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1-Triphenylstannyl-*nido*-pentaborane(9): An Example of ^{119}Sn–^{11}B Coupling in a Pyramidal Borane

Lawrence Barton* and Dileep K. Srivastava
Department of Chemistry, University of Missouri-St. Louis, St. Louis, MO 63121, USA

When $K[B_5H_8]$ is stirred with $SnClPh_3$ at room temperature for 12 h, it affords only the 1-$(SnPh_3)B_5H_8$ isomer, for which ^{119}Sn and ^{11}B NMR spectra exhibit ^{119}Sn–^{11}B coupling, the first such observation for a pyramidal borane.

There are not many examples of tin-containing moieties bonded to boron atoms in pyramidal boranes. The known species include some bridge-substituted small pyramidal *nido*-carbaboranes,[1] several bipyramidal *closo*-carbaboranes with Sn replacing an apical boron,[2] larger stannaboranes based on incorporation of tin into a decaborane cage,[3] and the species 2,3-μ-$(SnMe_3)B_5H_8$ in which the $SnMe_3$ group has replaced a bridging hydrogen atom.[4] We have prepared some bridge-substituted tin derivatives of B_6H_{10} and B_5H_9,[5] but in this communication we describe the preparation and NMR spectra of 1-$(SnPh_3)B_5H_8$, **1**, shown in Fig. 1, and provide the first example of ^{119}Sn–^{11}B NMR coupling in a pyramidal borane from both ^{11}B and ^{119}Sn spectra.

Compound **1** is prepared according to equations (1) and (2).

$$B_5H_9 + KH \xrightarrow[\text{thf}]{-78\,^\circ C} K[B_5H_8] + H_2 \qquad (1)$$

$$K[B_5H_8] + SnClPh_3 \xrightarrow[\text{thf, 12 h}]{20\,^\circ C} 1\text{-}(SnPh_3)B_5H_8 + KCl \qquad (2)$$

In a typical experiment, B_5H_9 (3.5 mmol) was condensed onto excess of KH at −196 °C on a vacuum line. Tetrahydrofuran (thf, 10 cm^3) was then added and the reaction flask warmed to −78 °C and the mixture stirred for 2 h. Hydrogen gas is formed quantitatively and was removed and measured on a Toepler pump. The solution was filtered at −78 °C to remove excess of KH, and $SnClPh_3$ (3.5 mmol, 1.35 g) added to the clear solution at −78 °C along with thf (7 cm^3). The solution was allowed to warm to ambient temperature, over a period of 1 h with continuous stirring, and then stirred for 12 h when an off-white turbid mixture was obtained. Work-up of the material afforded a yellowish white solid which we identified as 1-$(SnPh_3)B_5H_8$, obtained in 61% yield.

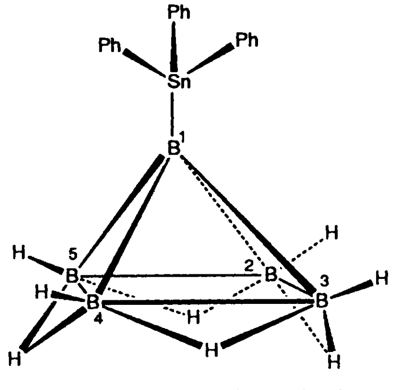

Fig. 1 Proposed geometry of 1-triphenylstannyl-*nido*-pentaborane(9) **1**

Compound **1** is soluble in CH_2Cl_2, $CHCl_3$, Me_2O, thf, and benzene, insoluble in pentane and hexane, and melts at 94–96 °C with decomposition. The infrared spectrum exhibits a strong B–H_t stretching band at 2595 cm^{-1}.† The mass spectrum, run as a solid probe sample at 70 eV (*ca.* 1.12 × 10^{-17} J), exhibits the expected B_5Sn envelope with a cut-off at m/z = 418 for $[^{12}C_8{}^1H_{23}{}^{11}B_5{}^{124}Sn]^+$, and NMR spectra were clearly indicative of a 1-substituted pyramidal pentaborane(9). The ^{11}B NMR spectra for 1-$(SnPh_3)B_5H_8$ are shown in Fig. 2. The doublet at $\delta = -10.5$, $J(^{11}B-^{1}H) = 164$ Hz, of area 4 is assigned to the four basal boron atoms and a singlet at $\delta = -54.6$, with ^{119}Sn satellites, $J(^{11}B-^{119}Sn) = 1123$ Hz, to the apical boron bearing the $SnPh_3$ group. On proton decoupling the low-field resonance becomes a singlet but the high-field resonance does not change. This suggests that the Sn atom is bonded to the apical boron which is expected to fall at higher field.[6] The ^1H NMR spectrum exhibits a 1 : 1 : 1 : 1 quartet of area 4 at δ 2.61, $J(^{1}H-^{11}B) = 160$ Hz, assigned to the basal terminal hydrogens coupled to $^{11}B(I = \frac{3}{2})$, and a broad single resonance of area 4 at δ −2.30, which we assign to the four bridging hydrogens. The ^{119}Sn NMR spectrum (Fig. 3) exhibits a single 1 : 1 : 1 : 1 quartet at $\delta = -89.2$, $J(^{119}Sn-^{11}B) = 1117$ Hz, and clearly visible is the 1 : 1 : 1 : 1 : 1 : 1 : 1 septet, $J(^{119}Sn-^{10}B) = 391$ Hz, which arises from coupling to the ^{10}B nucleus ($I = 3$). This suggests that the tin atom is σ bonded to a single boron atom rather than bridging the basal borons as is the case for the other known tin–pentaborane species, μ-$(SnMe_3)B_5H_8$. In order to check this we prepared the latter species using the procedure described in ref. 4. The ^{119}Sn NMR spectrum of 2,3-μ-$(SnMe_3)B_5H_8$ gives a single somewhat broad resonance at δ 15.3 confirming that the spectra for bridge- and terminally substituted species are, as expected, quite different and distinct.

We believe that **1** is the first example of a pyramidal borane with a tin atom bonded to the apical boron atom. We presume

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† IR data (KBr pellet): 3000m, 3058m, 2967w, 2595s, 1950w, 1879w, 1847m, 1806w, 1578w, 1478m, 1456w, 1427s, 1400m, 1328w, 1294w, 1260m, 1189w, 1156w, 1100m (br), 1072m, 1021m, 996m, 904s, 872w, 857m, 806m, 728s, 699s, 683s (sh), 650m (sh), 600w, 450s and 441s cm^{-1}. Mass spectrum [m/z (relative intensity)] 418 (35.2), 417 (33.52), 416 (37.43), 415 (37.43), 414 (66.48), 413 (94.97), 412 (96.09), 411 (100), 410 (79.33), 409 (60.34) and 408 (37.43). NMR data ($CDCl_3$, 25 °C): ^1H (300 MHz, relative to $SiMe_4$); δ 7.48 [m, 6 H, *o*-H of Ph, $^3J(^{119}Sn-^{1}H) = 46.5$], 7.24 (m, 9 H, *m*-, *p*-H of Ph), 2.61 [q, 4 H, basal H_t, $^1J(^{1}H-^{11}B) = 160$], and −2.30 (s, br, 4 H, H_μ); ^{11}B (96.3 MHz, relative to external $BF_3 \cdot OEt_2$); δ −10.5 [d, 4 B, basal BH_t, $J(^{11}B-^{1}H) = 164$ Hz] and −54.6 [s, 1 B, $BSnPh_3$, $^1J(^{11}B-^{119}Sn) = 1123$]; ^{13}C (76.6 MHz, relative to $SiMe_4$); δ 141.2 [q, *ipso*-C_6H_5, $^2J(^{13}C-^{11}B) = 8.2$], 137.1 [s, br, *o*-C of Ph, $^2J(^{119}Sn-^{13}C) = 33.8$], and 128.2 [s, br, *m*-, *p*-C of Ph, $^3J(^{119}Sn-^{13}C) = 62$]; ^{119}Sn (111.7 MHz, relative to $SnMe_4$); δ −89.2 [q, $^1J(^{119}Sn-^{11}B) = 1117$, $^1J(^{119}Sn-^{10}B) = 391$ Hz].

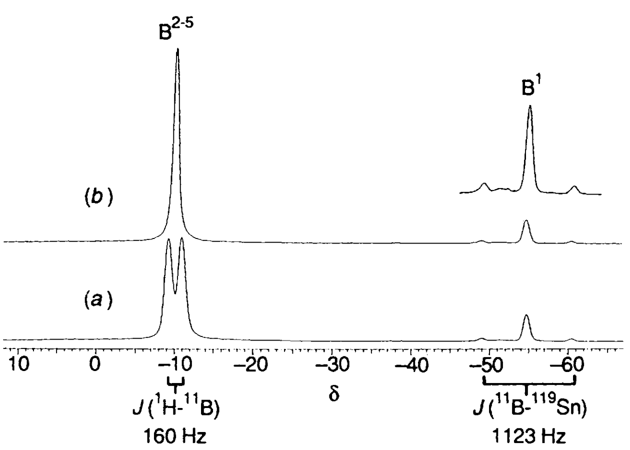

Fig. 2 96.3 MHz ^{11}B NMR spectra of compound **1**: (*a*) coupled, (*b*) ^1H decoupled

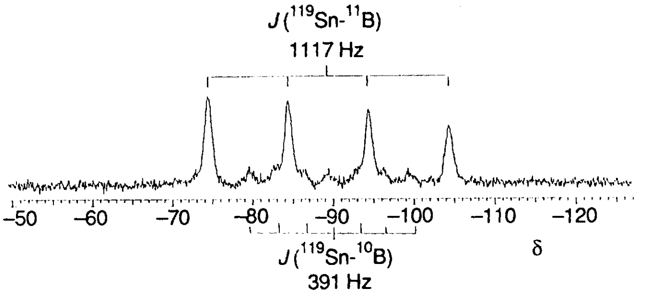

Fig. 3 111.7 MHz $^{119}Sn-\{^1H\}$ NMR spectrum of compound **1**

that the reaction proceeds *via* the initial formation of the bridge-substituted species 2,3-μ-$(SnPh_3)B_5H_8$. Such reactions are well documented and several examples exist in which the smaller Group 14 element-containing moieties replace a bridging hydrogen atom in B_5H_9.[4,5,7] In these latter systems the bridge-substituted isomer rearranges, in the presence of base, to form the 2-substituted species which is thermodynamically much more stable.[8a,b] Gaines and co-workers,[8c,d] in a series of elegant experiments, demonstrated that in the presence of base an equilibrium between the 2- and 1-substituted species exists, and that for several of the systems studied heretofore the 2-substituted isomer appears to be the thermodynamically stable product, and the rearrangement takes place without scission of the boron–substituent bond. These workers also found that 2,3-μ-$(SiMe_3)B_5H_8$ rearranges irreversibly to 2-$(SiMe_3)B_5H_8$ and that the latter is converted into the one isomer in the presence of very strong bases such as hexamethylenetetramine, or at elevated temperatures, but that the final equilibrium mixture contains a 4:1 mixture of the 1- and 2-substituted isomers respectively.[9] The species 2,3-μ-$(SnMe_3)B_5H_8$, is reported not to isomerize to the 2-substituted isomer but that some degradation occurs.[4] However we understand that this was not studied to any great extent.[10] We repeated the experiments and confirmed that indeed 2,3-μ-$(SnMe_3)B_5H_8$ does not rearrange when treated with ethers, 2,6-dimethylpyridine, or hexamethylenetetramine but that degradation occurs. In the case of the $SnPh_3$-substituted species the $SnPh_3$ moiety is sufficiently sterically hindered to render the 2- less stable than the 1-substituted isomer. Thus initial formation of the bridging isomer is followed by isomerization to the 2-substituted isomer, and after 12 h the product is exclusively 1-$(SnPh_3)B_5H_8$, the thermodynamically more stable isomer. If the ^{119}Sn NMR spectrum is run at ambient temperature, after stirring the $SnClPh_3$–$K[B_5H_8]$ mixture at 0 °C for 5 h, the spectrum contains two quartets and a broad resonance. This suggests that all three isomers, 2,3-μ-, 2- and 1-$(SnPh_3)B_5H_8$ are present, and supports our conclusion that the process proceeds as 2,3-μ-$(SnPh_3)B_5H_8 \longrightarrow$ 2-$(SnPh_3)B_5H_8 \longrightarrow$ 1-$(SnPh_3)B_5H_8$.

We also report the first observation of $^{119}Sn-^{11}B$ coupling in a pyramidal borane. There are several reports in the literature of ^{119}Sn NMR spectra of tin bonded to boron.[11,12] The magnitudes of the $J(^{119}Sn-^{11}B)$ range from 554 to 1007 Hz, so our value 1117 Hz, although the highest reported so far, is clearly within the normal range. This is confirmed by our observation of ^{119}Sn satellites in the ^{11}B NMR spectra which give a value of 1123 Hz for $J(^{11}B-^{119}Sn)$. It is well established that resonances involving nuclei with quadrupole moments are substantially broadened due to quadrupolar relaxation.[13] For pyramidal boranes, the more highly symmetrical apical borons provide the least favourable environment for such relaxation and the relaxation times are the longest.[14] Thus it is not unexpected that we were able to observe $^{119}Sn-^{11}B$ coupling only for the apical resonance. These observations portend well for further study of polyhedral boranes containing tin atoms.

Acknowledgements

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