Crystal and Molecular Structure of μ,2′-SnPh$_2$(B$_5$H$_8$)$_2$ and μ,1′-SnPh$_2$(B$_5$H$_8$)$_2$: The First Structurally Characterized Examples of Two Pentaborane Cages Linked by a Single Heteroatom

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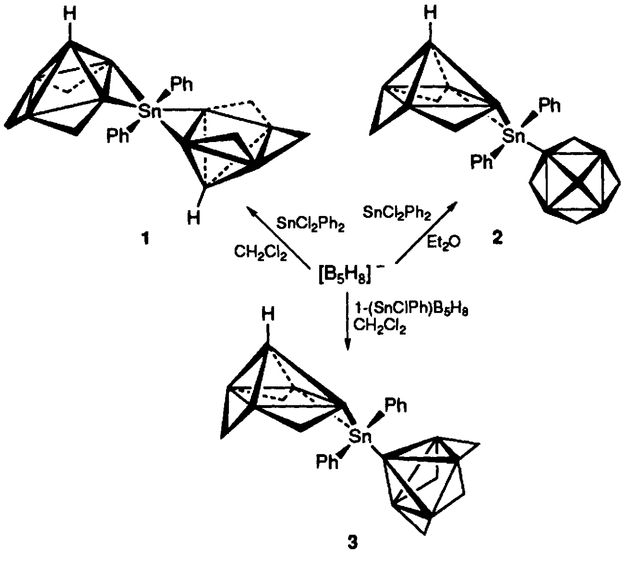
The synthesis and characterization of three of the six possible linkage isomers of SnPh$_2$(B$_5$H$_8$)$_2$ is reported, reaction between K[B$_5$H$_8$] and SnCl$_2$Ph$_2$, in 2 : 1 molar ratio, affording either μ,μ′-SnPh$_2$(B$_5$H$_8$)$_2$, **1**, μ,2′-SnPh$_2$(B$_5$H$_8$)$_2$, **2**, or μ,1′-SnPh$_2$(B$_5$H$_8$)$_2$, **3**, depending on the choice of solvent and conditions; the crystal structures of **2** and **3** are reported and **3** is also prepared in the reaction between K[B$_5$H$_8$] and 1-SnClPh$_2$B$_5$H$_8$.

Examples of borane clusters linked by single heteroatoms are quite rare and the only known systems contain the heteroatoms Cu^{I},[1] Pt^{II},[2] Au^{I},[3] O,[4] Hg^{II},[5] Si and Ge.[6] Of these examples, the last three were characterized by low field NMR spectroscopy and crystal structure determinations are only available for the large B$_{10}$ cages systems [Cu(1-B$_{10}$H$_9$N$_2$)$_2$]$^-$, [Pt(B$_{10}$H$_{12}$)$_2$]$^{2-}$, [Au(B$_{10}$H$_{12}$)$_2$]$^-$, [(B$_{10}$H$_{12}$)Au(B$_{10}$H$_{13}$)]$^{2-}$ and (B$_{10}$H$_{13}$)$_2$O. We have demonstrated recently the utility of ^{119}Sn and ^{11}B NMR spectroscopy, combined with X-ray crystallography, in the characterization triphenylstannyl-*nido*-pentaboranes(9).[7] We now report that selection of solvent allows individual isolation of three of the six possible linkage isomers of SnPh$_2$(B$_5$H$_8$)$_2$ and we also describe the crystal and molecular structure of μ,2′-SnPh$_2$(B$_5$H$_8$)$_2$ and μ,1′-SnPh$_2$(B$_5$H$_8$)$_2$.

Two B$_5$H$_8$ cages may be coupled *via* a SnPh$_2$ moiety by treatment of K[B$_5$H$_8$] with SnCl$_2$Ph$_2$ in 2:1 molar ratio in CH$_2$Cl$_2$ at −35 °C. Stirring the reaction mixture for 4 h and then at 25 °C for 1 h, allows the isolation of μ,μ′-SnPh$_2$(B$_5$H$_8$)$_2$, **1**, as a white solid in 59% yield. Recrystallization from hexane affords colourless needles suitable for X-ray diffraction. Elemental analysis gave unsatisfactory results, probably since **1** is air-sensitive.† **1** decomposes above 98 °C, is very soluble in THF, CH$_2$Cl$_2$ and CHCl$_3$ and is moderately soluble in C$_5$H$_{12}$, C$_6$H$_{14}$ and Me$_2$O. NMR and IR spectra identify **1** as the μ,μ′-isomer.† An X-ray structure determination of **1** was hampered by twinning but the preliminary refinements are consistent with the proposed structure, that is the two B$_5$H$_8$ cages are linked by a SnPh$_2$ group which replaces a bridging H atom in each B$_5$H$_9$ molecule. Details will be reported elsewhere.[8]

If **1** is stored in CDCl$_3$ at 25 °C for several weeks, changes are observed in the NMR spectra. After about one month the ^{119}Sn NMR spectrum shows diminution of the single broad resonance at −40.1 ppm and a 1:1:1:1 quartet appears at −138.5 ppm which we assign to the μ,2′-(SnPh$_2$)(B$_5$H$_8$)$_2$ isomer, **2**. **2** is also formed if the initial reaction between K[B$_5$H$_8$] with SnCl$_2$Ph$_2$ in 2:1 mole ratio is carried out in Et$_2$O. Work up affords a white solid in 64% yield which melts at 74–75 °C. NMR spectra† and a crystal structure determination confirm the identity of **2** whose solubility properties resemble those of **1**. Recrystallization of **2** from hexane affords colourless rectangular crystals which allowed a crystal structure determination.‡ The structure of **2** is given in Fig. 1 along with some structural parameters. The crystal structure of **2** contains two independent molecules which differ in their relative orientation of the B$_5$ cages as indicated by the torsion angles of 72.9 and 63.9 for B(13)–Sn(1)–B(22)–B(21) and B(33)–Sn(2)–B(42)–B(41) respectively. **2** consists of a SnPh$_2$ group coupled to one B$_5$H$_8$ cage at the basal boron B(22) and to the other cage by bridging the basal boron atoms B(12)–B(13). The Sn atom lies well below the basal plane of the cage in which it occupies a bridging position.

If the NMR spectrum of the solution of **1** in CDCl$_3$ is observed after standing for four months a second 1:1:1:1 quartet at −80.1 ppm, assigned to a third isomer, μ,1′-(SnPH$_2$)(B$_5$H$_8$)$_2$, **3**, is observed. Alternatively, **3** is prepared in the reaction between 1-(SnClPh$_2$)B$_5$H$_8$ and K[B$_5$H$_8$] in CH$_2$Cl$_2$ at −35 °C. Workup allows isolation of **3** in 52% yield as an off-white solid. Slow evaporation of a solution in hexane afforded colourless rectangular crystals, suitable for X-ray study. **3** melts at 86–88 °C. It is much more air-sensitive than **1**



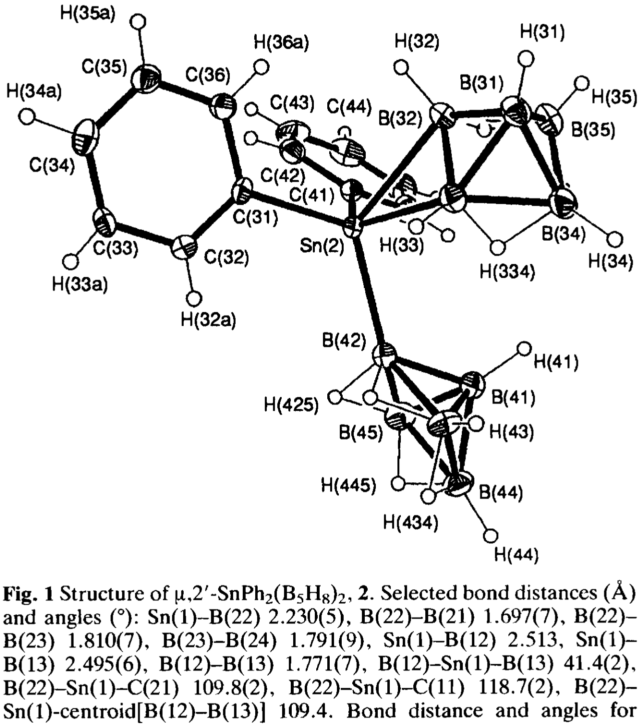


Fig. 1 Structure of μ,2′-SnPh$_2$(B$_5$H$_8$)$_2$, **2**. Selected bond distances (Å) and angles (°): Sn(1)–B(22) 2.230(5), B(22)–B(21) 1.697(7), B(22)–B(23) 1.810(7), B(23)–B(24) 1.791(9), Sn(1)–B(12) 2.513, Sn(1)–B(13) 2.495(6), B(12)–B(13) 1.771(7), B(12)–Sn(1)–B(13) 41.4(2), B(22)–Sn(1)–C(21) 109.8(2), B(22)–Sn(1)–C(11) 118.7(2), B(22)–Sn(1)-centroid[B(12)–B(13)] 109.4. Bond distance and angles for molecule 2 lie within 3σ of these values.

and **2**, and has similar solubility properties to **1** and **2**. Spectral data† are consistent with the identification of **3** as the μ,1′-isomer. The structure of **3**‡ is shown in Fig. 2. The B_5 cage which is bonded to the Sn *via* a bridging site has its open face pointing away from the other B_5 cage. Presumably this position is favoured for steric reasons over the alternative structure in which the open face of the cage points toward the second B_5 cage.

2 and **3** represent the first structurally characterized small borane cages linked by a single heteroatom group. Structures of 2-substituted *nido*-B_5H_9 cages are rare; the only other examples are *trans*-$(PMe_3)_2Br_2(CO)IrB_5H_8$,[9a] [$\mu$-$(Ph_2P)B_5H_7FeCp(CO)_2$][9b] and 2,3-$Me_2B_5H_7$, determined many years ago.[9c] Formation of **1** as the sole product when the reaction is carried out in CH_2Cl_2 clearly is a consequence of the low basicity of the solvent. In the presence of Lewis bases, 2,3-μ-substituted pentaboranes isomerize to the 2- and then the 1-isomers.[10] It is interesting to note that in the presence of a moderately strong base such as Et_2O, rearrangement **1** to **3** does not occur. The alternative preparation of **3** from 1-$(SnClPh_2)B_5H_8$ and $[B_5H_8]^-$ in CH_2Cl_2, is analogous to our original preparation of 2,3-μ-$(SnPh_3)B_5H_8$.[7b] The electrophile $[1\text{-}SnPh_2)B_5H_8]^+$ inserts into the vacant bridging site in $[B_5H_8]^-$ and in CH_2Cl_2 further rearrangement does not occur. There are only two other fully characterized systems with a heteroatom in the 1-position of *nido*-B_5H_9. They are 1-$(SnPh_2Cl)B_5H_8$[7b] and the halogeno-systems, 1-Br-2,3-μ-$(SiMe_3)B_5H_7$[11a] and 1-IB_5H_8.[11b] Several bis(pentaboranyl) species of the type $(B_5H_8)_2MRR'$ (M = Si, Ge; R = H, CH_3) are known and they were assigned as the μ,2′ or 2,2′ isomers on the basis of NMR spectra. Similarly the species μ,μ'-$(B_5H_8)_2Hg$ is known[5] but complexes of the type μ,1′-$(B_5H_8)_2MRR'$ have not, to our knowledge, been described prior to this work.

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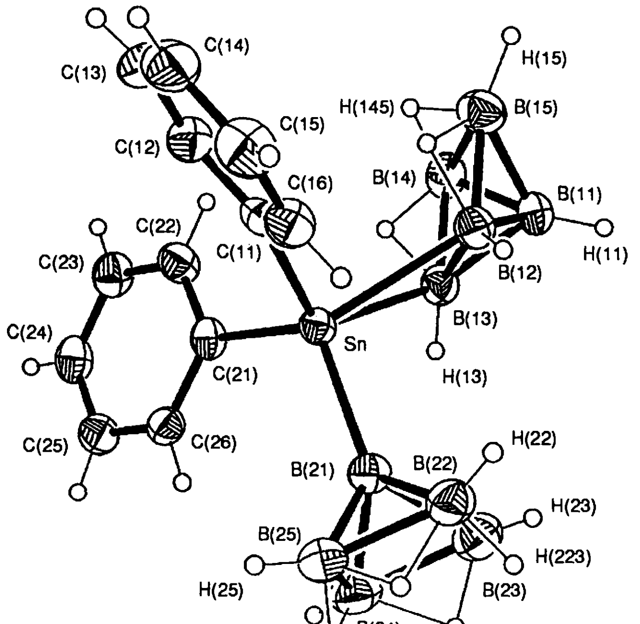

Fig. 2 Structure of μ,1′-$SnPh_2(B_5H_8)_2$, **3**. Selected bond distances (Å) and angles (°): Sn–B(21) 2.197(3), B(22)–B(23) 1.783(5), Sn–B(12) 2.532(3), Sn–B(13) 2.504(3), B(12)–B(13) 1.752(4), B(13)–B(14) 1.801(4), B(14)–B(15) 1.803(5), B(21)–Sn–C(21) 114.3(1), B(21)–Sn–C(11) 113.6(1), B(21)–Sn–centroid[B(12)–B(13)] 105.6

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Footnotes

† *Selected NMR data* for **1** ($CDCl_3$, 25 °C): ^1H NMR (300.1 MHz) 1.5–3.7 [m, br, 8H, H_t(2–5), {H_t(2′–5′)}], 0.90 [q, br, 2H, H(1), {H(1′)}, $J(^{11}B-^1H)$ = 180 Hz], −1.98 [s, br, 2H, H_μ(4,5), {H_μ(4′,5′)}], −2.72 [s, br, 4H, H_μ(2,5) {H_μ(2′,5′)}, H_μ(3,4), {H_μ(3′,4′)}]; ^{11}B (96.3 MHz): −7.4 [d, 4B, B(2,3), {B(2′3′)} $J(^{11}B-^1H)$ = 155 Hz], −10.8 [d, 4B, B(4,5), {(4′,5′)} $J(^{11}B-^1H)$ = 155 Hz], −45.8 [d, 2B, B(1), {B(1′)}, $J(^{11}B-^1H)$ = 176 Hz]; ^{119}Sn (111.5 MHz): −40.1 (s, br, fwhm = 187 Hz); IR/cm^{-1} ν_{BH} = 2592 (s, br). **2**. NMR ^1H: 1.5–3.80 [m, br, 7H, H_t(2–5) {H_t(3′–5′)} *J*unres], 0.85 [q, br, 1H, H(1) $J(^{11}B-^1H)$ = 176 Hz], 0.65 [q, br, 1H, H(1), $J(^{11}B-^1H)$ = 176 Hz], −1.70 [s, br, 2H, H_μ(2′,3′; 2′,5′)], −2.0 [s, br, 3H, H_μ(4,5; 3′,4′; 4′,5′), −2.75 [s, br, 2H, H_μ(3,4; 2,5)]; ^{11}B: −2.6 [d, 1B, B(4′) $J(^{11}B-^1H)$ = 164 Hz], −6.8 [d, 2B, B(2,3), $J(^{11}B-^1H)$ = 155 Hz], −8.2 [d, 2B, B(3′,5′), $J(^{11}B-^1H)$ = 164 Hz]; −10.5 [s, 1B, B(2′ *J*unres], −48.0 [d, 2B, B(1), B(1′), $J(^{11}B-^1H)$ = 177 Hz]; ^{119}Sn: −138.5 [q, $J(^{11}B-^{119}Sn)$ = 900 Hz, fwhm = 244 Hz]; IR/cm^{-1} ν_{BH} = 2589 (s, br). **3**. NMR ^1H: 1.4–3.5 [m, br, 8H, H_t(2–5), {H_t(2′–5′)}], 0.60 [q, br, 1H, H(1), $J(^{11}B-^1H)$ = 175 Hz], −2.15 [s, br, with shoulder, 5H, H_μ(2′,3′; 3′,4; 4′,5′; 2′,5′), shoulder H_μ(4,5)], −2.75 [s, br, 2H, H_μ(3,4; 2,5)], ^{11}B: −10.1 [d, br with shoulder, 8B, B(2–5) {B(2′–5′)}, $J(^{11}B-^1H)$ = 156 Hz], −48.2 [d, 1B, B(1), $J(^{11}B-^1H)$ = 171 Hz], −51.6 [s, 1B, B(1′), $J'(^{11}B-^{119}Sn)$ = 1174 Hz]; ^{119}Sn: −80.1 [q, $J(^{11}B-^{119}Sn)$ = 1174 Hz, fwhm = 200 Hz]; IR/cm^{-1} ν_{BH} = 2596 (s, br).

‡ *Crystal data for* **2** and **3**. $C_{12}H_{26}B_{10}Sn$, *M* = 397.16, $\omega/2\theta$ scan data, 2θ range 3–55°, Mo-Kα radiation, (λ = 0.71073 Å), using a Siemens R3m/V diffractometer. Structure solution by direct methods; semi-empirical absorption correction, refinement by full matrix least squares (SHELXTL PLUS). μ,2′-$(SnPh_2)(B_5H_8)_2$, **2**: monoclinic, *C*2/*c* (No. 15), a = 38.506(14), b = 11.379(2), c = 19.096(6) Å, β = 106.12(2)°, V = 8038(4) Å^3, Z = 16, D_c = 1.313 g cm^{-3}, μ = 1.26 mm^{-1}; T = 125(5) K. 9903 data collected, 9291 independent, 6442 [$F > 4.0\sigma(F)$ used in the refinement, 571 parameters]. R_F = 0.037, R_{wF} = 0.31, S_F = 1.15. μ, 1′-$(SnPh_2)(B_5H_8)_2$, **3**: monoclinic, *P*2$_1$/*c*, (No. 14), a = 9.662(2), b = 9.868(2), c = 21.009(2) Å, β = 92.07(2)°, V = 1993.6(7) Å^3, Z = 4, D_c = 1.323 g cm^{-3}, μ = 1.27 mm^{-1}, T = 184(5) K, 5162 data collected, 4609 independent, 3813 [$F > 4.0\sigma(F)$] used in refinement, 286 parameters. R_F = 0.026, R_{wF} = 0.026, S_F = 1.41 Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for authors, Issue No. 1.

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