

Preliminary communication

A stannaethene with a planar environment of the tricoordinated tin and carbon atoms^{1,2}

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Abstract

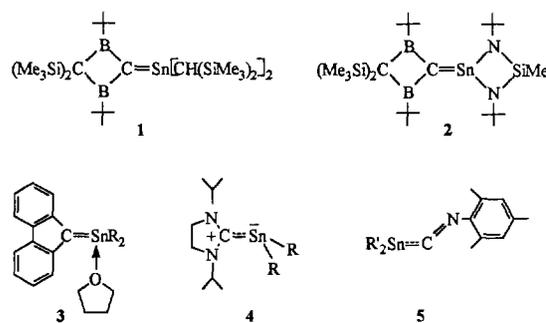
Addition of the diarylstannylene R'_2Sn ($R' = 2\text{-}^i\text{Bu-4,5,6-Me}_3\text{C}_6\text{H}$) to the cryptodiborylcarbene $(\text{Me}_3\text{Si})_2\text{C}(\text{B}^i\text{Bu})_2\text{C}$ furnishes the stannaethene $(\text{Me}_3\text{Si})_2\text{C}(\text{B}^i\text{Bu})_2\text{C}=\text{SnR}'_2$ (**10**). The X-ray structure analysis of **10** reveals a strictly planar environment of the tricoordinated tin and carbon atoms and a slight twisting of the $\text{Sn}=\text{C}$ double bond.

Keywords: Tin; Stannaethene; Carbene; Stannylene

1. Introduction

Compounds with a tin/carbon double bond are still extremely rare [2]. Besides **1**, the sole known stannaethene for which the structure has been confirmed [3], merely the molecules **2** [4] and **3** [5] have been reported, although the former can only be isolated as the adduct with diethyl ether or THF. Other compounds with tricoordinated tin atoms can better be described as Lewis acid–base adducts on account of their geometries and large $\text{Sn}-\text{C}$ bond lengths of approximately 230–240 pm, which are markedly longer than the corresponding single bond lengths. Examples of such compounds are products of the type **4**, prepared from the reaction of a nucleophilic carbene with tin(II) chloride [6] or a diaryl-

stannylene [7], and **5** [8], obtained from the reaction of a stable diarylstannylene with an isocyanide.



$R = 2,4,6\text{-}^i\text{Pr}_3\text{C}_6\text{H}_2$, $R' = 2,4,6\text{-}(\text{CF}_3)_3\text{C}_6\text{H}_2$

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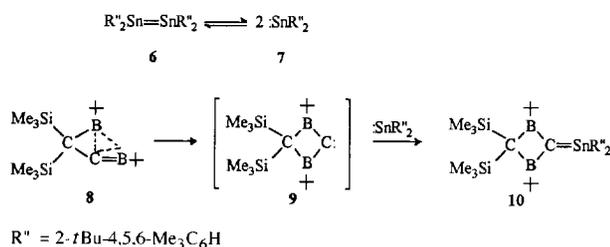
¹ Dedicated to Professor Peter Sartori on the occasion of his 65th birthday.

² Compounds of Germanium and Tin, Part XIX. For Part XVIII see Ref. [1].

We now report on the synthesis and unequivocal characterization of a further, genuine stannaethene exhibiting both similarities and pronounced differences in comparison with **1**.

2. Results and discussion

We recently isolated the distannene **6** which is characterized by a large Sn–Sn bond length and an unsymmetrical environment of the two tin atoms [9]. Compound **6** is stable in the solid state, while in solution the black crystals of **6** decompose to give the stannylene molecules **7**. Treatment of **7** with the non-classical boriranylideneborane **8** [10], which behaves like the electrophilic carbene **9** in reactions of this type, leads smoothly to the stannaethene **10**.



The differences in NMR data between **1** and **10** are not large. The chemical shifts of the boron atoms [$\delta(^{11}\text{B}) = 63$] and the Sn=C carbon atom [$\delta(^{13}\text{C}) = 137$] in **10** are in the same regions as the shifts determined for the corresponding atoms in **1**. However, the ^{119}Sn NMR spectrum [$\delta(^{119}\text{Sn}) = 374$] does reveal a significantly lower deshielding than is the case for the tin atom in **1** [$\delta(^{119}\text{Sn}) = 835$]. The higher shielding of the tin nucleus in **10** in comparison with that in **1** is presumably attributable mainly to the aryl groups, since the tin atoms in the tetraaryldistannene $\text{R}_2\text{Sn}=\text{SnR}_2$, where $\text{R} = 2,4,6\text{-}i\text{Pr}_3\text{C}_6\text{H}_2$, also exhibit a chemical shift of only approximately 400 ppm [11].

An X-ray crystal structure analysis of **10** (Fig. 1,

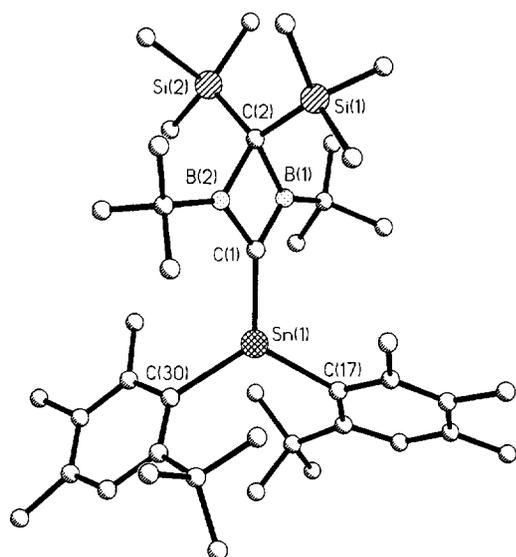


Fig. 1. Molecular structure of **10** in the crystal (hydrogen atoms omitted).

Table 1
Selected bond lengths (pm) and angles ($^\circ$) (standard deviations) for **10**

Sn–C(1)	203.2(5)	Sn–C(17)	218.9(5)
Sn–C(30)	217.3(5)	C(1)–B(1)	150.2(8)
C(1)–B(2)	151.0(8)	B(1)–C(2)	165.1(8)
B(2)–C(2)	163.4(8)		
C(1)–Sn–C(17)	119.1(3)	C(1)–Sn–C(30)	122.2(2)
C(17)–Sn–C(30)	118.5(2)	Sn–C(1)–B(1)	137.1(4)
Sn–C(1)–B(2)	135.9(2)	B(1)–C(1)–B(2)	86.7(4)
C(1)–B(1)–C(2)	97.2(4)	C(1)–B(2)–C(2)	97.7(4)
B(1)–C(2)–B(2)	78.0(4)	Si(1)–C(2)–Si(2)	115.3(3)

Table 1) also reveals some similarities with **1**, while at the same time clearly showing some major differences between the two stannaethenes. The Sn=C bond length of 203.2 pm is considerably shortened in comparison with the normal single bond length, and corresponds approximately to the bond length in **1**. Conspicuous in both stannaethenes is the fact that the bonds from C(1) to the two boron atoms are about 14 pm shorter than the bonds from the boron atoms to carbon C(2). This is indicative of a considerable ylidic character of the C^-Sn^+ type.

However, the tin atom in the stannaethene **1** exhibits only a slight and the Sn=C carbon atom a pronounced pyramidalization, the corresponding two atoms in **10** have planar environments with angular sums of 359.7° and 359.8° . Compound **10** is thus the first stannaethene to approach the planarity theoretically deduced for the parent compound $\text{H}_2\text{Sn}=\text{CH}_2$ [12–14]. Accordingly, the torsion of the double bond, which amounts to 61° in **1**, is markedly less in **10** with an average twist angle of 36° .

3. Experimental section

3.1. General procedures

All reactions were carried out in oven-dried glassware under an atmosphere of dry argon. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AM 300 spectrometer, whereas the ^{11}B , ^{29}Si and ^{119}Sn NMR spectra were recorded on a Bruker AMX 300 spectrometer using C_6D_6 or toluene- d_8 as solvents. Mass spectra were obtained with a Varian-MAT 212 instrument. The UV–vis spectrum was recorded on a Shimadzu UV 260 spectrometer.

3.2. Synthesis of the stannaethene $(\text{Me}_3\text{Si})_2\text{C}(\text{tBu})_2\text{C}=\text{SnR}'$ (**10**)

A solution of 0.26 g (0.55 mmol) of the stannylene **7** in 20 ml of *n*-hexane was added dropwise to a solution

of 0.17 g (0.55 mmol) of the cryptocarbene **8** in 10 ml of *n*-hexane over a period of 30 min. The mixture was stirred at room temperature for 2 h and the solvent removed. Recrystallization of the residue from 10 ml of *n*-pentane at 4 °C yielded 0.18 g (42%) of the stan-naethene **10**: yellow rectangular crystals, m.p. 152–155 °C (decomp.). ¹H NMR (C₆D₆): δ 0.56 (s, 18H, Si–CH₃), 1.09 (s, 18H, ¹BuB), 1.32 (s, 18H, ¹Bu), 1.88 (s, 6H, CH₃), 1.96 (s, 6H, CH₃), 2.87 (s, 6H, CH₃), 7.11 (s, 2H). ¹³C NMR (C₆D₆): δ 5.79 (C_p), 15.92 (C_p), 21.04 (C_p), 27.89 (C_p), 31.13 (C_p), 33.04 (C_p), 35.93 (C_q), 134.88 (C_q), 139.21 (C_q), 140.39 (C_q), 148.76 (C_q), 152.15 (C_q). C_p and C_q refer to primary and quaternary carbon atoms. The carbon atoms of the four-membered ring, which are omitted from this list, were observed in toluene-*d*₈ solution at –40 °C as broad signals at 37 (CSiMe₃) and 137 (C=Sn). ¹¹B NMR (C₆D₆): δ 63 (broad). ²⁹Si NMR (C₆D₆): δ –7.73. ¹¹⁹Sn NMR (C₆D₆): δ 374.2. MS (CI, isobutane): *m/z* 776 (M⁺, 3), 762 (MH⁺ – CH₃, 35). UV-vis: λ_{max} 284 nm (broad, tailing off into the visible region). Compound **10** was too sensitive against air and moisture for a satisfactory elemental analysis to be obtained.

3.3. X-ray structure analysis of **10**

Empirical formula C₄₂H₇₄B₂Si₂Sn, molar mass 775.50 g mol^{–1}, *a* = 968.30(10), *b* = 1300.60(10), *c* = 1859.7(2) pm, α = 94.260(10), β = 96.570(10), γ = 102.940(10)°, *V* = 2255.5(4) × 10⁶ pm³, *Z* = 2, *D*_{calc} = 1.142 g cm^{–3}. Crystal system triclinic, space group *P*1, crystal size 0.23 × 0.23 × 0.19 mm³, 2θ_{max} 46°, number of reflections 8184, number of unique reflections 6251, number of reflections *I* > 2σ(*I*) 4517, linear absorption coefficient 0.645 mm^{–1}, number of parameters 424, *R*(*I* > 2σ(*I*)) 0.051, *wR*₂ (all data) 0.1106.

Data collection was performed at room temperature on a Siemens-Stoe AED 2 diffractometer using graphite monochromated Mo Kα radiation. The structure was solved by direct phase determination using the SHELXS 86 program system and refined by full-matrix least-squares techniques using the SHELXL 93 program system [15]. Hydrogen atoms were placed in calculated positions, and all other atoms were refined anisotropically.

Further details of the crystal structure investigation

may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, upon quoting the depository number CSD-405489.

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