Reductive and Non-reductive Insertions of Silicon Atoms into Carbaborane Cages: Synthesis and Structure of a Carbaborane Analogue of Bis(cyclopentadienyl)silicon

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The silacarbaboranes $[(Me_3Si)_2C_2B_4H_4]Si^{II}$ (**1**) and $[(Me_3Si)_2C_2B_4H_4]_2Si^{IV}$ (**2**) have been prepared and the structure of (**2**) has been determined by *X*-ray crystallography.

The group 4 atoms (Ge, Sn, and Pb) in their +2 oxidation states have been inserted into carbaborane cages.[1] The reactions involving these atoms in their +4 oxidation states generated bridge-substituted complexes in which the hetero-atom was η^2 linked to the carbaborane cages by a three-centre B–M–B bond.[2] The only reported example in which a group 4 atom is in a doubly bridged position is $\mu,\mu'\text{-}SiH_2(C_2B_4H_7)_2$.[3] Recently, preliminary results on the syntheses and structures of carbaborane analogues of bis(cyclopentadienyl)germanium, $[(Me_3Si)_2C_2B_4H_4]_2Ge$, and bis(cyclopentadienyl)silicon, $[C_2B_9H_{11}]_2Si$, have been reported by Hosmane *et al.*[4] and Hawthorne *et al.*[5] In both compounds, the group 4 atom is in its +4 oxidation state and ten-co-ordinated. We report (i) the first reductive insertion of Si into the carbaborane cage to prepare $[(Me_3Si)_2C_2B_4H_4]Si^{II}$ (**1**), (ii) a synthesis of $[(Me_3S_i)_2C_2B_4H_4]_2Si^{IV}$ (**2**) *via* a non-reductive insertion of Si, and (iii) the crystal structure of (**2**).

Both (**1**) and (**2**) were isolated in 1.0 and 18% yields, respectively from a reaction involving $SiCl_4$ and $Na^+Li^+[(Me_3Si)_2C_2B_4H_4]^{2-}$ in tetrahydrofuran (THF).† The proposed structure of (**1**) (Figure 1) is consistent with its spectroscopic data‡ which are quite similar to those of stannacarbaboranes[1f] and germacarbaboranes.[4] The reductive insertion of Si into a carbaborane cage in the synthesis of (**1**) would be expected, since tin and germanium atoms, in the same series, undergo reduction from +4 to +2 oxidation states during the syntheses of stannacarbaboranes[6] and germacarbaboranes,[4] respectively. Furthermore, the structure of bis(pentamethylcyclopentadienyl)silicon, the first π-complex with Si^{II} as the central atom, is now well documented by *X*-ray crystallography.[7]

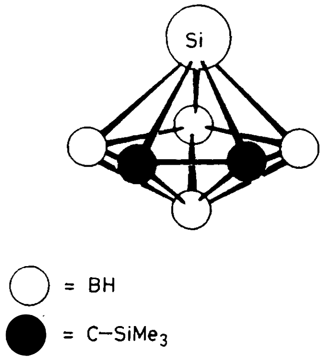

Figure 1. Proposed structure of (**1**).

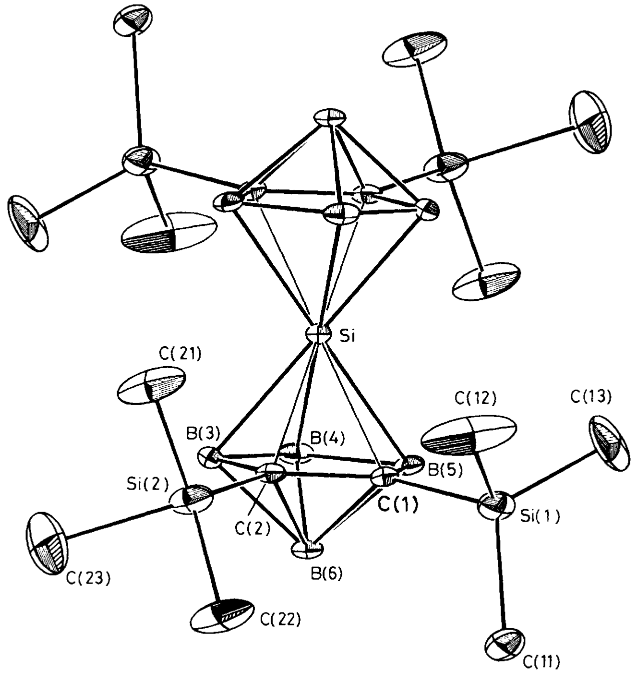

Figure 2. ORTEP view of (**2**) showing the atomic numbering scheme. Bond distances involving the central Si atom are: Si–C(1) 2.23(1), Si–C(2) 2.25(1), Si–B(3) 2.10(1), Si–B(4) 2.03(1), and Si–B(5) 2.10(1) Å.

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† A THF solution of $Na^+[(Me_3Si)_2C_2B_4H_5]^-$ (5.92 mmol) was added to a THF solution of BuLi (6.0 mmol) *in vacuo* and the resulting mixture was allowed to react with $SiCl_4$ (2.96 mmol) with constant stirring at 0 °C for 6 h. After removal of THF at 0 °C *via* vacuum distillation for 4 h, the reaction flask was attached to a high-vacuum U-trap sublimator. With identical sublimation procedures and times as described for stannacarbaboranes[1f] compound (**1**) (0.061 mmol), as an air-sensitive colourless liquid, compound (**2**) (0.52 mmol), as moderately air-stable transparent crystals, and *nido*-$[(Me_3Si)_2C_2B_4H_6]$ (2.48 mmol) were obtained in traps held at 0, 25, and −23 °C, respectively. Compounds (**1**) and (**2**) (m.p. 118 °C) are highly soluble in both polar and non-polar organic solvents.

‡ The mass spectra of both (**1**) and (**2**) exhibit characteristic groupings corresponding to their molecular ions, and the i.r. spectra are identical to those of corresponding germanium analogues. Fourier transform n.m.r.: (**1**), ^1H ($CDCl_3$, relative to external Me_4Si) δ 3.8 [q (br. overlapping), 3H, basal H_t, $^1J(^1H-^{11}B)$ 110 Hz], 0.73 [q (br.), 1H, apical H_t, $^1J(^1H-^{11}B)$ 170 Hz], and 0.43 [s(br.), 18H, Me_3Si]; ^{11}B ($CDCl_3$, p.p.m. relative to external $BF_3\cdot OEt_2$) δ 15.56 [d, 2B, basal BH, $^1J(^{11}B-^1H)$ 160 Hz], 6.82 [d, 1B, basal BH, $^1J(^{11}B-^1H)$ 150 Hz], and −16.79 [d, 1B, apical BH, $^1J(^{11}B-^1H)$ 175 Hz]; ^{13}C ($CDCl_3$, relative to external Me_4Si) δ 110.43 [s(br.), cage C] and 2.41 [q, Me_3Si, $^1J(^{13}C-^1H)$ 120 Hz]; (**2**), ^1H ($CDCl_3$, relative to Me_4Si) δ 3.86 [q (br. overlapping), 6H, basal H_t, $^1J(^1H-^{11}B)$ 110 Hz], 0.91 [q(br.), 2H, apical H_t, $^1J(^1H-^{11}B)$ 170 Hz], and 0.41 [s(br.), 36H, Me_3Si]; ^{11}B ($CDCl_3$, p.p.m. relative to external $BF_3\cdot OEt_2$) δ 20.39 [d, 4B, basal BH, $^1J(^{11}B-^1H)$ 110 Hz], 4.16 [d, 2B, basal BH, $^1J(^{11}B-^1H)$ 112 Hz], and −43.35 [d, 2B, apical BH, $^1J(^{11}B-^1H)$ 156 Hz]; ^{13}C ($CDCl_3$, relative to external Me_4Si) δ 123.85 [s(br.), cage C] and 1.36 [q, Me_3Si, $^1J(^{13}C-^1H)$ 120 Hz]; ^{29}Si ($CDCl_3$, p.p.m. relative to external Me_4Si) δ −1.25 [m, Me_3Si, $^2J(^{29}Si-^1H)$ 6.1 Hz], −137.92 [s(br.), cage Si].

The *X*-ray crystal structure of (**2**),§ shown in Figure 2, reveals that the silicon atom adopts an essentially η^5-bonding posture with respect to each of the C_2B_3 faces. However, the Si–C distances of 2.23(1) and 2.25(1) Å are substantially longer than the Si–B distances [2.10(1), 2.03(1), and 2.10(1) Å]. This type of slippage from η^{10} to η^6 has been observed in the structures of $[(Me_3Si)_2C_2B_4H_4]_2Ge^{IV}$,[4] $[C_2B_9H_{11}]_2Si^{IV}$,[5] and $(Me_5C_5)_2Si^{II}$.[7] The $[C_2B_4H_4]^{2-}$ moiety is isoelectronic with $[C_5H_5]^-$ by contributing 16 valence electrons [3 and 2 electrons from each of the C(R) and BH groups, respectively] to the cage or ring. Consequently, (**2**) can be regarded as an analogue of $(Me_5C_5)_2Si^{II}$ which also features an η^{10}-bonded Si atom and possesses 32 valence electrons.

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§ *Crystal data for* (**2**): $C_{16}H_{44}B_8Si_5$, $a = 10.101(3)$, $b = 11.460(2)$, $c = 13.486(2)$ Å, $\beta = 90.72(2)°$, $U = 1560.9(6)$ Å^3, monoclinic, space group $P2_1/n$, $Z = 2$, $D_c = 0.986$ g cm^{-3}, μ(Mo-K_α) = 2.27 cm^{-1}. Data were collected on a Syntex P2$_1$ diffractometer to $2\theta = 43°$. No decay was observed. The data were corrected for Lorentz-polarisation, but not for absorption. 1804 unique reflections were measured of which 1021 were considered as observed $[I > 3\sigma(I)]$ and only these were used subsequently. Refinement started with the co-ordinates of the non-H atoms of its Ge analogue, these two compounds being isostructural. All non-H atoms were refined anisotropically. None of the methyl H atoms could be located but the four cage H atoms were located and refined isotropically. Final full-matrix least-squares refinement converged to $R = 0.088$ and $R_w = 0.095$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

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