Eleven-vertex Polyhedral Stannadicarbaborane Chemistry. 'Naked Tin' {*closo*-1,2,3-SnC_2B_8}-cluster Compounds

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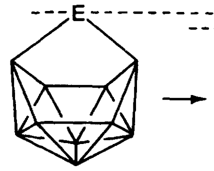
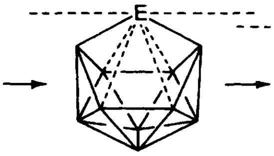
Reaction of anhydrous $SnCl_2$ with the *nido* ten-vertex anions $[6,9\text{-}C_2B_8H_{10}]^{2-}$, $[6\text{-Me-}6,9\text{-}C_2B_8H_9]^{2-}$, $[6\text{-Ph-}6,9\text{-}C_2B_8H_9]^{2-}$ or $[6,9\text{-Me}_2\text{-}6,9\text{-}C_2B_8H_8]^{2-}$ in tetrahydrofuran solution results in the formation of [*closo*-1,2,3-$SnC_2B_8H_{10}$] (59%), [2-Me-*closo*-1,2,3-$SnC_2B_8H_9$] (34%), [2-Ph-*closo*-1,2,3-$SnC_2B_8H_9$] (21%) or [2,3-Me_2-*closo*-1,2,3-$SnC_2B_8H_8$] (10%) respectively as volatile white solids. Their NMR properties suggest that the compounds are best regarded as true *closo* species analogous to *closo*-2,3-$C_2B_9H_{11}$.

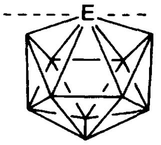
We have become interested in the variety of electronic structures available to the idealised C_{2v} eleven-vertex heteroborane cluster structure **I** when it flexes within the constraints of its basic cluster connectivity.[1-3] We have found that so far there appear to be five increasingly compact (**IA** ⟶ **IB** ⟶ **IC**) structure types that range from bridged *arachno* (*e.g.* the $[1,1\text{-Ph}_2\text{-}1\text{-PB}_{10}H_{12}]^-$ anion[4]), through bridged *nido* (*e.g.* $[1,1\text{-Me}_2\text{-}1,2,3\text{-SnC}_2B_8H_{10}]$[1,3]) and classical true *closo* (*e.g.* $[1,1\text{-}\{P(OMe)_3\}_2\text{-}1,2,3\text{-PtC}_2B_8H_{10}]$[3]), to two successively more compact types {*e.g.* $[1,1\text{-}(PMe_2Ph)_2\text{-}1,2,3\text{-PtC}_2B_8H_{10}]$[1,2] and $[1,1\text{-}(PMe_2Ph)_2\text{-}1,2\text{-}\mu\text{-H-}2,3\text{-}(OMe)_2\text{-}1\text{-RhB}_{10}H_8]$[5] respectively}. The last two are of interest because both deviate from the classical Williams–Wade[6,7] borane cluster formalism. The numbering scheme is shown in structure **II**.



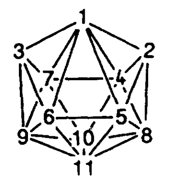
IA



IB

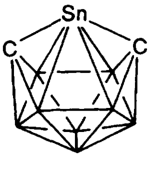


IC

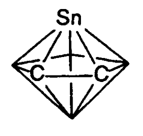


II

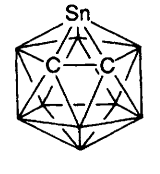
Incidental to our work[3] on the tin(IV) bridged *nido* species $[1,1\text{-Me}_2\text{-}1,2,3\text{-SnC}_2B_8H_{10}]$ we noted that it decomposed in air to give a product that appeared to be a non-methylated 'naked tin' species, $[1,2,3\text{-SnC}_2B_8H_{10}]$ (schematic structure **III**; all boron and carbon atoms have *exo*-terminal hydrogen atoms bound to them). This species also appeared to be a significant product from the treatment of the tin(IV) species $[SnPh_2Cl_2]$ with the [*nido*-6,9-$C_2B_8H_{10}$]$^{2-}$ anion, and the predominant product from the analogous reaction with $[SnBu^t{}_2Cl_2]$. We surmised that a better route to these potentially interesting compounds would be *via* a direct stoichiometric halide displacement on the tin(II) starting material $SnCl_2$ by [*nido*-6,9-$C_2B_8H_{10}$]$^{2-}$. Seven- and twelve-vertex 'naked tin' congeners $[SnC_2B_4H_6]$[8] and $[SnC_2B_9H_{11}]$[9,10] (of schematic structures **IV** and **V** respectively) have been known for some time. These compounds were also prepared from $SnCl_2$ and the appropriate dicarbaborane anion; interestingly, the formation of $[SnC_2B_9H_{11}]$ from bis(organo)tin(IV) dichlorides was also observed.[9] Subsequently, some substituted derivatives of $[SnC_2B_4H_6]$ and $[SnC_2B_9H_{11}]$ have been reported.[11-14]



III



IV



V

There has also been some recent interest in 'carbons apart' dicarbaborane ligands[15] and in this context it is interesting that the new stannadicarbaboranes reported here represent the first examples of 'carbons apart' stannadicarbaboranes.

Results and Discussion

The reaction of the [*nido*-6,9-$C_2B_8H_{10}$]$^{2-}$ anion (disodium salt) with $SnCl_2$ in tetrahydrofuran (thf) solution for a short period (minutes), followed by chromatographic separation, resulted in the isolation of [*closo*-1,2,3-$SnC_2B_8H_{10}$] **1** as a volatile white crystalline solid in 59% yield (reaction scale *ca.* 500 μmol). The 2-methyl- (**2**, 34%), 2-phenyl- (**3**, 21%) and 2,3-dimethyl- (**4**, 10%) derivatives were similarly prepared from [6-Me-*nido*-6,9-$C_2B_8H_9$]$^{2-}$, [6-Ph-*nido*-6,9-$C_2B_8H_9$]$^{2-}$ and [6,9-Me_2-*nido*-6,9-$C_2B_8H_8$]$^{2-}$ respectively. All of the compounds were somewhat air- and moisture-sensitive but could be handled in the ambient atmosphere for short periods. Prolonged dissolution in thf and other oxygen-donor solvents resulted in decomposition. In this context we tried to prepare compound **1** using benzene as the solvent rather than thf; however, this gave a lower yield (22%) and also required a longer reaction time of 1 week.

In its 70 eV ($\approx 1.12 \times 10^{-17}$ J) electron-impact mass spectrum, each compound had a high mass cut-off corresponding to the molecular ion, although the spectrum of one sample of the *C,C*-dimethyl compound **4** showed trace amounts of $[Sn_2C_2B_8H_8Me_2]^+$ (presumably originating from a twelve-vertex *closo* compound) at high detector sensitivities. For all four compounds, generation of Sn^+ was the most apparent

Table 1 NMR data for [*closo*-1,2,3-$SnC_2B_8H_{10}$] **1**, [2-Me-*closo*-1,2,3-$SnC_2B_8H_9$] **2**, [2-Ph-*closo*-1,2,3-$SnC_2B_8H_9$] **3** and [2,3-Me_2-*closo*-1,2,3-$SnC_2B_8H_8$] **4** in $CDCl_3$ solution at 294–297 K

	1		2				3		4	
Assignment	$\delta(^{11}B)$	$\delta(^{1}H)$	$\delta(^{11}B)$	$\delta(^{1}H)$	Observed [^{11}B–^{11}B]-COSY cross peaks	Observed [^{1}H–^{1}H]-COSY cross peaks^{a}	$\delta(^{11}B)$	$\delta(^{1}H)$	$\delta(^{11}B)$	$\delta(^{1}H)$
8^{b}	+0.5	$+3.83^{c}$	$+5.2^{d}$	+3.95	4,5w 10,11s	4,5vw 10,11s	+5.0	+4.12	+0.1	$+3.74^{c}$
9^{b}	+0.5	$+3.83^{c}$	-4.6^{e}	$+3.66^{c}$	6,7w 10,11s	10,11m 3vw	−3.4	+3.77	+0.1	$+3.74^{c}$
$4,5^{f}$	+0.2	+2.48	+1.9	+2.54	8w, 6,7s, 10,11m	8vw	0.0	+2.90	+1.3	+2.49
$6,7^{f}$	+0.2	+2.48	−0.4	+2.46	9w, 4,5s 10,11m	3s	−0.3	+2.57	+1.3	+2.49
$10,11^{g}$	−6.1	+1.96	−6.3	+2.01	8s 9s 4,5m 6,7m	8s 9m	−5.9	+2.15	−6.6	+2.03
2	[CH]	$+6.28^{h}$	[CMe]	$+2.71^{d,i}$	[CMe]	—	[CPh]	*j*	[CMe]	$+2.64^{i}$
3	[CH]	$+6.28^{h}$	[CH]	$+6.04^{e,h}$	[CH]	9vw 6,7s	[CH]	$+6.14^{h}$	[CMe]	$+2.64^{j}$

[a] Measured under conditions of complete {^{11}B} decoupling. [b] $^{1}J(^{11}B–^{1}H)$ *ca.* 165 Hz. [c] $^{3}J(^{119}Sn–^{1}H)$ *ca.* 35 Hz. [d] Possible selective sharpening of $\delta(^{1}H)$(CMe) at +2.71 upon irradiation at $\nu(^{11}B)$ corresponding to $\delta(^{11}B)$ +5.2. [e] Selective sharpening of $\delta(^{1}H)$(CH) at +6.04 upon irradiation at $\nu(^{11}B)$ corresponding to $\delta(^{11}B)$ −4.6. [f] $^{1}J(^{11}B–^{1}H)$ *ca.* 155 Hz. [g] $^{1}J(^{11}B–^{1}H)$ *ca.* 150 Hz. [h] $^{2}J(^{119}Sn–^{1}H)$ *ca.* 45 Hz. [i] $^{3}J(^{119}Sn–^{1}H)$ *ca.* 24 Hz. [j] Aromatic $\delta(^{1}H)$ centred at *ca.* +7.35 (3 H) and *ca.* +7.80 (2 H).

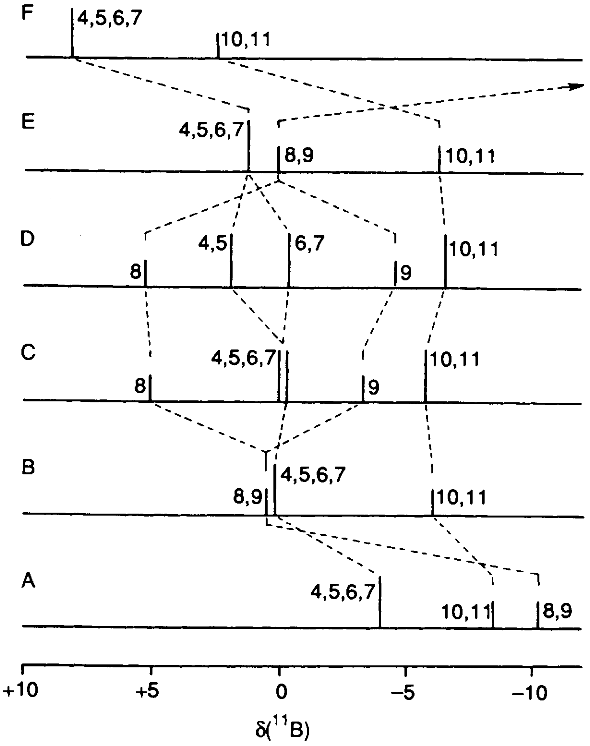


Fig. 1 Stick representations of the chemical shifts and relative intensities in the ^{11}B NMR spectra of A, *closo*-2,3-$C_2B_9H_{11}$ [B(1) is off-scale at δ −15.2]; B, unsubstituted compound **1**; C, the *C*-phenyl compound **3**; D, the *C*-methyl compound **2**; E, the *C,C*-dimethyl compound **4**; and F, the bridged *nido* compound [1,1-Me_2-1,2,3-$SnC_2B_8H_{10}$] [B(8) and B(9) are off-scale at δ −25.3]. Hatched lines join equivalent positions for the six compounds

fragmentation, $^{120}Sn^{+}$ being the base peak in all the spectra. For the two monoorganyl-substituted species **2** and **3** the $[M - Sn]^{+}$ fragment envelope was the second most significant fragmentation.

The ^{11}B and ^{1}H NMR spectra (Table 1 and Fig. 1) were also consistent with the formulations. The ^{11}B spectra are characterised by a very close grouping of the resonances around $\delta(^{11}B)$ *ca.* zero, and there is a somewhat low ^{1}H shielding associated with the BH(8,9) positions. Compared to unsubstituted **1**, the $\delta(^{11}B)$ values for the *C*-monosubstituted compounds **2** and **3** show an interesting adjacent–antipodal imbalance at the 8,9 positions, which is restored on *C,C*-disubsitution (compound **4**). However, these $\delta(^{11}B)$ changes are not large, and occur within the context of a total shielding range of only *ca.* 12 ppm, which is small for a polyhedral boron compound.

The close grouping of the resonances in the ^{11}B NMR spectra, and also the ordering, are markedly at variance with the pattern[1,3] for the tin(IV) 'bridged *nido*' species [1,1-Me_2-1,2,3-$SnC_2B_8H_{10}$] which spans over 30 ppm [$\delta(^{11}B)$: B(4,5,6,7) +8.1, B(10,11) +2.5 and B(8,9) −25.5]. In particular the extreme high-field *nido* $^{11}B(8,9)$ resonance is absent. These differences indicate a different cluster electronic structure. The ^{11}B spectra of compounds **1**–**4** are in fact much more similar to those[1] for the classical *closo* compound *closo*-2,3-$C_2B_9H_{11}$ [$\delta(^{11}B)$: B(1) −15.2, B(4,5,6,7) −4.0, B(8,9) −10.3 and B(10,11) −8.5], suggesting a parallel in bonding and a true *closo* descriptor for these stannadicarbaboranes. This implies that the 'naked' tin(II) vertex behaves in cluster terms rather like the BH(1) vertex in conventional closed eleven-vertex *closo*-2,3-$C_2B_9H_{11}$. This is in accord with the behaviour discussed some time ago[16] for the 'naked' tin vertex in the twelve-vertex analogue [*closo*-3,1,2-$SnC_2B_9H_{11}$].

Experimental

General.—The starting compounds Na_2[*nido*-6,9-$C_2B_8H_{10}$], Na_2[6-Me-*nido*-6,9-$C_2B_8H_9$] and Na_2[6-Ph-*nido*-6,9-$C_2B_8H_9$] were made as described elsewhere;[1,17] Na_2[6,9-Me_2-*nido*-6,9-$C_2B_8H_8$] [previously unreported; $\delta(^{11}B)$: B(5,7,8,10) −3.9, B(1,3) −8.1 and B(2,4) −29.2] was synthesised by essentially the same route.[18] NMR spectroscopy was performed at *ca.* 2.12, 2.35 and 9.4 T using commercially available JEOL FX-90, JEOL FX-100 and Bruker AM-400 instrumentation respectively. The general techniques, and the techniques of [^{11}B–^{11}B]-correlation spectroscopy (COSY),[19,20] and ^{1}H-{^{11}B} NMR spectroscopy,[22] were essentially as described and illustrated in other recent papers from our laboratories.[21–25] Chemical shifts (δ) are given in ppm positive to high frequency (low field) of Ξ100 ($SiMe_4$) for ^{1}H (quoted ±0.05 ppm) and Ξ31.083 971 MHz (nominally $BF_3 \cdot OEt_2$ in $CDCl_3$) for ^{11}B (quoted ±0.5 ppm), Ξ being defined as in ref. 26. Spectra were calibrated using solvent resonances as internal secondary standards. Mass spectra were recorded in the electron-impact ionisation mode (70 eV) on a VG Autospec instrument.

Preparation of Compounds.—The procedure for all four compounds was similar. That for [2-Ph-*closo*-1,2,3-$SnC_2B_8H_9$] **3** is described in detail.

Anhydrous tin(II) chloride (100 mg, 527 μmol) was stirred with a slight excess of Na_2[6-Ph-*nido*-6,9-$C_2B_8H_9$] (140 mg, 580 μmol) in thf (*ca.* 20 cm^3) for 120 min. After this time the thf was removed (rotary evaporator, water-pump pressure, room temperature), CH_2Cl_2 (*ca.* 20 cm^3) added, and the mixture filtered over SiO_2 (TLC grade, Fluka type GF254), washing through with more CH_2Cl_2 (*ca.* 40 cm^3). The clear colourless filtrate was reduced in volume (rotary evaporator, water-pump pressure, room temperature) to *ca.* 5 cm^3, and applied to two preparative TLC plates (silica gel G, Fluka type GF254, 200 × 200 × 1 mm, made on glass plates from a water slurry and dried in air at 80 °C), which were developed using CH_2Cl_2–hexane (70:30). One main component band (R_f 0.23), colourless in daylight, but visible under UV light, was apparent. This was released from the silica by washing with CH_2Cl_2 (3 × *ca.* 20 cm^3), and reduction of the resulting liquid to dryness (rotary evaporator, water-pump pressure, room temperature) yielded [2-Ph-*closo*-1,2,3-$SnC_2B_8H_9$] **3** as a white, moderately air-stable, crystalline solid (35 mg, 111 μmol, 21%), characterised by mass spectrometry and NMR spectroscopy.

The compounds [*closo*-1,2,3-$SnC_2B_8H_{10}$] **1** (reaction time 30 min, R_f 0.33, yield 74 mg, 59%), [2-Me-*closo*-1,2,3-$SnC_2B_8H_9$] **2** (reaction time 10 min, R_f 0.61, yield 44 mg, 34%) and [2,3-Me_2-*closo*-1,2,3-$SnC_2B_8H_8$] **4** (reaction time 60 min, R_f 0.84, yield 14 mg, 10%) were prepared on the same scale in an analogous manner from Na_2[*nido*-6,9-$C_2B_8H_{10}$], Na_2[6-Me-*nido*-6,9-$C_2B_8H_9$] and Na_2[6,9-Me_2-*nido*-6,9-$C_2B_8H_8$] respectively.

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References

1 J. D. Kennedy, B. Štíbr, T. Jelínek, X. L. R. Fontaine and M. Thornton-Pett, *Collect. Czech. Chem. Commun.*, 1993, in the press.

2 J. D. Kennedy, B. Štíbr, M. Thornton-Pett and T. Jelínek, *Inorg. Chem.*, 1991, **30**, 4481.

3 J. D. Kennedy, K. Nestor, B. Štíbr, M. Thornton-Pett and G. S. A. Zammit, *J. Organomet. Chem.*, 1992, **477**, C1.

4 M. A. Beckett and J. D. Kennedy, *J. Chem. Soc., Chem. Commun.*, 1983, 575; M. Thornton-Pett, M. A. Beckett and J. D. Kennedy, *J. Chem. Soc., Dalton Trans.*, 1986, 303.

5 H. Fowkes, N. N. Greenwood, J. D. Kennedy and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1986, 517.

6 K. Wade, *J. Chem. Soc., Chem. Commun.*, 1971, 273; *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 1.

7 R. E. Williams, *Inorg. Chem.*, 1971, **10**, 210; *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 64.

8 K.-S. Wong and R. N. Grimes, *Inorg. Chem.*, 1977, **16**, 2053.

9 T. L. Voorhees and R. W. Rudolph, *J. Am. Chem. Soc.*, 1969, **91**, 2173.

10 R. W. Rudolph, R. L. Voorhees and R. E. Cochoy, *J. Am. Chem. Soc.*, 1970, **92**, 3351.

11 M. S. Islam, U. Siriwardane, N. S. Hosmane, J. A. Maguire, P. de Meester and S. S. C. Chu, *Organometallics*, 1987, **6**, 1936.

12 N. S. Hosmane, N. N. Sirmokadam and R. H. Herber, *Organometallics*, 1984, **3**, 1665.

13 A. H. Cowley, P. Galow, N. S. Hosmane, P. Jutzi and N. C. Norman, *J. Chem. Soc., Chem. Commun.*, 1984, 1564.

14 P. Jutzi and P. Galow, *J. Organomet. Chem.*, 1987, **319**, 139.

15 N. S. Hosmane, L. Jia, H. Zhang, J. W. Bausch, G. K. Surya Prakash, R. E. Williams and T. P. Onak, *Inorg. Chem.*, 1991, **30**, 3793.

16 R. W. Rudolph and V. Chowdhry, *Inorg. Chem.*, 1974, **13**, 248.

17 B. Štíbr, J. Plešek and S. Heřmánek, *Collect. Czech. Chem. Commun.*, 1973, **38**, 338.

18 B. Štíbr and T. Jelinek, unpublished work.

19 T. Venable, W. C. Hutton and R. N. Grimes, *J. Am. Chem. Soc.*, 1984, **106**, 29.

20 D. Reed, *J. Chem. Res.*, (*S*), 1984, 198.

21 X. L. R. Fontaine and J. D. Kennedy, *J. Chem. Soc., Dalton Trans.*, 1987, 1573.

22 M. Bown, X. L. R. Fontaine and J. D. Kennedy, *J. Chem. Soc., Dalton Trans.*, 1988, 1467.

23 M. A. Beckett, M. Bown, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1988, 1969.

24 M. Bown, J. Plešek, K. Baše, B. Štíbr, X. L. R. Fontaine, N. N. Greenwood and J. D. Kennedy, *Magn. Reson Chem.*, 1989, **27**, 947.

25 G. Ferguson, J. D. Kennedy, X. L. R. Fontaine, Faridoon and T. R. Spalding, *J. Chem. Soc., Dalton Trans.*, 1988, 2555; X. L. R. Fontaine, J. D. Kennedy, M. McGrath and T. R. Spalding, *Magn. Reson. Chem.*, 1991, **89**, 711.

26 W. McFarlane, *Proc. R. Soc.* (*London*), *Ser. A*, 1965, **306**, 185.

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