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# A SPECTROSCOPIC STUDY OF 1,3-DIMETHYL-2-(TRIMETHYLSTANNYL)-1,3-DIAZA-2-BORACYCLOALKANES

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## SUMMARY

The vibrational spectra of 1,3-dimethyl-2-(trimethylstannyl)-1,3-diaza-2-boracyclopentane and the corresponding diazaboracyclohexane derivative as well as those of some other 1,3-diaza-2-boracycloalkanes have been recorded. Boron–nitrogen valence vibrations are observed in the 1500 ± 10 $cm^{-1}$ frequency region and boron–tin stretching is assigned near 760 $cm^{-1}$. These data are discussed in conjunction with the $^{11}B$ and $^{1}H$ NMR spectra of the various heterocycles and the tin Mössbauer spectra of the two boron–tin species.

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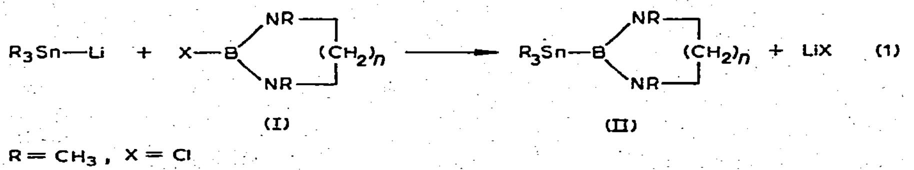
## INTRODUCTION

Organic derivatives of boron in which a boron atom is also bonded to metals are exceedingly rare and little is known about the chemistry of such species. In particular, organoboron heterocycles containing exocyclic boron–metal bonds have not yet been explored in detail.

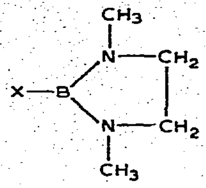
Recently[1], the reaction of 1,3-dimethyl-2-chloro-1,3-diaza-2-boracyclopentane [(I), $n=2$] with trimethylstannyllithium was found to yield 1,3-dimethyl-2-(trimethylstannyl)-1,3-diaza-2-boracycloalkane [(II), $n=2$] and the corresponding diazaboracyclohexane [(II), $n=3$] has now been prepared by an analogous procedure.



One of the features of (II), $n=2$, was the observation that the compound is fairly stable towards attack by oxygen, which is in contrast to the behavior of the

TABLE 1

VIBRATIONAL SPECTRA OF 2-SUBSTITUTED 1,3-DIMETHYL-1,3-DIAZA-2-BORACYCLOPENTANES[a]



| *X=H* | | *X=Cl* | | *X=Sn(CH₃)₃* | |
|---|---|---|---|---|---|
| *Raman* | *IR* | *Raman* | *IR* | *Raman* | *IR* |
| 2977 wm, dp | 2971 m | | 2975 wm | 2970 w, dp | 2969 s |
| 2942 wm, dp | 2940 (sh) | | | | |
| 2909 (sh), dp | | 2898 w, p | 2895 (sh) | 2906 ms, p | |
| 2899 m, p | | | | | |
| 2886 ms, p | 2883 s | 2878 wm, p | | | 2882 vs |
| 2867 s, p | | | | | |
| 2861 (sh), p | 2859 s | 2855 m, p | 2860 vs | | |
| 2845 (sh), p | | | | 2842 ms, p | 2838 s |
| 2839 s, p | | | | | |
| 2816 m, p | | | | | |
| 2794 w, p | 2792 ms | 2797 m, p | 2793 m | 2785 w, p | |
| 2735 vw, dp | | | | | |
| | 2689 w | | | | |
| | 2607 (sh) | | | | |
| | 2598 wm | | | | |
| 2553 w, p | 2550 ms | | | | |
| 2517 w, p | 2518 m | | | | |
| | 2491 (sh) | | | | |
| | | | 1867 vw | | |
| | | | | | 1688 wm (br) |
| | 1561 wm | | | | |
| | 1518 (sh) | | 1526 (sh) | | 1522 (sh) |
| | 1508 s | | 1511 vs | | 1507 (sh) |
| | 1498 (sh) | | 1498 (sh) | 1493 w, dp | 1491 vs |
| | 1475 m | | 1472 wm | | 1472 ms |
| 1448 wm, dp | 1448 s | 1449 w, dp | 1448 ms | 1438 w, dp | 1436 vs |
| 1434 (sh), p | | | | | |
| 1408 ms, p | 1410 s | 1412 w, p | 1409 s | 1405 w, dp | 1398 vs |
| | | | | | 1336 m |
| | | | 1305 (sh) | | |
| 1300 vw, p | 1293 s | | 1295 s | 1285 vw, dp | 1283 vs |
| | 1244 ms | | 1240 ms | 1235 vw, p | 1232 vs |
| 1222 vw | 1222 m | | 1207 m | | |
| 1208 vw, dp | 1200 (sh) | | | | |
| | | 1180 vw | 1182 (sh) | 1192 ms, p | 1192 ms |
| | | | | 1183 ms, p | 1180 (sh) |
| | | | | | 1162 (sh) |
| 1133 vw, dp | 1126 w | | | 1126 vw, dp | 1121 vw |
| | | | 1104 (sh) | | |

(*Continued*)

TABLE 1 (*continued*)

| *X=H* | | *X=Cl* | | *X=Sn(CH$_3$)$_3$* | |
|---|---|---|---|---|---|
| *Raman* | *IR* | *Raman* | *IR* | *Raman* | *IR* |
| | 1084 (sh), ? | 1094 vw | 1090 s | 1087 (sh), dp | 1081 (sh) |
| 1068 m, p | 1064 m | | 1068 (sh) | 1076 w, dp | 1071 s |
| | | | | | 1050 wm |
| | | | | | 1036 m |
| 1020 vw | 1017 wm | | 1005 vw | | 1017 (sh) |
| 990 vw | | | 982 wm | 979 w, p | 975 w |
| 964 w, dp | 960 w | | | | |
| | | 940 w, p | 935 vw | 947 vw | 948 vw |
| | | | | 920 (sh) | |
| | | | | 913 w, p | 912 (sh) |
| | | | | | 908 m |
| 896 m, p | 891 w | | | | |
| 885 vs, p | 880 wm | | | | |
| | 870 wm | | | | |
| 807 vw | 860 m | | 862 vw (br) | | 832 (sh) |
| | | | | | 760 vs (br) |
| 695 vw | | | | | 699 ms |
| 604 w, dp | 596 wm | 612 vw, ? | 609 wm | 610 w, dp | 606 m |
| | | 574 s, p | 569 m | 589 w, p | |
| 549 s, p | | 549 ms | 549 ms | 553 w, p | 549 w |
| | | | | 515 (sh), p | |
| | | | | 507 vs, p | 511 vs |
| | | 435 m, p | 430 m | | |
| | | | | | 412 wm |
| 378 wm, dp | 370 m | | | | |
| 364 (sh), dp | | | | | |
| | | | | 315 w, p | 313 w |
| | | 258 vw, p | | | |
| 245 vw | | | | | |
| | | | | | 212 (sh) |
| 204 vw | | 194 w, dp | | 194 ms, p | 194 w |
| | | | | 155 s, dp | 154 wm |
| | | | | 147 s, dp | |

[a] Neat liquids, frequencies in cm$^{-1}$; w, weak; m, medium; s, strong; v, very; (br), broad; (sh), shoulder; p, polarized; dp, depolarized.

closely related acyclic R$_3$Sn–B(NR$_2$)$_2$ (R=CH$_3$)[2]. This observation may be indicative of changes in the bonding about the boron by incorporating the latter into a cyclic system. In the present work spectroscopic data on the two cited 1,3-dimethyl-2-(trimethylstannyl)-1,3-diaza-2-boracycloalkanes are reported with particular attention being devoted to the derivative of the five-membered heterocycle.

## RESULTS AND DISCUSSION

### *The vibrational spectrum of* 1,3-*dimethyl*-2-(*trimethylstannyl*)-1,3-*diaza*-2-*boracycloalkane*

The vibrational spectrum of 1,3-dimethyl-2-(trimethylstannyl)-1,3-diaza-2-

boracyclopentane together with those of the corresponding 2-hydrido and the 2-chloro derivatives are listed in Table 1. A complete assignment of such multiband spectra cannot readily be accomplished and, in the present context, major attention was devoted only to the identification of vibrational motions involving the boron atoms, and, in particular, of the trimethylstannyl derivative.

In 1,3-dimethyl-2-(trimethylstannyl)-1,3-diaza-2-boracyclopentane boron is bonded to two nitrogen atoms and one tin atom. No information is available on boron–tin vibrational modes but $\sigma$-bonded, boron–nitrogen vibrations are known to occur in the 1350–1525 $cm^{-1}$ region[3]. Of the inner vibrations of the trimethyltin moiety, only CH deformational modes and the tin–carbon stretching might impair the assignment of vibrational modes involving the boron atom.

A strong and polarized Raman line at 510 $cm^{-1}$ with a counterpart in the IR spectrum has been assigned to a tin–carbon stretching mode in the spectra of various trimethyltin derivatives, and a strong but diffuse Raman line near 160 $cm^{-1}$ has been associated with the corresponding deformational vibration[4–6], and the Sn–C stretch of organotin species appears to be fairly insensitive to the nature of the organic groups bonded to the tin atom.

On that basis it seems reasonable to assign $\nu$(SnC) of 1,3-dimethyl-2-(trimethylstannyl)-1,3-diaza-2-boracyclopentane to the IR band observed at 511 $cm^{-1}$ with a counterpart in the Raman spectrum at 507 $cm^{-1}$. This assignment is supported by the complete lack of any absorption in this region in the spectra of the tin-free 1,3-diaza-2-boracyclopentanes listed in Table 1. Moreover, an identical band is observed at 508 $cm^{-1}$ in the IR spectrum of 1,3-dimethyl-2-(trimethylstannyl)-1,3-diaza-2-boracyclohexane (Raman spectrum: 507 $cm^{-1}$) thus lending credence to the suggested assignment (see Table 2).

Assuming simple mass effects, the boron–tin stretch is expected at somewhat higher frequencies, probably in the 520–800 $cm^{-1}$ region. There appear to be five prime candidates for assignment to $\nu$(BSn) in the spectrum of 1,3-dimethyl-2-(trimethylstannyl)-1,3-diaza-2-boracyclopentane: 549, 606, 699, 760 and 908 $cm^{-1}$ respectively. Of these, the frequencies at 549 and 606 $cm^{-1}$ have counterparts in the spectra of the tin-free heterocycles (see Table 1) and hence are likely to be fundamentals of the heterocyclic system. Furthermore, the band at 908 $cm^{-1}$ appears to be somewhat high for a boron–tin stretching mode and, hence, it is suggested to assign $\nu$(BSn) at 760 $cm^{-1}$. The shape of this band is similar to that observed for other vibrations involving boron atoms. It is fairly broad, as one would expect for a B–Sn mode on the basis of isotopic effects, and an identical band is seen in the spectrum of 1,3-dimethyl-2-(trimethylstannyl)-1,3-diaza-2-boracyclohexane at 762 $cm^{-1}$ (see Table 2). It is possible then that the 699 $cm^{-1}$ line may be due to a combination, *e.g.*, (194+511) or (154+549) $cm^{-1}$.

The assignment of $\nu$(BN) in the compound under consideration can now be attempted. On the basis of spectroscopic studies on borazines[7–9] and a variety of 1,3-diaza-2-boracycloalkanes[10–13] two such bands are expected to occur in the indicated range of 1350–1550 $cm^{-1}$. Usually, the higher one of these is exhibited by a strong IR absorption and a weak Raman line, whereas the lower frequency often is not readily identified.

In the higher range of the frequencies cited there are four IR bands of major intensity observed in the spectrum of 1,3-dimethyl-2-(trimethylstannyl)-1,3-diaza-2-

TABLE 2

THE VIBRATIONAL SPECTRUM OF 1,3-DIMETHYL-2-(TRIMETHYLSTANNYL)-1,3-DIAZA-2-BORACYCLOHEXANE[a]

| *Raman* | *IR* | *Raman* | *IR* |
|---|---|---|---|
| 2984 vw, dp ? | | 1100 vw | 1097 m |
| 2970 vw, p ? | 2975 w | 1071 w, dp | 1068 ms |
| | 2950 (sh) | | 1029 vw |
| 2929 (sh), p | 2928 (sh) | 1010 vw | 1009 w |
| 2907 wm, p | | 920 vw, p | 918 vw |
| 2885 (sh), dp | 2890 s | | 908 vw |
| 2841 w, p | 2850 s | | 863 mw |
| | 2824 (sh) | 803 vw, p | 804 (sh) |
| 2793 vw, p | 2788 w | | 762 s (br) |
| | 2362 (sh) | | 698 w |
| | 2348 w | | 631 vw |
| | 1684 w | 581 w, p | 579 w |
| | 1510 (sh) | 507 s, p | 508 s |
| 1484 vw | 1501 s | 478 m, p | |
| | 1468 w | | 430 w |
| 1443 w, dp | 1442 ms | | 349 vw |
| 1392 w, dp | 1404 s | | 301 w |
| | 1352 m | 188 mw, p | |
| 1324 vw, dp | 1321 s | 160 (sh) | |
| 1276 vw, dp | 1272 mw | 155 m, dp | |
| | 1228 (sh) | | |
| 1211 vw, dp | 1211 ms | | |
| | 1204 s | | |
| 1194 mw, p | | | |
| 1184 w, p | 1176 m | | |
| | 1139 w | | |

[a] See footnote, Table 1.

boracyclopentane, *i.e.*, at 1398, 1436, 1472, and 1491 cm$^{-1}$. On the basis of previous studies on 1,3-diaza-2-boracycloalkanes[7-10] the bands observed at 1398, 1436 and 1472 cm$^{-1}$ should be assigned to CH deformations of nearly constant frequency. Hence, only the 1491 cm$^{-1}$ band is left for assignment to the boron–nitrogen stretch. Conveniently, this absorption has a weak counterpart in the Raman spectrum and, in particular, it also has a shoulder observed at 1507 cm$^{-1}$ which is indicative of a $^{10}$B isotope effect. Assignment of the 1491 cm$^{-1}$ to the higher $\nu(BN_2)$ is also supported by the fact that in the spectra of other 1,3-diaza-2-boracycloalkanes the corresponding mode is always found at 1500 ± 10 cm$^{-1}$ and it always has the same band shape.

It is known that the lower $BN_2$ stretch is usually highly mixed and, consequently, much less constant in frequency. Possibly this second $\nu(BN_2)$ may be the IR band at 1336 cm$^{-1}$. However, a positive identification of this mode can only be accomplished by a complete normal coordinate analysis which, in the absence of crystallographic data, seems to be a futile undertaking.

Above 1550 cm$^{-1}$, only CH stretching modes, overtones and combination bands are expected. Assignments of most of the other fundamentals of 1,3-dimethyl-2-(trimethylstannyl)-1,3-diaza-2-boracyclopentane can be based on previous spectroscopic studies of 1,3-diaza-2-boracycloalkane derivatives[10-13] and will not be considered in detail here.

*Magnetic resonance spectra*

The $^1$H NMR spectra of the two 1,3-dimethyl-2-(trimethylstannyl)-1,3-diaza-2-boracycloalkanes are readily interpreted. For the five-membered heterocycle a chemical shift $\delta$ 3.24 ppm (singlet) was obtained for the protons of the annular methylene groups and protons of the *N*-bonded methyl group gave a resonance signal at $\delta$ 2.73 ppm (singlet). The protons of the trimethyltin group (the natural abundances of $^{117}$Sn and $^{119}$Sn are large enough that the splitting they cause is indeed observed) consists of a central singlet ($\delta$ 0.05 ppm) with two doublets symmetrically disposed about the singlet since: $J(^{117}\text{Sn–C–H})$ 45 Hz; $J(^{119}\text{Sn–C–H})$ 48 Hz.

The $^1$H NMR spectrum of 1,3-dimethyl-2-(trimethylstannyl)-1,3-diaza-2-boracyclohexane is quite similar to that of the five-membered ring derivative. Again, the *N*-bonded methyl groups cause a singlet with $\delta$ 2.73 ppm but mutual coupling of the methylene protons gives rise to a triplet ($\delta$ 2.83 ppm) and a quintuplet ($\delta$ 1.88 ppm); resonance signals of the Sn-bonded methyl groups are centered at $\delta$ 0.04 ppm [$J(^{119}\text{Sn–C–H})$ 45 Hz; $J(^{117}\text{Sn–C–H})$ 43 Hz] and are analogous to those of the five-membered heterocycle.

In both spectra the tin–hydrogen coupling constants are quite small; in fact, they appear to be some of the lowest reported coupling constants for four-coordinate trimethyltin derivatives. A decrease in coupling constant has been attributed to a decrease in the *s*-character of the bonding orbitals and the values reported here are comparable to those of tin–metal derivatives indicating a similar bonding in the two types of compounds.

Observation of simple spectra for the annular methylene protons can be inter-

TABLE 3

$^{11}$B CHEMICAL SHIFT DATA[a] ON 1,3-DIAZA-2-BORACYCLOALKANES (I)

| *X* | *R* | *n* | $\delta$ $^{11}B$ |
|---|---|---|---|
| I | $CH_3$ | 2 | −21.3 |
| Br | $CH_3$ | 2 | −26.0 |
| $N(CH_3)_2$ | $CH_3$ | 2 | −26.1 |
| Cl | $CH_3$ | 2 | −27.0 |
| H | $CH_3$ | 2 | −28.3 |
| $CH_3$ | $CH_3$ | 2 | −31.6 |
| $Sn(CH_3)_3$ | $CH_3$ | 2 | −36.5 |
| H | H | 3 | −25.1[b] |
| I | $CH_3$ | 3 | −21.4 |
| Br | $CH_3$ | 3 | −24.8 |
| $N(CH_3)_2$ | $CH_3$ | 3 | −25.1 |
| Cl | $CH_3$ | 3 | −25.2 |
| H | $CH_3$ | 3 | −26.0[c] |
| $CH_3$ | $CH_3$ | 3 | −29.2 |
| $Sn(CH_3)_3$ | $CH_3$ | 3 | −34.6 |
| H | $C_2H_5$ | 3 | −25.5[d] |

[a] Relative to $BF_3$-etherate. [b] $J$(B–H) 131 Hz. [c] $J$(B–H) 132 Hz. [d] $J$(B–H) 128 Hz.

preted to indicate a virtually planar structure for the heterocyclic system in consonance with earlier[14] findings including low temperature studies.

The $^{11}B$ chemical shift data of various 1,3-diaza-2-boracycloalkanes follow a clear pattern. The data compiled in Table 3 seem to indicate that the size of the nitrogen substituents does not have a major influence on the $^{11}B$ chemical shift values. However, the nature of the boron substituents shows the anticipated effects which seem to be quite independent of the ring size.

The effect of the tin atoms on the boron spectra should be comparable with those observed for the proton spectra. However, the large line widths observed in the boron spectra prevent identification of the two different $J(^{117}Sn-^{11}B)$ and $J(^{119}Sn-^{11}B)$ and a (broad) singlet surrounded by two symmetrically spaced but quite broad peaks of lower intensity is observed.

### $^{119}$*Sn Mössbauer spectra*

The liquid nitrogen temperature Mössbauer spectra of 1,3-dimethyl-2-(trimethylstannyl)-1,3-diaza-2-boracyclopentane (a) and the corresponding six-membered derivative (b) are shown in Fig. 1. The spectrum of (a) consists of a broadened resonance line in which the quadrupole splitting (*QS*) is not directly resolved, but can be inferred from the line broadening data, while in (b), the *QS* is clearly resolved in the spectrum. The isomer shifts [(a): 1,375±0.010 mm/sec, (b): 1.368±0.010 mm/sec)] are typical of trimethyltin (IV) compounds in which the metal–ligand bond is essentially covalent and in which the fourth ligand has the effective electronegativity of a halogen, being comparable with the isomer shifts observed for $(CH_3)_3SnCl$ (1.43 mm/sec), $(CH_3)_3SnBr$ (1.38 mm/sec) and $(CH_3)_3SnI$ (1.38 mm/sec).

The *QS* calculated for (a) from the full width at half maximum and a single resonance line width of 0.976±0.020 mm/sec (thickness broadening corrected; the zero thickness full width at half maximum for the $BaSnO_3$ source used under essentially identical conditions is 0.783±0.006 mm/sec) is 0.466 mm/sec. The *QS* observed for (b) is 0.852±0.010 mm/sec. While the *QS* interaction between the metal atom and its nearest neighbor environment is small compared with that observed in trialkyltin halides, pseudohalides or chalcogenides, it is larger than that observed in compounds

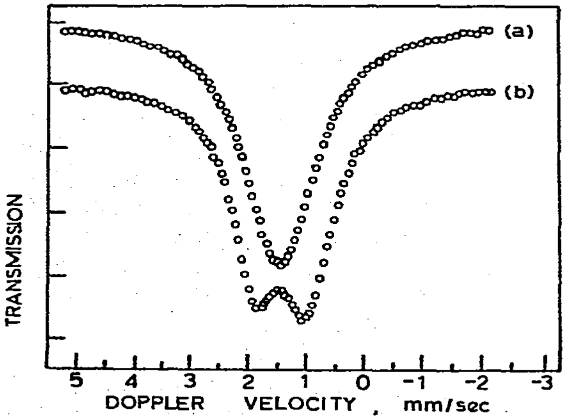


Fig. 1. $^{119}$Sn Mössbauer spectra of 1,3-dimethyl-2-(trimethylstannyl)-1,3-diaza-2-boracyclopentane (a) and 1,3-dimethyl-2-(trimethylstannyl)-1,3-diaza-2-boracyclohexane (b).

of the type $(CH_3)_3SnR$ where R is H, $C_6H_5$, $Sn(CH_3)_3$, etc., *i.e.*, a group lacking a lone pair on the heteroatom bonded to the trimethyltin group. On the other hand, appreciable *QS* interactions have been observed in compounds of this type where R is electron withdrawing such as $CF_3$, $CCl_3$, $C_6F_5$ or $C_6Cl_5$, which show a splitting of 1.1 to 1.6 mm/sec, and such *QS* values are presumed to reflect the inductive effects transmitted through the σ-bonding framework of the metal–ligand bonds. Whatever the detailed description of the electron density in the metal–ligand bond is, it is clear that the magnitude of the quadrupole interaction arises from an imbalance in this density between the three tin–carbon bonds and the tin–boron bond. Assuming that the steric hindrance between the methyl groups bonded to the tin atom and those bonded to the nitrogen atoms in the heterocyclic ligand are negligible, it is apparent that the electron density available in the boron–tin orbital overlap differs significantly in the two compounds (a) and (b), presumably due to the change in the N–B–N bond angle in the five-membered compared to the six-membered ring. The observed quadrupole splitting data show that the field gradient at the metal atom lattice site is about twice as large when the $Sn(CH_3)_3$ moiety is bonded to the six-membered boron heterocycle compared to its five-membered analog. This difference presumably arises from the difference in the inductive effect transmitted to the metal atom in the two cases. The small differences in $J(^{117}Sn–H)$ and $J(^{119}Sn–H)$ observed in the $^1H$ NMR spectra of the tin-bonded methyl group protons are in agreement with this interpretation. Additional systematic variations in the influence of the geometry around the boron atom in these ligands will have to be examined to elucidate this point further.

## CONCLUSION

Vibrational spectroscopic data on the two 1,3-dimethyl-2-(trimethylstannyl)-1,3-diaza-2-boracycloalkanes suggest the assignment of a boron–tin stretching frequency near 760 $cm^{-1}$. As expected, considerable B–N double bonding is evidenced by a B–N stretching frequency observed near 1490 $cm^{-1}$. Consequently, the $^1H$ NMR data indicate an essentially planar structure for the boron–nitrogen–carbon heterocycles as required for good bonding overlap. The $^{11}B$ chemical shift of the two compounds is similar to those heterocycles where the exocyclic substituent is an alkyl group.

$^{119}Sn$ Mössbauer spectra of the 1,3-dimethyl-2-(trimethylstannyl)-1,3-diaza-2-boracycloalkanes indicate that as far as the field gradient generated at the metal atom is concerned the heterocyclic ligand by itself does not differ very much from what is observed for compounds of the type $R_3SnR'$ where R is an alkyl group and R' is either a different alkyl, an aryl, or a trialkyltin moiety (as in hexamethylditin), or hydrogen. As far as the isomer shift is concerned, the values reported here for the cited two compounds are quite comparable with those observed for trimethyltin halides. Compared with tetramethyltin, the isomer shift in the boron derivatives is slightly more positive, thus indicating a greater electron density at the tin nucleus in these compounds than in $Sn(CH_3)_4$.

## EXPERIMENTAL

IR spectra were recorded under standard operating conditions on the neat liquids on a Perkin–Elmer Model 621 double-beam spectrophotometer using cesium iodide windows. The spectrum of 1,3-dimethyl-2-(trimethylstannyl)-1,3-diaza-2-boracyclopentane also was recorded on a Perkin–Elmer Model 180 instrument, courtesy of Perkin–Elmer Corporation, Norwalk, Connecticut.

The Raman spectra of the compounds were excited by a 50 mW Spectraphysics He–Ne laser, Model 125. The spectra were recorded on a Jarrell–Ash Raman spectrometer, Model 25-300 at spectral slit widths of 2.5–4.0 $cm^{-1}$. Each sample was contained under vacuum in a break-off tip, the bottom of which was fashioned into a simple lens by flame polishing. The sample is held vertically, polished end down, and the laser beam travels vertically upward, entering the polished end for a single pass of 2 cm. Right-angle scattering is observed and back-scattered radiation along the horizontal is collected and is focused on the entrance slit by a spherical mirror which has a focal length of 37 mm and a diameter of 50 mm.

$^1H$ NMR spectra were recorded with a Varian spectrometer Model HA60-IL and (or) Model T-60 on solutions of the compounds in carbon tetrachloride and using neopentane as an internal reference. Chemical shift data were recalculated and are listed for TMS as reference using a conversion factor of 0.927 ppm.

$^{11}B$ NMR resonance spectra were recorded at 19.3 Hz on the HA-60IL instrument on the neat liquids using boron trifluoride–etherate as external standard.

$^{119}Sn$ Mössbauer spectra were obtained using a constant acceleration spectrometer as described earlier[15]. Spectrometer calibration was effected using 0.85 mil NBS-SRM 1541 natural iron foil and the usual magnetic hyperfine interaction calculations[16]. The source used in these measurements was $BaSnO_3$ (New England Nuclear Corp.) at room temperature, and all isomer shifts are reported with respect to the center of a room temperature $BaSnO_3$–$BaSnO_3$ spectrum. The liquid samples were injected into Mylar window-fitted copper sample holders using a hypodermic syringe and immediately cooled to liquid nitrogen temperature and maintained at this temperature prior to the spectrum run. Sample temperatures during Mössbauer data accumulation (4–12 h) were monitored using a calibrated thermocouple and were constant to $\pm 2°$ during this interval. The total number of counts per channel accumulated was in excess of $1.2 \times 10^6$. Since the resonance effect magnitude in these runs is approximately 5%, the signal to (statistical) noise ratio is at least 60, and no data points (out of 200) were rejected in the final calculation.

Data reduction was effected using a least squares fitting program in which *n* Lorentzians are fitted using effect magnitude, line width and line positions as variable parameters*. Five iterations (7.3 sec CPU time) gave a value for the parameters which agreed to within 0.003% of the value obtained after ten iterations, and the former is sufficient to reduce the calculational error to well below the ±0.010 mm/sec experimental error quoted above.

Elemental analyses were provided by the Schwarzkopf Microanalytical Laboratory, Woodside, New York 11377.

### 1,3-*Dimethyl*-2-(*trimethylstannyl*)-1,3-*diaza*-2-*boracyclohexane*

First, 1.4 g (0.20 mol) of lithium ribbon and 20 ml of dry tetrahydrofuran were placed in a flask equipped with dropping funnel, reflux condenser, stirrer and dry

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* The authors are indebted to Dr. S. C. Chandra and to Mr. J. Fischer for development of this program. A program listing is available (R.H.H.) on request.

nitrogen flow. The system was cooled in an ice-bath and the flask was continuously flushed with nitrogen. Trimethyltin chloride (10.0 g, 0.05 mol) in 50 ml of tetrahydrofuran was added dropwise over a period of 10 min. The ice-bath was removed and the reaction mixture was stirred at room temperature for 3 h.

A solution of 7.3 g (0.05 mol) of 1,3-dimethyl-2-chloro-1,3-diaza-2-boracyclohexane in 10 ml of tetrahydrofuran was added to the reaction mixture which was filtered after stirring for 10 min. Solvent was stripped off the filtrate and subsequent vacuum distillation of the residue provided 5.5 g (45%) of the desired compound, b.p. 89–91° (4 mmHg). (Found: C, 35.0; H, 7.5; B, 3.8; N, 10.0; Sn, 43.3; mol.wt. cryoscopic in benzene, 271. $C_8H_{21}BN_2Sn$ calcd.: C, 35.0; H, 7.7; B, 3.9; N, 10.2; Sn, 43.2%; mol.wt., 274.8.)

1,3-Dimethyl-2-(trimethylstannyl-1,3-diaza-2-boracyclopentane and other 1,3-diaza-2-boracycloalkanes cited in the present work were prepared by the literature procedures[1,17–19].

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