 and references therein.

C(1s) region are planned. These studies will determine the molecular orientation with respect to the surface.²⁵ Gross differences in adsorption structure may yield insight into the chemical differences observed on the three W(100)-based surfaces.

Acknowledgment. C.M.F. acknowledges support from an IBM faculty development award (1983-1985) and an NSF Presidential Young Investigator Award. K.A.P. thanks the American Vacuum Society for an AVS Scholarship, 1983-1984. We also thank Professor T. N. Rhodin and the Cornell Materials Research Laboratory for the W(100) crystal. This work was supported in part by PRF-ACS Grant No. 14577-G5, Cottrell Grant No. 9787, and the Harvard Materials Research Laboratory, NSF DMR-80-20247.

(25) Stohr, J.; Jaeger, R. *Phys. Rev. B.* **1982**, 26, 4111.

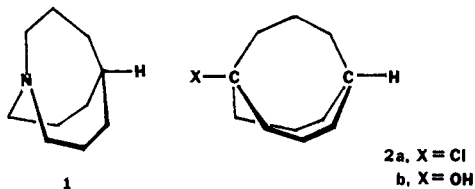
Photoelectron, Infrared, and Theoretical Study of 1-Aza-5-boratricyclo[3.3.3.0^{1,5}]undecane and Related Compounds

Kuei-Jen Lee, Peter D. Livant,* Michael L. McKee, and S. D. Worley

Contribution from the Department of Chemistry, Auburn University, Auburn, Alabama 36849.
Received April 2, 1985

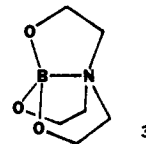
Abstract: 1-Aza-5-boratricyclo[3.3.3.0^{1,5}]undecane, **5**, has been studied by photoelectron spectroscopy and its association behavior studied by IR spectroscopy. The photoelectron results were interpreted with recourse to MNDO calculations on **5** and indicate a B-N bond similar electronically to that of Me₃N-BH₃. The previously reported photoelectron spectrum of 1-aza-4,6,11-trioxa-5-boratricyclo[3.3.3.0^{1,5}]undecane, **3**, has been reassigned based on MNDO calculations. The possibility that self-association of **5** in solution might involve extended p-orbital arrays has been ruled out based on IR spectra in a variety of solvents and in the gas phase. The B-N stretch is now believed to occur at 1039 cm⁻¹ rather than at 1271 cm⁻¹ as was earlier assigned. Despite reports that **5** did not form complexes, evidence for the existence of **5**·BBr₃ was obtained by NMR.

The bicyclo[3.3.3] skeleton is an inherently interesting ring system.¹ In manxine, **1**, various lines of evidence²⁻⁴ are indicative of planarity at nitrogen, an effect attributable to the idiosyncratic bicyclo[3.3.3]skeleton. The tertiary chloride **2a** undergoes sol-



volysis to the alcohol **2b** 10⁴ times faster than *tert*-butyl chloride under the same conditions,⁵ indicating that the planarity resulting from creation of a bridgehead carbonium ion is a welcome relief of angle strain present in the parent. A bridgehead-bridgehead attractive interaction allows both bridgeheads to pyramidalize

inward, as, for example, in boratran, **3**, where the X-ray structure⁶



reveals that the sum of angles around nitrogen and boron are 342.8° and 346.4°, respectively, and that these atoms are connected by a 1.693-Å bond. It is intriguing to visualize an intermediate situation in which the internal attractive interaction is weakened, resulting in bridgehead atoms sufficiently near planarity to take part in attractive intermolecular interactions. Such a possibility has been mentioned for **3**⁷ as well as **4**^{8,9} (eq 1). A report¹⁰ of the synthesis and properties of 1-aza-5-boratricyclo[3.3.3.0^{1,5}]undecane, **5**, included the observation that while **5** was monomeric in the gas phase, it was approximately hexameric in nonpolar solvents (Rast method), eq 2. Compound **5** thus

(1) Leonard, N. *J. Acc. Chem. Res.* **1979**, 12, 423.

(2) Halpern, A. M. *J. Am. Chem. Soc.* **1974**, 96, 7655.

(3) Wang, A. H.-J.; Missavage, R. J.; Byrn, S. R.; Paul, I. C. *J. Am. Chem. Soc.* **1972**, 94, 7100.

(4) Aue, D. H.; Webb, H. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1975**, 97, 4136.

(5) Parker, W.; Trantner, R. L.; Watt, C. I. F.; Chang, L. W. K.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1974**, 96, 7121.

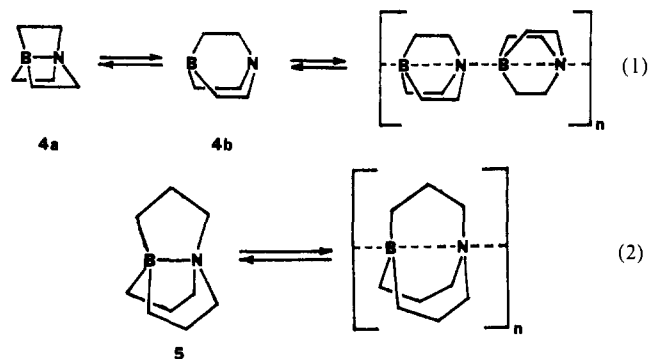
(6) Follner, H. *Monatsh. Chem.* **1973**, 104, 477.

(7) Hein, Fr.; Burkhardt, R. *Z. Anorg. Allg. Chem.* **1952**, 268, 159.

(8) Paddon-Row, M. N.; Radom, L.; Gregory, A. R. *J. Chem. Soc., Chem. Commun.* **1976**, 427.

(9) Gregory, A. R.; Paddon-Row, M. N.; Radom, L.; Stohrer, W.-D. *Aust. J. Chem.* **1977**, 30, 473.

(10) Greenwood, N. N.; Morris, J. H.; Wright, J. C. *J. Chem. Soc.* **1964**, 4753.

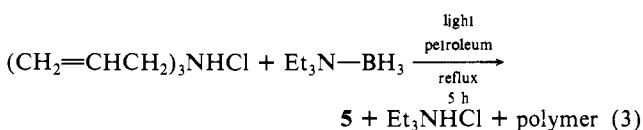


offered the possibility of being the intermediate situation alluded to earlier. That is, B-N interactions in *n*-meric **5** might no longer be pairwise but rather might occur by extended σ -type p-orbital overlap, as shown on the right-hand side of eq 2.

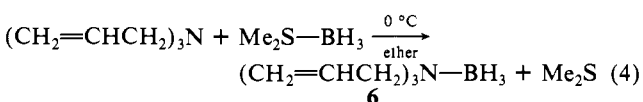
A thorough study of **5** is reported herein.

Results and Discussion

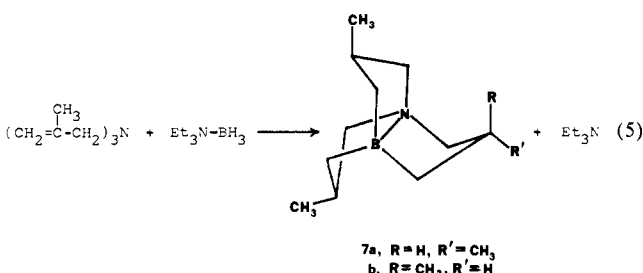
Synthesis of 5 and Related Compounds. Greenwood, Morris, and Wright¹⁰ reported an 18% yield of **5** by the route shown in eq 3. In these laboratories, the yield was much lower, when



sodium-dried toluene was used as the solvent. It was convenient to use preparative-scale HPLC to separate **5** from unreacted triethylamine-borane, as distillation proved ineffective. A variety of attempts were made to improve the synthesis of **5**; however, the use of alternate solvents such as heptane, xylene, diglyme (either refluxing during and after addition of triethylamine-borane, or addition at room temperature followed by a 6-h period of reflux), or the preparation of adduct **6** followed by reflux in various solvents¹¹ afforded no improvement in yield.



As might be expected tris(2-methylallyl)amine gave a higher yield (16%) of tricyclic product **7**, eq 5. The two diastereomers of **7** could be separated by either HPLC or by GC.



Photoelectron Spectroscopy. An important question is whether one may use photoelectron spectroscopy (PES) to assess the strength of the transannular bond in the bicyclo[3.3.3] systems of interest. This of course depends on being able to identify the band in the PE spectrum corresponding to ionization from the B-N bonding orbital. That done, one may compare that IP to the lone-pair IP of an appropriate amine, the difference representing something related to the B-N bond strength. This includes any effects of reorganizing geometry about nitrogen.

Simple B-N compounds have been studied previously by PES; these results are included in Table I. For $\text{Me}_3\text{N}-\text{BH}_3$, the dif-

Table I. Summary of Photoelectron Spectra

| compound | ionizat potent, eV | ref |
|--|--|-----------|
| $\text{Me}_3\text{N}-\text{BH}_3$ | 10.01 ($\sigma_{\text{B-H}}$), 10.63 ($\sigma_{\text{B-H}}$), 11.51 ($\sigma_{\text{B-N}}$) | a, b |
| Me_3N | 8.45 (N lone pair) | b |
| $\text{H}_3\text{N}-\text{BH}_3$ | 10.33, 10.90 sh ($\sigma_{\text{B-H}}$), 13.92 ($\sigma_{\text{B-N}}$) | a, b |
| H_3N | 10.84 (N lone pair) | c |
| $\text{N}(\text{CH}_2\text{CH}_2\text{O})_3\text{B}$, 3 | 9.8, 11.1 ^d | e |
| $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$ | 8.7 (N lone pair) | e |
| $\text{N}(\text{CH}_2\text{CH}_2\text{CH}_2)_3\text{B}$, 5 | 9.10, 10.15, 11.02 ^d | this work |
| $\text{N}(\text{CH}_2\text{CH}_2\text{CH}_3)_3$ | 7.92 (N lone pair) | c |
| $\text{N}(\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2)_3\text{B}$, 7a | 8.83 ($\sigma_{\text{B-C}}$) | this work |
| 7b | 8.87 ($\sigma_{\text{B-C}}$) | this work |

^aReference 12. ^bReference 13. ^cReference 4. ^dSee text for discussion of assignments. ^eReference 15.

Table II. MNDO Calculated Orbital Energies (eV) for Compounds **5**, **7a**, and **3**

| compd | orbital energy and description |
|-----------|---|
| 5 | -10.33, -10.35 ($\sigma_{\text{B-C}}$), -11.71 (π_{CH_2}), ^a -12.14 ($\sigma_{\text{B-N}}$), -12.26, -12.26 ($\sigma_{\text{C-C}}$) |
| 7a | -10.33, -10.34 ($\sigma_{\text{B-C}}$), -11.64 (π_{CH_2}), ^a -11.97, -11.98 ($\sigma_{\text{C-C}}$), -12.14 ($\sigma_{\text{B-N}}$) |
| 3 | -10.60, -10.60, -10.90 (0 lone pairs), -12.22, -12.24 (0 lone pairs), -12.29 ($\sigma_{\text{B-N}}$) |

^aCH₂ adjacent to boron.

ference between the ionization potential (IP) corresponding to $\sigma_{\text{B-N}}$ and the IP corresponding to the nitrogen lone pair of the free amine is 3.06 eV. For $\text{H}_3\text{N}-\text{BH}_3$, the analogous difference is 3.08 eV. These quantities may be calculated by the MNDO semiempirical method and are found to be 3.34 and 3.50 eV, respectively. Thus, MNDO seems to overestimate the nitrogen lone-pair stabilization due to interaction with boron by about 11% on the average.

We may use MNDO, with correction, to predict the IP corresponding to the B-N orbital of **5**. A suitable reference base is tri-*n*-propylamine. MNDO calculations on tri-*n*-propylamine and **5** yield a lone-pair stabilization value of 2.80 eV, which may be corrected to 2.52 eV (11% reduction as noted above). The observed IP due to $\sigma_{\text{B-N}}$ of **5** is predicted to be 2.52 eV higher than the lone-pair IP of tri-*n*-propylamine, or 10.44 eV.

The PE spectrum of **5** is shown in Figure 1, and the band positions are listed in Table I. On the basis of the foregoing considerations, one may tentatively assign either the 10.15-eV or 11.02-eV band to the $\sigma_{\text{B-N}}$ ionization.

A full consideration of the MNDO results for **5** favors the assignment of the 11.02-eV band to the $\sigma_{\text{B-N}}$ ionization. Table II lists the first six highest occupied MO's calculated for **5**, **7a**, and **3**. The first IP observed in the spectrum of **5** at 9.10 eV must correspond to the pair of degenerate HOMO's best described as $\sigma_{\text{B-C}}$ orbitals. This is also consistent with the B-C ionization previously observed for tri-*t*-butylborane, 9.15 eV.¹⁴ The second observed IP of **5** at 10.15 eV is best assigned as an orbital of local π symmetry centered on each of the CH₂ groups adjacent to boron. The third observed IP at 11.02 eV then corresponds to the $\sigma_{\text{B-N}}$ orbital.

Compound **7** can be viewed as **5** perturbed by the addition of three methyl groups virtually perpendicular to the B-N axis. Therefore, the calculated energy of the $\sigma_{\text{B-N}}$ orbital of **7a** is expected to be identical with that of **5**, and (Table II) this is the result found. The fairly highly delocalized $\sigma_{\text{C-C}}$ orbital which was calculated to be lower in energy than the $\sigma_{\text{B-N}}$ orbital of **5** is, in the case of **7a**, higher in energy than $\sigma_{\text{B-N}}$. Therefore, one may interpret the observed PE spectrum of **7a** (Figure 1) as basically identical with that of **5** with an additional band ($\sigma_{\text{C-C}}$) between the π_{CH_2} and $\sigma_{\text{B-N}}$ ionization bands. The $\sigma_{\text{C-C}}$ band is sufficiently

(12) Lloyd, D. R.; Lynaugh, N. *J. Chem. Soc., Chem. Commun.* **1970**, 1545.

(13) Lloyd, D. R.; Lynaugh, N. *J. Chem. Soc. Faraday Trans. 2* **1972**, *68*, 947.

(14) Noth, H.; Taeger, T. *J. Organomet. Chem.* **1977**, *142*, 281.

(11) Baboulene, M.; Torregrosa, J.; Speziale, V. *Bull. Soc. Chim. Fr.* **1980**, 565.

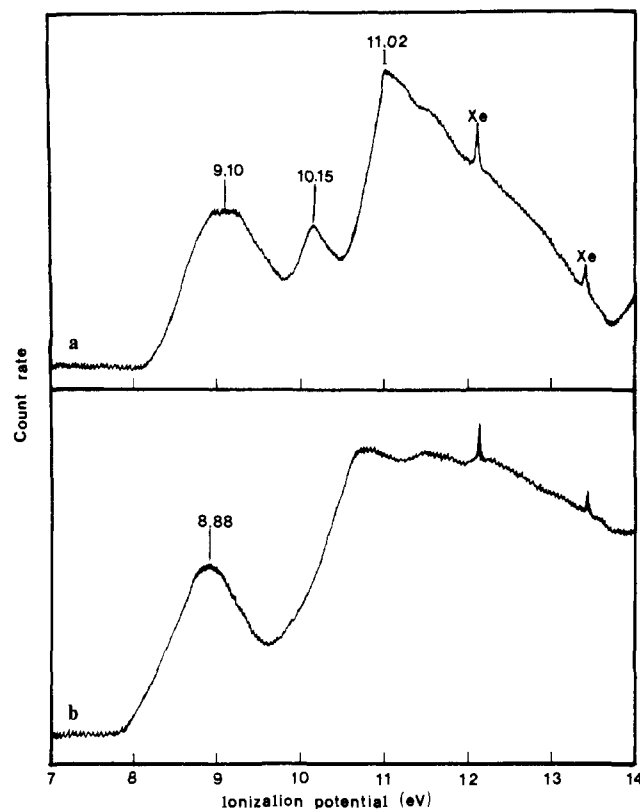


Figure 1. Photoelectron spectra of compounds **5** (a) and **7a** (b). The photoelectron spectrum of **7b** was identical with that of **7a**. The excitation source was the He I resonance line.

Table III. Stabilization of the Nitrogen Lone Pair on Formation of the B-N Bond

| compd | | IP, eV | | |
|-----------------------------------|-------|---------------------|---------------------|--------------|
| | | free amine | B-N compd | stabiliz, eV |
| H ₃ N-BH ₃ | exptl | 10.84 ^a | 13.92 ^b | 3.08 |
| | MNDO | 11.19 | 14.69 | 3.50 |
| Me ₃ N-BH ₃ | exptl | 8.45 ^c | 11.51 ^c | 3.06 |
| | MNDO | 9.49 | 12.83 | 3.34 |
| 5 | exptl | 7.92 ^{a,d} | 11.02 | 3.10 |
| | MNDO | 9.34 | 12.14 | 2.80 |
| 3 | | (9.31) ^e | (2.83) | |
| | exptl | 8.7 ^f | 11.1 ^{f,g} | 2.4 |
| | MNDO | 10.07 ^h | 12.29 | 2.22 |

^aReference 4. ^bReference 12. ^cReference 13. ^dAmine is tri-*n*-propylamine. ^e"Long B-N" isomer of **5** (see text). ^fReference 15. ^gRevised assignment (see text). ^h"Long B-N" isomer of **3** (see text).

strong and broad as to render the σ_{CH_2} and $\sigma_{\text{B-N}}$ irresolvable. Therefore, the orbital energies of $\sigma_{\text{B-N}}$ of **7a** and **7b** are unavailable from PE spectra.

For **5**, the experimental lone-pair stabilization is 3.10 eV which compares well with lone-pair stabilizations mentioned for N-H₃-BH₃, 3.08 eV, and Me₃N-BH₃, 3.06 eV, Table III.

The photoelectron spectrum of **3** has been reported.¹⁵ The main features of this spectrum are a large band at 9.8 eV and a smaller band at 11.1 eV, followed by a typical ill-resolved envelope encompassing the range 11.9–18 eV. The authors assigned the 9.8-eV band to ionization from three orbitals—an e combination of oxygen lone-pair orbitals and what was called the nitrogen "lone"-pair orbital (here denoted $\sigma_{\text{B-N}}$). The 11.1-eV band was taken as ionization from an oxygen lone-pair orbital of a symmetry. By this assignment, the stabilization of the nitrogen lone pair upon B-N bond formation is 1.1 eV. In light of the lone-pair stabilizations discussed above for other B-N compounds, 1.1 eV seems

Table IV. Ionization Potentials of Trimethyl Borate (eV)

| expt ^a | MNDO ^b | expt ^a | MNDO ^b |
|-------------------|-------------------|-------------------|-------------------|
| 10.40 | 10.68 | | 12.29 |
| 11.38 | 11.41 | 14.4 (sh) | 14.48 |
| 12.33 | 12.11 | 14.88 | 14.68 |

^aKroner, J.; Nolle, D.; Noth, H. *Z. Naturforsch., B* 1973 28B, 416.
^b-(orbital energy - 0.60).

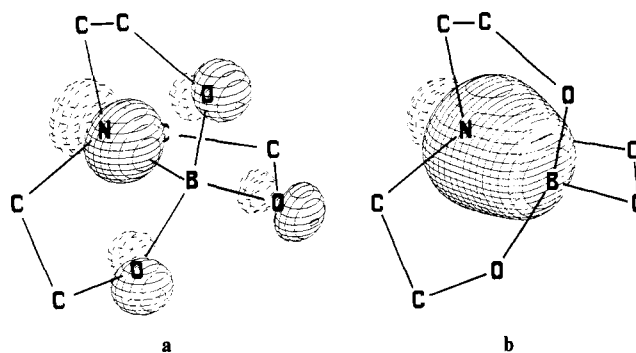
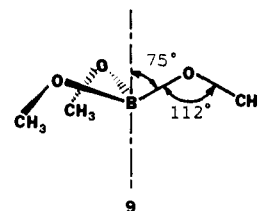


Figure 2. (a, left) Boron-nitrogen σ orbital of **3** calculated by MNDO. (b, energy = -12.29 eV. (b, right) Boron-nitrogen bonding molecular orbital resulting from Boys localization of the set of orbitals calculated for **3** by MNDO.

exceptionally low. To determine whether such a small stabilization could be reproduced by theory, **3** was examined by using MNDO.

The approach which was taken was to model the B(OCH₂)₃ moiety of **3** by performing a calculation on trimethyl borate, **8**, fixed in an appropriate geometry, and to use those results to understand the calculation of **3**. Table IV shows that MNDO is able to satisfactorily reproduce the PE spectrum of **8**.

A MNDO calculation on **9**, in which angles were chosen to closely represent the corresponding angles found experimentally^{6,16} for **3**, gave the required six oxygen lone-pair orbitals at -11.4 (e), -11.5 (a), -13.0 (e), and -17.1 (a) eV. The very low-lying oxygen



lone-pair orbital at -17.1 eV contains a substantial contribution from boron 2p. It is clear from this calculation that (i) the first three orbitals of **9** (of energies -11.4 and -11.5 eV) would generate one band in a PE spectrum and (ii) the first oxygen lone-pair ionization band and the second oxygen lone-pair ionization band would be separated by a gap of about 1.5 eV.

In the MNDO calculation on **3**, the first three orbitals (see Table II) were oxygen lone pair in nature (-10.6 eV, e; -10.9 eV, a), as expected from the model calculation on **9**. Clearly then, the lowest IP band in the PE spectrum of **3** must be assigned to ionization of three oxygen lone-pair orbitals, and the original assignment which included ionization from $\sigma_{\text{B-N}}$ in this band must be considered wrong.

As predicted by the calculation on **9**, a degenerate pair of e oxygen lone-pair orbitals is found at -12.2 eV in **3**, about 1.5 eV lower in energy than the first three orbitals. The next lowest orbital, at -12.3 eV, does not correspond to any in the model calculation, and inspection of the atomic orbital coefficients reveals a large contribution to the MO from nitrogen. To our initial surprise, the contribution of boron to this orbital was very small. A plot¹⁷ of this orbital is shown in Figure 2a.

The lack of significant boron contribution to the B-N bonding orbital results from near cancellation of (i) in-phase mixing of the nitrogen lone pair with the higher-energy boron 2p and (ii)

(15) Cradock, S.; Ebsworth, E. A. V.; Muiry, I. B. *J. Chem. Soc. Dalton Trans.* 1975, 25.

(16) Taira, Z.; Osaki, K. *Inorg. Nucl. Chem. Lett.* 1971, 7, 509.

(17) Jorgensen, W. L. QCPE Program No. 340, 1977.

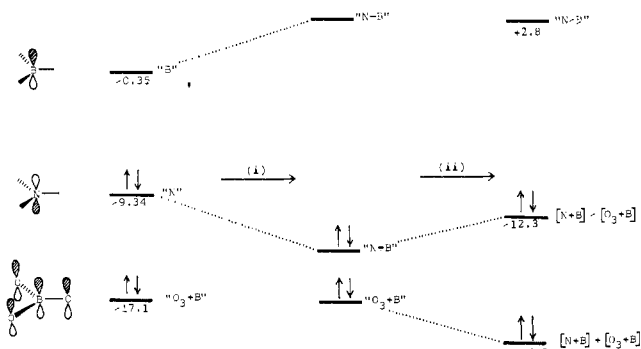


Figure 3. Interactions of B, N, and O orbitals parallel to the B–N axis of **3**. Steps indicated by (i) and (ii) are described in the text. Orbital energies on the left-hand part of the figure were taken from MNDO calculations on **9** and tri-*n*-propylamine, while those on the right-hand part result from a calculation on **3**.

Table V. Calculated and Observed B–N Stretching Frequencies (cm^{-1})

| compd | MNDO | obsd |
|-----------------------------------|------|------------------|
| H ₃ N–BH ₃ | 966 | 968 ^a |
| H ₃ N–BMe ₃ | 761 | 683 ^b |
| Me ₃ N–BH ₃ | 776 | 680 ^c |

^aSmith, J.; Seshadri, K. S.; White, D. J. *Mol. Spectrosc.* **1973**, *45*, 327. ^bSawodny, W.; Goubeau, J. *Z. Phys. Chem.* **1965**, *44*, 227. ^cOdom, J. D.; Barnes, J. A.; Hudgens, B. A.; Durig, J. D. *J. Phys. Chem.* **1974**, *78*, 1503.

antiphase mixing of the nitrogen lone pair with the orbital in **3** corresponding to the lowest-lying of the six oxygen lone-pair orbitals of **9** (which has significant boron 2p character). This argument is shown in Figure 3. Note that the signs of the two boron contributions are opposite in the -12.3-eV orbital. Although no MO in the calculation on **3** is clearly a typical $\sigma_{\text{B-N}}$ orbital, when the canonical orbitals are transformed to a localized set using the Boys criterion, one orbital is obviously B–N bonding (Figure 2b). Furthermore, the degree of bonding¹⁸ between B and N is calculated for **3** to be 0.514, which may be compared to a value of 0.669 for **5**, 0.687 for **7a**, and to several simple B–N compounds calculated by us: Me₃N–BH₃ 0.706, Et₃N–BH₃ 0.692, and Me₃N–BMe₃ 0.605. The orbital of **3** at -12.3 eV , despite its odd appearance, may be labeled $\sigma_{\text{B-N}}$.

The 11.1-eV band in the PE spectrum of **3** is most likely due to ionization of three orbitals—a degenerate pair of oxygen lone-pair orbitals (-12.2 eV) and the $\sigma_{\text{B-N}}$ orbital shown in Figure 2a (-12.3 eV). According to this revised assignment, the lone-pair stabilization is 2.4 eV , which is more in keeping with other stabilizations summarized in Table III.

Infrared Spectrum of 5. If indeed **5** were to take part in associative behavior depicted in eq 2, an important diagnostic parameter would be the value of the B–N stretching frequency. Thus, it was important to identify this band in the IR spectrum. Greenwood, Morris, and Wright¹⁰ assigned a strong absorption at 1271 cm^{-1} to the B–N stretch. A cursory survey of other simple B–N compounds (see Table V) casts doubt on the validity of the 1271-cm^{-1} assignment in **5**. Also, boron-containing compounds automatically provide the spectroscopist with an isotopic substitution experiment, viz. the presence of both ¹⁰B and ¹¹B isotopes. Therefore, the main ¹¹B–N stretch must be accompanied by a ¹⁰B–N stretch at higher wavenumber and of roughly one quarter the intensity of the ¹¹B–N peak. No such peak was assigned by Greenwood et al.

MNDO was used to calculate an IR spectrum for the simple B–N compounds in Table V, and the results indicate that the MNDO method is reliable as a tool for predicting the IR spectra of such compounds. The full normal mode analysis of **5** was therefore undertaken, and the results are presented in Table VI,

Table VI. Calculated and Observed IR Absorption of **5** (cm^{-1})

| Original Assignment ^a | frequency | | revised assign |
|--|-------------------|------|--|
| | obsd ^a | MNDO | |
| ¹¹ B–C ₃ sym str | 660 | 742 | ¹¹ B–C ₃ sym str + B–N str |
| ¹⁰ B–C ₃ sym str | 668 | 749 | ¹⁰ B–C ₃ sym str + B–N str |
| N–C ₃ antisym str | 1039 | 983 | ¹¹ B–N str + B–C ₃ sym str |
| ? ring vibration | 1082 | 1003 | ¹⁰ B–N str + B–C ₃ sym str |
| ¹¹ B–C ₃ antisym str | 1135 | 1377 | ¹¹ B–C ₃ antisym str |
| ¹⁰ B–C ₃ antisym str | 1144 | 1407 | ¹⁰ B–C ₃ antisym str |
| B–N str | 1271 | 1439 | N–C ₃ antisym str |

^aReference 10.

Table VII. Major IR Absorptions (cm^{-1}) of **5** Under a Variety of Measurement Conditions

| assign | hexane | CCl ₄ | CDCl ₃ | KBr | gas phase |
|--|--------|------------------|-------------------|------|-----------|
| N–C ₃ antisym str | 1268 | 1269 | 1269 | 1269 | 1271 |
| ¹⁰ B–N str | 1080 | 1081 | 1080 | 1080 | 1082 |
| ¹¹ B–N str | 1034 | 1035 | 1034 | 1034 | 1038 |
| N–C ₃ sym str | 900 | 901 | 896 | 901 | 901 |
| ¹¹ B–C ₃ sym str | 661 | 660 | 661 | 661 | 662 |

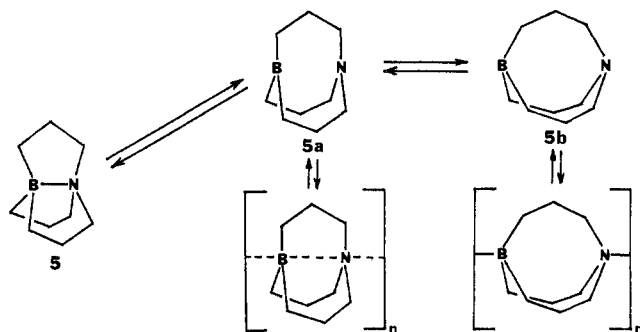
alongside the assignments of Greenwood et al.¹⁰

The B–C₃ symmetric stretching and B–N stretching modes are significantly mixed. The vibration observed at 660 cm^{-1} and calculated at 742 cm^{-1} is mainly the ¹¹B–C₃ symmetric stretch with a substantial amount of ¹¹B–N stretch admixed. The vibration observed at 1039 cm^{-1} and calculated at 983 cm^{-1} is mainly the ¹¹B–N stretch with a substantial amount of ¹¹B–C₃ symmetric stretch admixed. The isotope shift calculated for the former peak, 7 cm^{-1} , is in good agreement with experiment, 8 cm^{-1} , and that calculated for the latter, 20 cm^{-1} is in fairly good agreement with experiment, 43 cm^{-1} . We assert that the peak at 1039 cm^{-1} should be assigned as the ¹¹B–N stretch, with the peak at 1082 cm^{-1} (originally assigned as a “ring vibration”) assigned to the ¹⁰B–N stretch. The strong 1271-cm^{-1} peak is more satisfactorily assigned as the N–C₃ antisymmetric stretch.

The IR spectrum of **5** was obtained in a variety of solvents, namely, hexane, CCl₄, and CDCl₃, and as a KBr disk and in the gas phase. Table VII lists these results. Obviously, the IR spectrum is virtually identical whether in a polar solvent (CDCl₃), nonpolar solvent (hexane), or the gas phase.

This means that the presence or absence of association has no consequences on the B–N bond. (In fact, most vibrations were unaffected by the state of measurement and, by extension, the degree of association.) Clearly, the equilibrium depicted in eq 2, in which boron and nitrogen are approximately planar and there is an extended σ -type overlap of p orbitals, although intriguing, is in fact not the case here. A more reasonable picture of the association is simply a cluster held together by dipolar attractions, with no difference in geometry about B or N between the monomeric and oligomeric species.

Bond Stretch Isomerization in the Bicyclo[3.3.3] Skeleton. The equilibrium depicted in eq 2 shows the B–N bond partially stretched, **5a**. We have shown by IR that the process $\mathbf{5} \rightleftharpoons [\mathbf{5a}]_n$ is not observed. What prediction may be made for the process



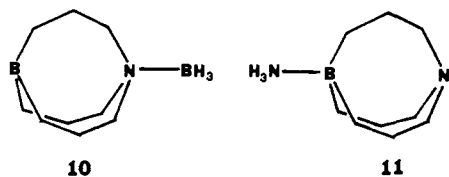
$\mathbf{5} \rightleftharpoons (\mathbf{5b})_n$? This question may be explored by using MNDO. The equilibrium $\mathbf{5} \rightleftharpoons \mathbf{5b}$ is called “bond stretch isomerization”.

(18) Armstrong, D. R.; Perkins, P. G.; Stewart, J. J. P. *J. Chem. Soc., Dalton Trans.* **1973**, 838.

Bond stretch isomers have been studied theoretically for bicyclo[2.2.2] systems, notably **4a** \rightleftharpoons **4b**.^{8,9} An ab initio calculation using an STO-3G basis indicates **4a** and **4b** in separate energy minima with the barrier to the B–N bond stretch 0.72 kcal/mol and the barrier to the B–N bond contraction 9.56 kcal/mol. The MNDO method essentially reproduces the energy difference between **4a** and **4b**, 8.3 kcal/mol, as well as the barrier to the B–N stretch, 0.8 kcal/mol, and contraction 9.1 kcal/mol. Therefore the MNDO method was applied to **3** and **5**.

For **3**, no “no-bond” isomer could be found in even a shallow energy minimum. The energy vs. B–N distance curve was flat in the region of geometrically reasonable “no-bond” distances, around 2.4 Å, and was roughly 10 kcal/mol above the short B–N bond isomer. It is interesting to note that the cleavage of the B–N bond of **3**, here calculated to cost roughly 10 kcal/mol, was identified as the rate-determining step in the hydrolysis of **3**.¹⁹ The no-bond form of **3** may be trapped, so to speak, by complexation to a Lewis acid. Complexes of **3** with SnCl₄, H₃BO₃, and SbCl₅ for example have been prepared.²⁰ A thermochemical study of **3** yielded a value for the B–N bond energy of 14.1 kcal/mol,²¹ with which our result of 10 kcal/mol agrees remarkably well. The nitrogen lone-pair orbital energy of a “long B–N” form of **3** (and **5** see below) was used to calculate the lone-pair stabilization reported in Table III.

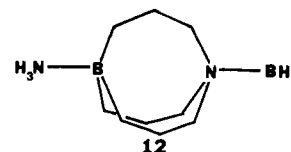
MNDO treatment of the B–N bond stretch of **5** yielded an energy vs. B–N bond length curve qualitatively similar to that calculated for **3**. That is, no no-bond isomer is found to be the occupant of even a shallow energy minimum. In the region of B–N bond distances reasonable for the no-bond form, 2.5–3.0 Å, the curve was very flat and was 17.6 kcal/mol above the minimum, which had a B–N distance of 1.70 Å. Even though the “long B–N” form of **5** was found to be 17.6 kcal/mol less stable than the “short B–N” form, and no barrier to bond contraction was found, it was wondered whether the “long B–N” form could be stabilized by complexation to either a Lewis acid or base. Accordingly, the structures **10** and **11** were examined by MNDO.



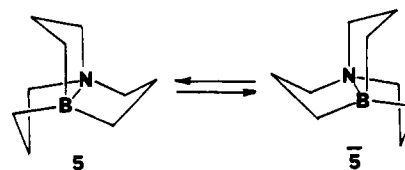
Structure **10** was found to be less stable than the long B–N form of **5** ($d_{\text{B-N}} = 3.11$ Å) plus BH₃ by only 1.7 kcal/mol. Furthermore, when a series of calculations was done in which the exocyclic B–N bond of **10** (originally 1.69 Å) was progressively lengthened while all other geometrical parameters were optimized, a transition state for exocyclic B–N bond cleavage (exocyclic B–N = 2.20 Å; endocyclic B–N = 3.03 Å) was found 7.3 kcal/mol higher in energy than **10**. Therefore, although **10** is slightly thermodynamically unstable relative to the long B–N form of **5** + BH₃, it is in a well 7.3 kcal/mol deep and may be kinetically stable to exocyclic B–N cleavage.

The analogous calculation of the exocyclic bond cleavage of **11** revealed a transition state (exocyclic B–N = 2.30 Å; endocyclic B–N = 2.93 Å) 14.4 kcal/mol higher in energy than **11** (exocyclic B–N = 1.65 Å; endocyclic B–N = 3.19 Å). Compound **11** furthermore was thermodynamically stable relative to the long B–N version of **5** plus NH₃ by 1.8 kcal/mol.

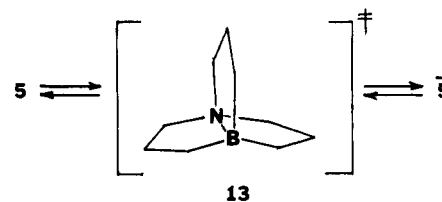
To model hypothetical polymer (**5b**)_n calculations were done on **12**. Compound **12** is calculated to be 21.8 kcal/mol less stable than **5** (short B–N) plus BH₃ plus NH₃. However, one would expect **12** to be trapped in an energy well at least as deep as the shallower of the two wells trapping **10** and **11**—that is 7.3 kcal/mol.



Barrier to Racemization in the Bicyclo[3.3.3] Skeleton. Compound **5** is chiral which is evident when viewed down the B–N axis. Enantiomers of **5** are interconverting rapidly at room temperature as shown by NMR; each of the two protons of each CH₂ group is equivalent to the other. By MNDO, **13**, in which each



B–C–C–N bridge is planar, is only 2 kcal/mol higher in energy than **5**. Structure **13** was purposely chosen to represent the highest energy pathway connecting **5** and **5**; pathways involving flips of one bridge at a time would have barriers even lower than 2 kcal/mol. Although MNDO has been acknowledged to un-



derestimate eclipsing interactions,²² the qualitative conclusion that the barrier to racemization of **5** is exceedingly low is probably valid. This remarkable assertion was partially verified by our observation that the ¹H NMR spectrum of **5** was unchanged down to a temperature of –95 °C (at 80 MHz). The low barrier to racemization indicates a substantial amount of strain in **5**.

For **7a**, a barrier of 1.2 kcal/mol is calculated. For **3**, an entirely unexpected result was encountered: the C_{3v} form with all bridges planar was found to be the global minimum. The energy surface was, however, exceedingly flat in this region. Introducing a C–O–B–N dihedral angle of 25° resulted in an energy increase of only 0.9 kcal/mol. Therefore, the observation of nonplanar bridges in X-ray crystal studies is reasonable since small packing forces could easily deform the bridges. It would be intriguing to have the structure of **3** (and **5**) determined by electron diffraction.

Complexes of 5 with Lewis Acids. Greenwood, Morris, and Wright¹⁰ reported that **5** did not form a complex with NH₃ or triethylphosphine. Even though the MNDO calculations suggested that Lewis acid complexes of **5** (e.g., **10**) should dissociate easily, we explored the chemistry of **5** with several Lewis acids. It should be noted that the results here presented are of a preliminary nature and further that all experiments were done on an NMR scale.

The ¹H NMR spectrum of **5** in CDCl₃ consists of triplets at 0.40 and 2.65 ppm, due to CH₂'s adjacent to boron and nitrogen, respectively, and a quintet at 1.62 ppm due to the remaining CH₂. In CD₃CN, these resonances occur at 0.34, 2.68, and 1.59 ppm. Addition at room temperature of SbCl₅ to a CD₃CN solution of **5** resulted in a triplet at 0.84 ppm (CH₂–B), a quintet at 1.77 ppm (C–CH₂–C), and a complex multiplet at 3.00 ppm (N–CH₂). Additional small unidentified multiplets appeared at 2.55 and 3.40 ppm. When the reaction of **5** with SbCl₅ was carried out in dry CDCl₃ solvent, a white precipitate resulted, which, after removal of CDCl₃ in vacuo and dissolution in CD₃CN, gave a spectrum nearly identical with that obtained in the CD₃CN reaction. We presume that the new spectrum is that of B(CH₂CH₂CH₂)₃N–SbCl₅.

Compound **5** does not react with BBr₃ in CD₃CN solvent, as evidenced by an unchanged ¹H NMR spectrum, but does give a

(19) Zimmerman, H. K.; Weidmann, H. *Ann.* **1959**, *628*, 37.

(20) Fenske, D.; Becher, H. J. *Chem. Ber.* **1972**, *105*, 2085.

(21) (a) Vorob'eva V. P.; Miroshnichenko, E. A.; Lebedev, Yu. A.; Solomenikova, I. I.; Zelcans, G.; Lukevics, E. *Latv. PSR Zinat. Akad. Vestis, Kim. Ser.* **1978**, *233*; *Chem. Abstr.* 89:59550v. (b) Vorob'eva, V. P. *Fiz.-Khim. Protssy Gazov. Kondens. Fazakh.* **1979**, *35*; *Chem. Abstr.* 93:167376j.

(22) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4907.

new product with BBr_3 when the solvent is CDCl_3 . The NMR spectrum undergoes changes, both in chemical shift—1.01 ppm ($\text{CH}_2\text{-B}$), 1.65 ppm ($\text{C-CH}_2\text{-C}$), and 2.88 ppm ($\text{CH}_2\text{-N}$)—and in appearance of the signals. The signal at 1.01 ppm is still a triplet. However, the signals at 1.65 and 2.88 ppm are complex multiplets, indicating additional coupling to the boron of BBr_3 . Miller and co-workers²³ reported a downfield shift of the methyl resonance of 0.52 ppm on going from $(\text{CH}_3)_3\text{N-BH}_3$ to $(\text{C-H}_3)_3\text{N-BBr}_3$. In the present case, the shift from the N-CH_2 's of **5** (2.65 ppm) to the N-CH_2 's of **5-BBr}_3** (2.88 ppm) is substantially less. This indicates that the B-N bond of **5** is stronger than the B-N bond of $(\text{CH}_3)_3\text{N-BH}_3$.

Conclusions. The data in Table III indicate roughly the "electronic" strength of B-N bonds, with steric factors excluded. It is significant that **5** appears to possess a normal B-N bond, while **3** (its PE spectrum now correctly assigned) appears to have a substantially weaker one.

The hypothesis that **5** might engage in an extended p-orbital array, as in eq 2, has been tested experimentally and found false. This involved a major reassignment of the IR spectrum of **5**, which was made possible by a full normal-mode analysis based on MNDO results.

The possibility that **5** might engage in bond stretch isomerization was explored theoretically, and no "long B-N " isomer was found. Calculations indicated that the long B-N form of **5** might be stabilized by complexation to an external Lewis acid or base, and NMR evidence for the existence of **5-SbCl}_5** and **5-BBr}_3** bears the calculations out.

The concept of an extended p-orbital array, as in eq 2, is still an intriguing one. Other possible building blocks are being considered in these laboratories.

Experimental Section

General. Unless otherwise specified, reagents were commercially available and, where feasible, were purified by distillation. Solvents were dried either by distillation from sodium (toluene) or from P_2O_5 (CHCl_3) and were stored over molecular sieves. NMR spectra were obtained at 80 MHz (^1H) with a Varian CFT-20 spectrometer, at 90 MHz (^1H) with a Varian EM-390 spectrometer, or, in the case of the BBr_3 complex of **5**, at 400 MHz (^1H) or 100 MHz (^{13}C) with a Bruker AM400 spectrometer. IR spectra were obtained on a Perkin-Elmer Model 983 spectrometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Gas chromatography was done on a Perkin-Elmer Model 990 chromatograph, with thermal conductivity detector, 6 ft \times $1/4$ in. column of 12% SE-30 on Chromosorb W. All samples for photoelectron spectroscopy were purified by preparative GC. Photoelectron spectra were obtained on a Perkin-Elmer Model PS-18 spectrometer, using Xe and Ar as internal calibrants in all runs. Ionization potentials reported are the averages of several spectra.

Synthesis of 1-Aza-5-boratricyclo[3.3.3.0^{1,5}]undecane (5). The method of Greenwood et al.¹⁰ was employed with several modifications. In a 1-L, three-necked flask equipped with Trubore stirrer, condenser, and gas inlet and outlet, 21.0 g (0.153 mol) of triallylamine (prepared by the method of Butler and Benjamin²⁴) was diluted with 300 mL of toluene (freshly distilled from sodium). The solution was cooled in an ice bath, and $\text{HCl}_{(\text{g})}$ was passed through the stirred liquid until the oily hydrochloride was completely formed. The reaction flask was attached to the water aspirator to remove excess HCl , and 6.0 g (0.043 mol) triallylamine was added to further ensure the absence of free HCl . Under nitrogen, the reaction mixture was brought to reflux, and, with vigorous stirring, a solution of 23.3 g (0.202 mol) of triethylamine-borane in 50 mL of dry

toluene was added via a Teflon needle by means of a syringe pump at the rate of 10 mL/h. The mixture was maintained at reflux temperature under nitrogen for 8 h after completion of the addition, at which time the ^1H NMR showed no olefinic peaks. The cooled reaction mixture was filtered in a dry-nitrogen-filled glovebox, the solid washed with several portions of toluene, and the toluene washings added to the filtrate. The combined toluene fraction was distilled under nitrogen at atmospheric pressure to remove toluene. The residual viscous liquid, which was a mixture of **5**, triethylamine-borane, and polymer, did not separate well on careful fractional vacuum distillation. The product could be obtained by preparative HPLC using silica gel and 100% hexane as eluent. The yield was 2.49 g (8.4%). The product could be further purified by preparative GC or by vacuum sublimation (40 °C, water aspirator pressure): ^1H NMR (CDCl_3) δ 0.40 (t, $\text{CH}_2\text{-B}$), 1.62 (quintet, $\text{C-CH}_2\text{-C}$), 2.65 (t, $\text{CH}_2\text{-N}$); ^{13}C NMR (CDCl_3) δ 20.5 ($\text{CH}_2\text{-B}$), 24.9 ($\text{C-CH}_2\text{-C}$), 61.6 ($\text{CH}_2\text{-N}$); ^{11}B NMR δ 9.8 (rel to B(OMe)_3).

Tris(2-methylallyl)amine Hydrochloride. In a 500-mL round-bottomed flask equipped with magnetic stirring bar, 26.6 g (0.148 mol) of tris(2-methylallyl)amine was diluted with 200 mL of anhydrous ether. The solution was cooled to 0 °C and stirred while $\text{HCl}_{(\text{g})}$ was passed through, resulting in precipitation of a white solid. Solvent was removed at the rotary evaporator and then on the vacuum line (0.1 mmHg), giving 24.5 g (77% yield) of the hydrochloride salt, mp 178–9 °C: ^1H NMR (CDCl_3) δ 2.05 (s, CH_3), 3.63 (s, $\text{CH}_2\text{-N}$), 5.30 (d, $=\text{CH}_2$).

3,7,10-Trimethyl-1-aza-5-boratricyclo[3.3.3.0^{1,5}]undecane (7). The method described for the preparation of **5** was used with the following exceptions. Tris(2-methylallyl)amine hydrochloride was used initially instead of generation of the hydrochloride in situ by passage of HCl . Triethylamine-borane was added at the rate of 20 mL/h, and refluxing after addition was for a period of 5 h. The viscous liquid obtained finally after removal of solvent (this time in air) proved amenable to purification by vacuum distillation. A colorless liquid was obtained, bp 40–50 °C/0.1 mmHg which solidified after standing overnight, 3.5 g (16% yield). Anal. Calcd for $\text{C}_{12}\text{H}_{24}\text{NB}$: C, 74.63; H, 12.53; N, 7.25. Found: C, 74.56; H, 12.66; N, 7.28. Diastereomers **7a** and **7b** could be separated by preparative GC (12% SE-30 on Chromosorb W, $1/4$ in. \times 6 ft; 150 °C).

For **7a**: ^1H NMR (CDCl_3) δ -0.2–0.9 (m, $\text{CH}_2\text{-B}$), 1.00 (d, CH_3), 2.00 (m, C-H), 2.1–2.9 (m, $\text{CH}_2\text{-N}$). Irradiation at 2.00 ppm caused the signal at 1.00 ppm to collapse to a singlet and multiplet at -0.2–0.9 ppm to appear as a simple AB quartet (0.32 ppm, $J_{\text{AB}} = 12$ Hz, $\Delta\nu_{\text{AB}} = 65$ Hz): IR (CCl_4) 2949, 2898, 2871, 2808, 1457, 1425, 1372 (CH_3), 1257 ($\text{C}_3\text{-N}$), 1125 (B-C_3), 1078 ($^{10}\text{B-N}$), 1031 ($^{11}\text{B-N}$) cm^{-1} .

For **7b**: ^1H NMR (CDCl_3) δ -0.2–0.8 (m, $\text{CH}_2\text{-B}$), 0.9 (d of d (apparent t), CH_3), 2.0–2.3 (br m, C-H), 2.3–3.1 (m, $\text{CH}_2\text{-N}$). Irradiation at 2.2 ppm caused a signal at 0.95 to appear as a doublet, while the multiplet at -0.2–0.8 was still complex: IR (CCl_4) 2952, 2905, 2813, 1457, 1430, 1370 (CH_3), 1234 ($\text{C}_3\text{-N}$), 1127 (B-C_3), 1073 ($^{10}\text{B-N}$), 1036 ($^{11}\text{B-N}$) cm^{-1} .

Triallylamine-Borane (6). In a 50-mL round-bottomed flask equipped with magnetic stirring bar and nitrogen flush, 2.74 g (20.0 mmol) of triallylamine was diluted with 20 mL of anhydrous ether. To this solution, cooled to 0 °C in an ice bath, was added dropwise by syringe 2.00 mL (20.0 mmol) of 10 M methyl sulfide-borane. After addition, volatiles were removed at the rotary evaporator and then on the vacuum line (0.1 mmHg). The residue was a slightly cloudy liquid, 2.60 g (86% yield): ^1H NMR (CDCl_3) δ 3.32 (d, $\text{CH}_2\text{-N}$), 5.27 (m, $=\text{CH}_2$), 6.15 (m, $-\text{CH}=\text{CH}_2$).

Complexes of 5 with Lewis Acids. In general, the NMR solvents (CDCl_3 and CD_3CN) were dried over molecular sieves, and all manipulations were performed at room temperature in a dry-nitrogen-filled glovebox. All reactions were on an NMR scale (total volume ca. 0.5 mL). The ratio of Lewis acid to **5** was always 1.0–1.3.

Acknowledgment. We acknowledge a generous gift of computer time by the Auburn University Computer Center. This work was supported in part by Grant CHE8204278 from the National Science Foundation and by Auburn University Energy Grant-In-Aid ER-83-03.

(23) Benton-Jones, B.; Davidson, M. E. A.; Hartman, J. S.; Klassen, J. J.; Miller, J. M. *J. Chem. Soc., Dalton Trans.* **1972**, 2603.

(24) Butler, G. B.; Benjamin, B. M. *J. Chem. Educ.* **1959**, *28*, 191.