Novel Bicyclic Organoboranes via 1,1-Organoboration

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Tris[ethynyl(dimethyl)silyl]methane **1** and tris[trimethylstannylethynyl(dimethyl)silyl]methane **2** react with triethylborane **3** via a threefold 1,1-ethylboration to give the new bicylic compounds **4** and **5** in good yields; the molecular structure of **5** was determined by a single crystal X-ray analysis.

The formation of macrobicyclic compounds is particularly straightforward if intramolecular reactions can be found to engage at least three functions of a noncyclic polyfunctional system.[1] Starting from suitably designed alkynyl–silicon or –tin compounds, 1,1-organoboration reactions[2] could serve this purpose. Therefore, we have prepared tris[ethynyl-(dimethyl)silyl]methane **1**† and tris[trimethylstannyl-ethynyl(dimethyl)silyl]methane **2**,† following literature methods[3–5] for some steps of the procedure. Tris[bromo-(dimethyl)silyl]methane, HC[Si(Me₂)Br]₃, was obtained as described,[3] and after treatment with 3 equiv. of HC≡CMgBr in THF[4] compound **1** was isolated (yield 58.5%). The reaction between **1** and 3 equiv. of Et₂N–SnMe₃, a general method for preparing alkynyltin compounds,[5] gave **2** in quantitative yield.

The reaction between **1** and Et₃B **3** in Et₃B as the solvent for several days at 100 °C afforded the tricyclic compound **4**‡ (Scheme 1) in 80% yield as a colourless, oily liquid. The reaction between **2** and **3** (Scheme 1) proceeded under much milder conditions (−78 °C to room temp.), and produced the analogous compound **5** as a colourless solid (crystalline material isolated in 55% yield). The characterization of **4** and **5** by multinuclear NMR in solution is straightforward (Table 1). The position of the substituents at the C=C bonds follows unambiguously from the observation of coupling constants $^1J(^{13}C^1H)$ (**4**), $^1J(^{29}Si^{13}C)$ (**4, 5**) and $^1J(^{119}Sn^{13}C)$ (**5**), and broad $^{13}C(BC)$ resonances[6] for the olefinic carbon atoms (see Fig. 1). The chirality of **5** is revealed by low-temperature NMR spectra showing the non-equivalence of the SiMe groups and the typical pattern of an ABM₃ spin system in the ^1H NMR spectrum for the ethyl groups.

In order to build the bicyclic compounds **4** and **5**, the stereochemistry of the first step, the intermolecular 1,1-organo-boration reaction, is of prime importance. In general, the boryl group and the other organometallic group end up in *cis*-positions at the C=C double bond.[2] Thus, in the case of **1**, the first step affords an intermediate in which further intramolecular 1,1-organoboration reactions lead directly towards the product **4**. If both a stannyl and a silyl group are present as in **2**, the

formation of mixtures of (*E*)- and (*Z*)-isomers must be expected in the first step.[2,7] However, for this particular pattern of
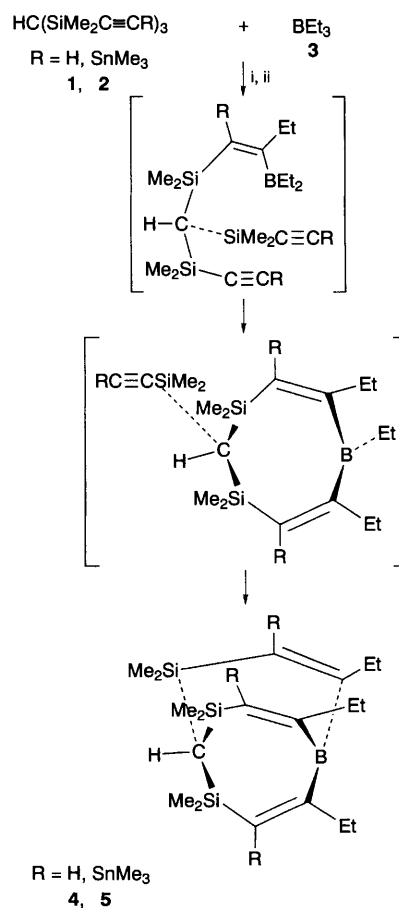
Scheme 1 *Reagents and conditions*: i, R = H: Et₃B serves as the solvent, 100 °C for 7 d; ii, R = SnMe₃: toluene, −78 °C to room temp., 1 h

Table 1 ^1H, ^{13}C, ^{29}Si and ^{119}Sn NMR data^a of compounds **4** and **5**

Parameters	4^b	5^c
δ ^{13}C (*C*=)	129.4 (67.6)^d	145.3 (56.3) [302.0]
δ ^1H (*H*C=)	5.87 {1.3, ^4J}	—
δ ^{13}C (=*C*B)	170.2, br	179.8, br [39.5]
δ ^{13}C (*H*C)^e	4.7 (38.1)	10.8 (24.2)
δ ^1H (*H*C)	−0.53 (9.9) {1.1, ^4J}	−0.44 (7.6)
δ ^{13}C (Si*Me₂*)	3.7 (52.3)	3.0 (50.5), 5.3 (52.0)
δ ^1H (Si*Me₂*)	0.19 (6.8)	0.00 (6.8), −0.05 (6.8)
δ ^{13}C (Sn*Me₃*)	—	−5.7 [306.2]
δ ^1H (Sn*Me₃*)	—	0.08 [51.3]
δ ^{13}C (*Et*)	30.0 (8.7), 12.9	33.0 (12.6) [98.9], 15.6
δ ^1H (*Et*)	2.12 {7.5, ^3J, 1.3, ^4J, 1.1, ^4J} 1.00 {7.5, ^3J}	2.25, 2.23 [9.3] {m} {7.5, ^3J} 0.90 {7.5, ^3J}
δ ^{11}B	78.1	f
δ ^{29}Si	−10.0	−5.2^g [92.7, ^2J (^{119}Sn, ^{29}Si)]

^{a} $^nJ(^{119}Sn^{13}C)$ in Hz are given in [ ]; $^nJ(^{29}Si^{13}C)$ in Hz are given in ( ); $^nJ(^1H^1H)$ in Hz are given in { }; br denotes broad signals due to partially relaxed scalar coupling $^1J(^{13}C^{11}B)$. ^{b} EI-MS *m/z* (%) 360 (M⁺) (8), 345 (M⁺ − Me) (26), 247 [M⁺ − SiMe₂C(H)=C(Et)] (100), 73 (SiMe₃) (17). ^{c} In CDCl₃ at 233 K; ΔG* [263 K, ^1H(Me₂Si)] = 56.3 ± 1 kJ mol⁻¹; EI-MS *m/z* (%) 848 (M⁺) (4), 685 (M⁺ − SnMe₃) (72), 165 (SnMe₃) (100). ^{d} $^1J(^{13}C^1H)$ = 137.9 Hz. ^{e} $^1J(^{13}C^1H)$ = 97.0 Hz **4**; $^1J(^{13}C^1H)$ = 100.1 Hz **5**. ^{f} ^{11}B NMR signal is too broad for accurate measurement. ^{g} δ ^{119}Sn −58.3.

substituents the 1,1-organoboration is readily reversible,[2] and the equilibrium is finally shifted towards compound **5** by further irreversible intramolecular 1,1-organoboration reactions. It has been found that the intermolecular 1,1-ethylboration of alky-
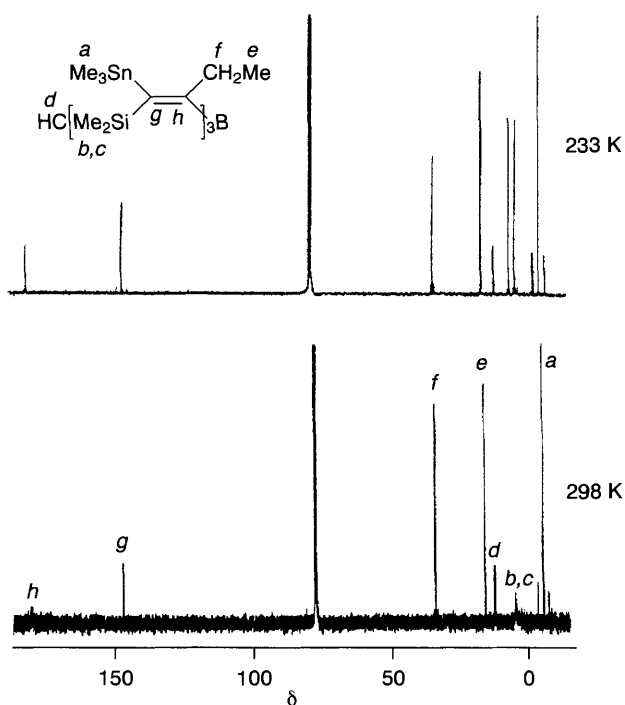

Fig. 1 75.5 MHz ^{13}C{^{1}H} NMR spectra of **5** in CDCl$_3$ at variable temperature. Note the appearance of two ^{13}C (SiMe) resonances (*b,c*) and the 'quadrupole decoupled' ^{13}C (=C–B) resonance (*h*) at low temperature.
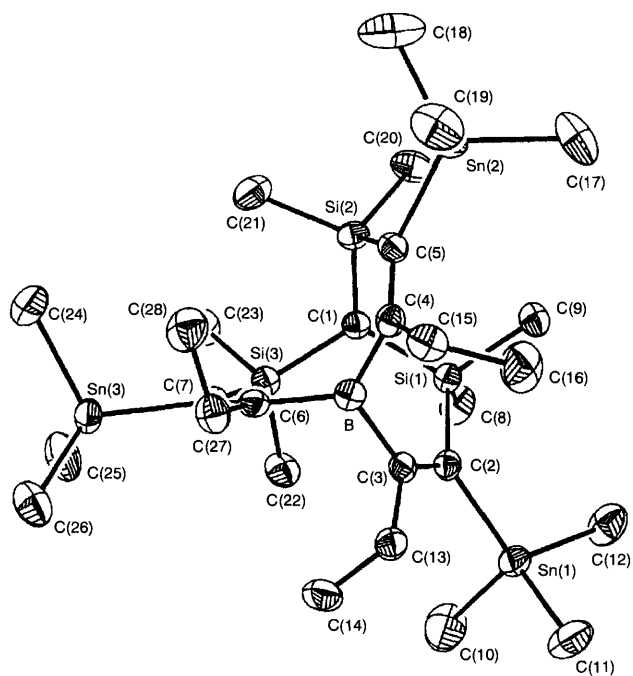

Fig. 2 Molecular structure of **5** as determined by X-ray analysis. Selected bond lengths [pm], bond angles and torsion angles [°]: B–C(3,4,6) 157.5, C(2,5,7)–C(3,4,6) 134.8, Si(1,2,3)–C(1) 189.6, Si(1,2,3)–C(2,5,7) 187.4, Si(1,2,3)–C(Me) 187.8, Sn(1,2,3)–C(2,5,7) 216.8, Sn(1,2,3)–C(Me) 215.1; B–C(3)–C(2) 124.8(3), Si(1)–C(2)–C(3) 119.1(2), Si(1)–C(2)–Sn(1) 117.8(1), Sn(1)–C(2)–C(3) 123.0(2), C(2)–C(3)–C(13) 123.3(2); C(1)–Si(1)–C(2)–C(3) −27.2, Sn(1)–C(2)–C(3)–B −179.9, Sn(1)–C(2)–C(3)–C(13) −2.3

nylsilanes requires rather harsh reaction conditions,[8] whereas intramolecular 1,1-ethylborations can be expected to proceed much more readily.[9] This favours the formation of the bicyclic structure over polymerization products which may result from intermolecular reactions. If the progress of the reaction between **1** and **3** is monitored by using ^{29}Si NMR, signals for potential intermediates are not detected. Only the signals for **1** and the final product **4** can be observed, thus confirming the expected[9] relative reaction rates of slow inter- and fast intra-molecular 1,1-organoboration of alkynylsilanes. In the case of **2**, the stereochemistry of the 1,1-organoboration is not defined,[2,7] and in addition, inter- and intra-molecular 1,1-organoboration may compete with each other[2,10] because of the mild reaction conditions required for the cleavage of the Sn–C≡ bond. By monitoring the reaction between **2** and **3** using ^{29}Si and ^{119}Sn NMR the presence of numerous intermediates becomes apparent. The unassigned ^{29}Si and ^{119}Sn NMR signals for these intermediates disappear after 1 h at room temperature in favour of those for the final product **5**.

The molecular structure of **5**§ is shown in Fig. 2. The geometry of the boron atom is close to trigonal planar [sum of bond angles C–B–C = 358.7(6)°]. The boron atom is shifted slightly by 10.5 pm out of the plane formed by the boron-bonded olefinic carbon atoms. The methane carbon atom possesses a distorted tetrahedral geometry with rather large bond angles Si–C–Si [116.7(1), 117.2(1) and 118.0(1)°], and it is shifted by 31.5 pm out of the Si(1)–Si(2)–Si(3) plane. The three C–C–Si bridges between the boron and the methane carbon atom are arranged with a helical twist which means that the molecule is chiral and the unit cell contains both enantiomers ($P\overline{1}$, $Z = 2$).

It is expected that extensions of 1,1-organoboration reactions to variants of **1** or **2** will open the way to other new bicyclic compounds. Considering the presence of various functionalities in compounds of types **4** or **5** there is much scope for further transformations.

Footnotes

† Satisfactory spectral and analytical data were obtained for **1** (bp 120 °C/2.5 × 10^3 Pa) and **2** (mp 167–169 °C). *Selected NMR data*: **1**: ^{29}Si NMR (25 °C, 59.63 MHz, C$_6$D$_6$) δ −18.4; **2**: ^{29}Si NMR (25 °C, 59.63 MHz, C$_6$D$_6$) δ −21.2 [^3J(^{119}Sn^{29}Si) 9.6 Hz]; ^{119}Sn NMR (25 °C, 111.9 MHz, C$_6$D$_6$) δ −72.9.

‡ *Physical data* for **4**: colourless liquid, bp >200 °C, 0.4 Pa, decomposition.

§ *Crystal data* for **5**: C$_{28}$H$_{61}$BSi$_3$Sn$_3$, mp >230 °C (decomp.) M = 848.94, triclinic, space group $P\overline{1}$, a = 990.2(2), b = 1148.8(2), c = 1773.5(2) pm, α = 77.39(2), β = 87.11(2), γ = 84.39(2)°, Z = 2, colourless, isometrically shaped crystal of dimensions 0.40 × 0.40 × 0.50 mm^3 sealed under argon in a Lindemann capillary; absorption coefficient μ(Mo-Kα) 2.0 mm^{-1}; Data collection and processing: Siemens P4 diffractometer (graphite monochromator), ω-mode, 8150 reflections measured in the range 3 ≤ 2θ ≤ 50°, 6846 unique, semi-empirical absorption correction by ψ-scans (min/max transmission factors: 0.112/0.154), measuring temperature 173 K; Structure solution and refinement: direct methods (Siemens SHELXTL PLUS system), full-matrix least squares refinement with all non-hydrogen atoms anisotropic and hydrogens in calculated positions with one overall temperature factor (U_{iso} = 0.08 Å^2); weighting scheme w = 1/σ^2(F_o), 317 refined parameters; convergence was achieved at the final R/wR value 0.028/0.020; residual electron density (max/min): 0.91/−0.67 e Å^{-3}. 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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