The Structures of Seven- and Twelve-vertex Stannacarbaboranes and their Relationship to Cyclopentadienyl Tin Cations

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The stannacarbaboranes, $Sn(Me_3Si)(Me)C_2B_4H_4$ (**1**), $Sn(Me)_2C_2B_9H_9$ (**2**), and $(C_{10}H_8N_2)Sn(Me)_2C_2B_9H_9$ (**4**) have been prepared and the structures of (**1**) and (**4**) have been determined by *X*-ray crystallography.

The group 4 carbaborane derivatives $MC_2B_4H_6$[1] and $MC_2B_9H_{11}$[2] (M = Ge, Sn, or Pb) have been prepared and assigned structures with capping (η^5) M atoms on the basis of spectroscopic data. We report (i) the first *X*-ray crystallographic data for group 4 carbaboranes of this type, (ii) a useful analogy between these compounds and capped cyclopentadienyl cations, $[(\eta^5\text{-}R_5C_5)Sn]^+$, and (iii) the structural consequences of treating these stannacarbaboranes with Lewis bases.

The stannacarbaboranes, $Sn(Me_3Si)(Me)C_2B_4H_4$ (**1**)† and $Sn(Me)_2C_2B_9H_9$ (**2**),† were prepared by the reaction of $SnCl_2$ with $Na[(Me_3Si)(Me)C_2B_4H_5]$[3] and $Na_2[Me_2C_2B_9H_9]$,‡ in tetrahydrofuran (THF) and benzene solutions, respectively. An *X*-ray crystal structure of (**1**)§ (Figure 1) reveals that the Sn atom adopts an essentially η^5-bonding posture with respect to the C_2B_3 face. However, there is a significant 'slippage' of the Sn away from the two C atoms and towards the three B atoms. *X*-Ray-quality crystals of (**2**) have not yet been obtained. However, since ^{11}B n.m.r. data for $PbC_2B_9H_{11}$ are indicative of the displacement of Pb towards the three B atoms,[2] it is reasonable to assume that the C_2B_3 faces of (**1**) and (**2**) are bonded to Sn in a similar manner. Slippages of this type have been observed in $1\text{-}MeGaC_2B_4H_6$ and for transition metal fragments on C_2B_3 faces.[4,5]

Possessing 14 valence electrons, the $C_2B_4H_5$ moiety is isoelectronic with $[C_5H_5]^+$; consequently (**1**) can be regarded as an analogue of $[(Me_5C_5)Sn]^+$ (**3**) which also features an η^5-bonded Sn atom.[6] It is obvious that this analogy should hold for the larger molecule, (**2**). Given this parallel, it is perhaps not surprising that compounds like (**1**) and (**2**) fail to function as Lewis bases.[2,3] It is, in fact, apparent that, like (**3**), (**1**) and (**2**) should behave as Lewis acids. Thus, *e.g.* (**2**) reacts

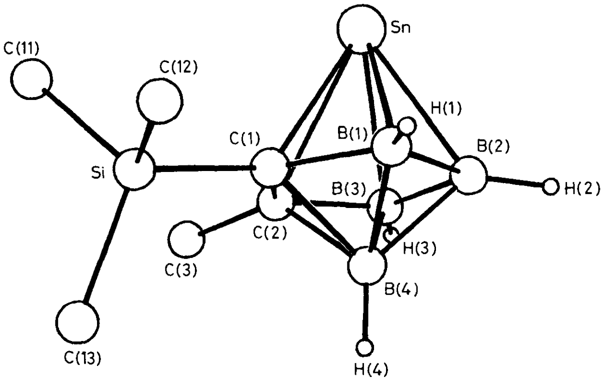

Figure 1. ORTEP view of (**1**) showing the atom numbering scheme. Pertinent parameters include Sn–C(1), 2.476(3); Sn–C(2), 2.489(4); Sn–B(1), 2.402(5); Sn–B(2), 2.378(6); Sn–B(3), 2.426(6) Å.

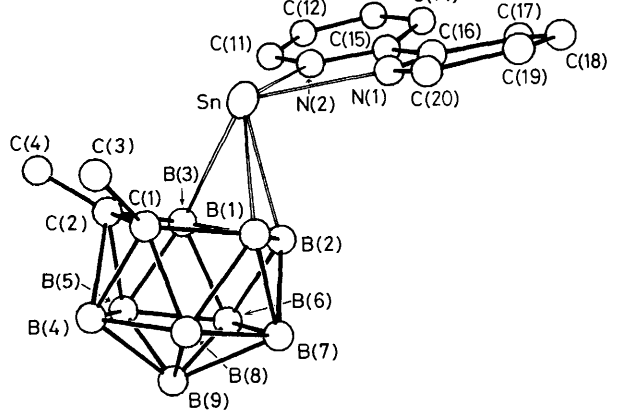

Figure 2. ORTEP view of (**4**) showing the atom numbering scheme. Pertinent parameters include Sn–N(1), 2.412(14); Sn–N(2), 2.374(15); Sn–B(1), 2.56(2); Sn–B(2), 2.35(3); Sn–B(3), 2.55(2); Sn–C(1), 2.88(2); Sn–C(2), 2.85(2) Å.

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† All new compounds had satisfactory chemical analyses and spectroscopic characteristics.

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§ *Crystal data* for (**1**): $C_6H_{16}B_4SiSn$, $a = 18.755(6)$, $b = 11.849(1)$, $c = 12.073(6)$ Å, $\beta = 112.38(3)°$, $U = 2481$ Å^3, monoclinic, space group *C*2/*c* (No. 15), $Z = 8$, $D_c = 1.49$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 22.0$ cm^{-1}. Data were collected on an Enraf-Nonius CAD4-F diffractometer over the range $2.0 \leqslant 2\theta \leqslant 50.0°$ at 293 K. Corrections for Lorentz and polarisation effects were applied but not for absorption or decay (<1.0%). From a total of 2218 unique measured reflections, 1658 $[I > 3.0\sigma(I)]$ were considered observed and used to solve (Patterson) and refine (difference Fourier, full-matrix least-squares) the structure of (**1**). This confirmed the choice of space group as *C*2/*c*. All non-hydrogen atoms were refined anisotropically. Final least squares refinement converged smoothly to give residuals $R = 0.0302$ and $R_w = 0.0424$.

Crystal data for (**4**): $C_{14}H_{23}B_9N_2Sn \cdot C_4H_8O$, $a = 12.502(3)$, $b = 10.502(2)$, $c = 18.627(6)$ Å, $\beta = 94.87(2)°$, $U = 2437$ Å^3, monoclinic, space group *P*2$_1$/*c* (No. 14), $Z = 4$, $D_c = 1.182$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 10.5$ cm^{-1}. Data were collected as described for (**1**) in the range $2.0 \leqslant 2\theta \leqslant 40.0°$. A decay correction was applied due to a 40% decay in standard reflections. The number of unique data measured, 2286, was thus low and only 1438 were considered observed, $I > 2.0\sigma(I)$. Only those atoms in the carbaborane cage and N(1) and N(2) were refined using anisotropic thermal parameters. All others, including the THF of crystallisation, were refined isotropically. Final least squares refinement converged to give residuals $R = 0.0767$ and $R_w = 0.0936$.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

with 2,2′-bipyridine to afford $(C_{10}H_8N_2)Sn(Me)_2C_2B_9H_9$ (**4**),† the structure of which is illustrated in Figure 2.§ As in the case of the pyridine or bipyridine complexes of (**3**), there is a distortion from η^5 towards η^2 or η^3 bonding.[7] In (**4**), the bonding of Sn is exclusively to the three boron atoms; consequently (**4**) can be regarded as an η^3-borallyl complex.

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