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The first supraicosahedral p-block metallacarboranes

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Reaction of $Na_2[7,9\text{-}C_2B_{10}H_{12}]$ or its C-dimethyl analogue with $SnCl_2$ in THF affords 4,1,6-*closo*-$SnC_2B_{10}H_{12}$ or 1,6-Me_2-4,1,6-*closo*-$SnC_2B_{10}H_{10}$ respectively, the first 13-vertex metallacarboranes involving p-block metals; spectroscopic, structural and theoretical studies, including an analysis of fluctionality in solution, are reported.

The 2-e reduction of 1,2-*closo*-$C_2B_{10}H_{12}$ or its C-derivatives followed by addition of a metal fragment has afforded a wide range of supraicosahedral metallacarboranes. Following the first such species, 4-Cp-4,1,6-*closo*-$CoC_2B_{10}H_{12}$, in 1971,[1] reports of 13-vertex metallacarboranes of early,[2] mid[3] and late[4] transition metals, of group 1[5] and group 2[6] metals, and of lanthanide[7] metals have all appeared. Notable by its absence, however, has been literature dealing with supraicosahedral metallacarboranes of the p-block elements. We now report the synthesis and characterisation of two such species, 4,1,6-*closo*-$SnC_2B_{10}H_{12}$ and 1,6-Me_2-4,1,6-*closo*-$SnC_2B_{10}H_{10}$, and a study of their fluctional behaviour in solution.

When a THF solution of $Na_2[7,9\text{-}C_2B_{10}H_{12}]$† (prepared by Na reduction of 1,2-*closo*-$C_2B_{10}H_{12}$) is allowed to react with 1 equiv. of $SnCl_2$ at 0 °C the colourless stannacarborane[8] 4,1,6-*closo*-$SnC_2B_{10}H_{12}$ (**1**) is formed in 44% yield after work-up involving crystallisation from CH_2Cl_2/40–60° petroleum ether. An analogous reaction starting with $Na_2[7,9\text{-}Me_2\text{-}7,9\text{-}C_2B_{10}H_{10}]$ afforded 1,6-Me_2-4,1,6-*closo*-$SnC_2B_{10}H_{10}$ (**2**) in 31% yield.‡

Compounds **1** and **2** were characterised by mass spectrometry, ^1H, ^{11}B and ^{13}C (and, in the case of **1**, by ^{119}Sn) NMR spectroscopies,‡ and by single-crystal X-ray diffraction studies.§ The crystallographic study of **1**, although sufficiently precise to characterise the species unambiguously as 4,1,6-*closo*-$SnC_2B_{10}H_{12}$, suffers from pseudosymmetry arising from the distribution of heavy (Sn) atoms, and consequently anisotropic refinement of all (non-H) atoms is unstable. In contrast, the structural study of **2** was routine and a view of a single molecule is given in Fig. 1.

The molecule shares the same basic polyhedral geometry observed in earlier 13-vertex metallacarboranes and identified as the ground state geometry for the parent borane $[B_{13}H_{13}]^{2-}$.[9] The heteroatom pattern is 4,1,6-MC_2, shown for $CpCoC_2B_{10}H_{12}$ to be the kinetic isomer (successive thermodynamic isomers being 4,1,8- and 4,1,12-MC_2).[1] Thus the Sn(4) and B(5) vertices are both 6-connected with respect to the polyhedron, whilst C(1) alone is 4-connected. Distances from Sn(4) to adjacent boron atoms are somewhat longer than those previously observed[10] in smaller stannacarboranes; the M(4)–C(6) and B(5)–B(2) and B(5)–B(3) connectivities are particularly long, consistent with the results of previous studies on 13-vertex MC_2B_{10} species.[11]

Thus compounds **1** and **2** represent the first reported examples of supraicosahedral p-block metallacarboranes. They are also unusual examples of Sn^{II} carboranes that are not stabilised by adduct formation (at least in the solid state¶) with Lewis bases,[12] the only previous such examples being 1,2,3-*closo*-SnC_2B_4 species.[9] In terms of cage size the nearest analogous compounds are (bipy)$SnMe_2C_2B_9H_9$ and (THF)$SnMe_2C_2B_9H_9$[13] which display highly slipped [away from the (adjacent) cage C atoms] structures. As heteroborane clusters containing naked tin atoms, compounds **1** and **2** provide a further conceptual bridge between boranes and Corbett's naked tin clusters.[14]

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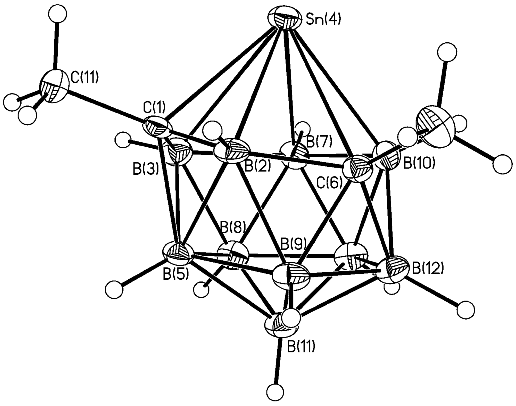

Fig. 1 Perspective view of compound **2**. Selected interatomic distances (Å) include: Sn(4)–C(1) 2.411(3), Sn(4)–B(2) 2.639(4), Sn(4)–C(6) 2.672(4), Sn(4)–B(10) 2.425(4), Sn(4)–B(7) 2.453(4), Sn(4)–B(3) 2.592(4), B(2)–B(5) 2.038(5), B(3)–B(5) 1.941(5), C(1)–C(11) 1.525(5), C(6)–C(61) 1.534(5).

The room temperature ^{11}B NMR spectra of **1** and **2** clearly indicate time-averaged C_s molecular symmetry although the crystallographic studies reveal asymmetric molecules. Unfortunately, variable temperature ^1H and ^{11}B NMR experiments on **1** in CD_2Cl_2 do not yield resolved spectra that could be interpreted in terms of the solid-state structure, even at −90 °C, and so we are not able to determine an activation energy experimentally.

Accordingly, we have studied the fluctional process in compound **1** computationally, using density functional calculations.‖ The fluctional nature of 4,1,6-MC_2B_{10} metallacarboranes has been recognised for many years and has been discussed[16] in terms of a C_s transition state related to the ground state molecule by a double diamond–square rearrangement (Fig. 2). However, to our knowledge, this process has not previously been studied theoretically, and nor has an activation energy been reported.

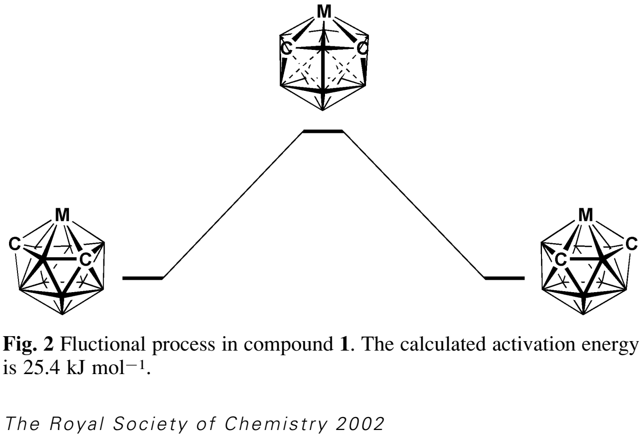

Fig. 2 Fluctional process in compound **1**. The calculated activation energy is 25.4 kJ mol^{-1}.

The optimised structure of **1** corresponds very closely to that determined crystallographically for **2** (the more accurate structure) with average and maximum disagreements on cage bond lengths of only 0.02 and 0.09 Å, respectively. Comparison with the transition state (optimised in C_s symmetry, one imaginary frequency) gives an activation energy of 25.4 kJ mol^{-1} (Fig. 2). Since NMR experiments can only usually be used to probe activation energies in the approximate range 35–100 kJ mol^{-1},[17] our inability to measure this barrier experimentally is thus explained. Finally, we note that it is interesting that the B–B connectivity formally broken in forming the transition state structure is B(2)–B(5), the longest such connectivity in the ground state, which is 2.038(5) Å in the crystal of **2** and 2.083 Å in the theoretical study of **1**.

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Notes and references

† We describe the species $Na_2[C_2B_{10}H_{12}]$ and $Na_2[Me_2C_2B_{10}H_{10}]$ in the conventional *nido* manner although there is recent evidence that they may be better formulated as, for example, (solvated) Na[4,1,6-*closo*-$NaC_2B_{10}H_{12}$]. See ref. 5.

‡ Experimental procedure: for **1**: a dry, oxygen-free, THF solution (20 mL) of 1,2-$C_2B_{10}H_{12}$ (1.01 g, 6.97 mmol) was treated with sodium metal (0.35 g, 15.4 mmol) for 18 h. The resulting solution of $Na_2[C_2B_{10}H_{12}]$ was added to a dry, oxygen-free THF solution (20 mL) of $SnCl_2$ (1.46 g, 7.70 mmol) at −196 °C. After the reaction had warmed to 0 °C all volatiles were removed *in vacuo*. The dark residue was extracted with CH_2Cl_2 (40 mL) and filtered. Concentration of the solution to *ca.* 10 mL, followed by slow addition of 40/60 petroleum ether gave white needles of the product (0.80 g, 44%). IR (KBr): ν_{max} at 2524 cm^{-1} (B–H). ^1H NMR (CD_2Cl_2, 298 K): δ5.51 (br, CH). $^{11}B\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ11.8 (1B), 11.2 (2B), 9.6 (2B), 7.8 (3B), −5.2 (2B). ^{13}C NMR (CD_2Cl_2, 298 K): δ 92.3 (br). ^{119}Sn NMR (CD_2Cl_2, 298 K, chemical shift rel. $SnMe_4$): δ431.0 (br). MS: *m*/*z* 257 (M^+), 143 (M − Sn), 119 (M − $C_2B_{10}H_{12}$). Satisfactory microanalytical data were obtained.

For **2**: similarly, 1,2-Me_2-1,2-$C_2B_{10}H_{10}$ (0.15 g, 0.87 mmol) in 20 mL dry, oxygen-free, THF was treated with sodium (0.06 g; 2.61 mmol) then added to a dry, oxygen-free THF solution (10 mL) of $SnCl_2$ (0.18 g, 0.97 mmol). The product was extracted with CH_2Cl_2 (30 mL), filtered, and crystallised by addition of 40/60 petroleum ether to give the product as white blocks (0.08 g, 31%). IR (KBr): ν_{max} at 2518 cm^{-1} (B–H). ^1H NMR (CD_2Cl_2, 298 K): δ2.39 (s, CH_3). $^{11}B\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ 14.3 (1B), 11.1 (3B), 8.1 (2B), 6.2 (1B), 4.1 (1B), −5.2 (2B). ^{13}C NMR (CD_2Cl_2, 298 K): δ 32.9 (s, CH_3). MS: *m*/*z* 291 (M^+), 171 (M − Sn), 119 (M − $Me_2C_2B_{10}H_{10}$). Satisfactory microanalytical data were obtained.

§ *Crystal data*: for **1**: $C_2H_{12}B_{10}Sn$, $M = 262.91$, monoclinic, Pc, $a = 15.315(4)$, $b = 10.023(4)$, $c = 9.917(2)$ Å, $\beta = 108.593(18)°$, $V = 1442.9(8)$ Å^3, $Z = 6$ (3 independent molecules), $D_c = 1.815$ Mg m^{-3}, $\mu = 2.581$ mm^{-1}, $F(000) = 744$. Data to $\theta_{max} = 25°$ collected at 160(2) K on a Bruker P4 diffractometer using Mo-Kα radiation. 2401 independent reflections, $R_1 = 0.0676$, $wR_2 = 0.1750$, $S = 1.082$, $x = 0.45(13)$ for a model with anisotropic Sn atoms.

For **2**: $C_4H_{16}B_{10}Sn$, $M = 290.96$, monoclinic, $P2_1/n$, $a = 7.0815(5)$, $b = 13.0311(9)$, $c = 12.5779(12)$ Å, $\beta = 94.228(8)°$, $V = 1157.61(13)$ Å^3, $Z = 4$, $D_c = 1.669$ Mg m^{-3}, $\mu = 2.153$ mm^{-1}, $F(000) = 560$. Data collection as for **1**. 2044 independent reflections, $R_1 = 0.0363$, $wR_2 = 0.0933$, $S = 1.068$, for a model with Sn, C and B allowed anisotropic refinement.

CCDC reference numbers 173828 and 173829.

See http://www.rsc.org/suppdata/cc/b1/b110490j/ for crystallographic data in CIF or other electronic format.

¶ However, NMR spectroscopy of a CD_2Cl_2 solution of **1** that had not previously been recrystallised revealed clear evidence of the 1 : 1 adduct **1**. THF in the ^1H spectrum and measurably different chemical shifts [δ 12.7 (1B), 10.3 (2B), 9.7 (2B), 7.3 (2B), 6.3 (1B), −6.2 (2B)] in the $^{11}B\{^1H\}$ spectrum.

‖ Calculations used the ADF1999 program[15] with the BP86 functional and incorporated a treatment of relativistic effects. A triple-ζ plus polarisation STO basis set was used for Sn and a double-ζ plus polarisation STO basis set for all other atoms. The frozen core approximation was applied (Sn: 4d; C, B: 1s). Stationary points were fully characterised *via* frequency analyses, and a correction for zero point energy was included in the calculated activation energy.

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