

A Cyclic Disilylated Stannylene: Synthesis, Dimerization, and Adduct Formation

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Supporting Information

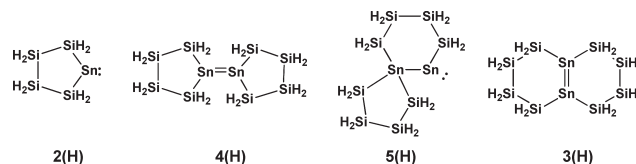
ABSTRACT: Reaction of 1,4-dipotassio-1,1,4,4-tetrakis(trimethylsilyl)tetramethyltetrasilane with $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Sn}$ led to the formation of an endocyclic distannene via the dimerization of a transient stannylene. In the presence of strong donor molecules such as PEt_3 , the stannylene could be trapped as adduct. Reaction of the PEt_3 derivative with $\text{B}(\text{C}_6\text{F}_5)_3$ gave rise to the formation of the stannylene $\text{B}(\text{C}_6\text{F}_5)_3$ adduct.

Stannylenes were among the first reported stable group 14 silylenes.^{1,2} In contrast to carbenes, they exhibit singlet ground states with a formal $5s^25p^2$ valence electron configuration. Early examples featured heteroatom (group 15 and 16) substituents providing stabilization via interaction of the heteroatom lone pair with the vacant p orbital. If these electronegative groups are replaced by alkyl groups, the p character of the lone pair is enhanced by the inductive effect of the electropositive substituents. The exchange with silyl groups should further amplify this effect.³ It is thus surprising that after the first examples of bis(silyl)-substituted stannylenes were reported by Klinkhammer and co-workers,^{4–6} no more efforts were undertaken in this direction to modify the reactivity of stannylenes.

To avoid dissociation of the silyl groups, the current study was directed toward the introduction of a bidentate silyl ligand. By reaction of a 1,4-dipotassiotetrasilane^{7,8} (**1**) with $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Sn}$,^{9,10} a cyclic disilylated stannylene structurally related to Klinkhammer's compound should be formed. However, instead of the expected stannylene **2**, the endocyclic distannene **3** was obtained (Scheme 1).

The formation of **3** likely involved the initial formation of the cyclic stannylene **2**. Dimerization of **2** generated an exocyclic distannene **4**, which after two 1,2-silyl shifts via the stannylstannylene **5** formed the endocyclic distannene isomer **3**. Precedent for the formation of stannylstannylenes such as **5** by dimerization of stannylenes has been given by Power and co-workers,¹¹ and a related reaction in silicon chemistry was recently reported by Kira and co-workers.¹² Further support for this proposed mechanism came from density functional theory (DFT) calculations at the MPW1K/SDD(Sn), 6-31G(d) level of theory.¹³ The results of the computations showed that distannenes **3** and **4** and stannylstannylene **5** are all significantly lower in energy than two molecules of stannylene **2** (**4** by 57.5 kJ mol^{-1} , **5** by

35.8 kJ mol^{-1} , and **3** by 58.7 kJ mol^{-1}). In addition, calculations for the model compounds **2(H)**, **3(H)**, **4(H)**, and **5(H)** indicated that the involved barriers for the 1,2 substituent shift are rather low [i.e., 29.5 kJ mol^{-1} for **4(H)** \rightarrow **5(H)** and 30.5 kJ mol^{-1} for **5(H)** \rightarrow **3(H)** at the MPW1K/Sn(SDD), 6-311+G(d,p) level].



As can be expected for the bicyclic structure of **3**, in which the two Sn atoms are held together, a typical distannene ¹¹⁹Sn NMR shift of +544.5 ppm was found; this lies between the value of +630.7 ppm reported for Sekiguchi's compound $(\text{Bu}_2\text{MeSi})_2\text{SnSn}(\text{SiMe}^t\text{Bu}_2)_2$ (**6**)¹⁴ and the values of +427.3 ppm for Masmune's tetrakis(2,4,6-triisopropylphenyl)distannene¹⁵ and +412 ppm for Wiberg's cyclotristannene,¹⁶ all of which are known to retain the distannene structure in solution. This is also consistent with a UV absorption at 626 nm, which is close to the reported value of 670 nm for **6**. A low-quality crystal structure of **3** (Figure 1) showed that the two Sn atoms are disordered over two positions each with very similar structural features. The resulting two $\text{Sn}=\text{Sn}$ double bonds of **3** have lengths of 268.9(5) and 268.6(4) pm, which are among the shortest of all structurally characterized stable distannenes.¹² The sums of the bond angles around the tricoordinated Sn atoms [$\Sigma^\circ(\text{Sn}) = 354.0(2)$, $352.2(2)$, $352.7(2)$, and $353.7(2)^\circ$] and the relatively large trans-bent angles ($\beta = 29.6$, 26.5 , 25.8 , and 28.5°) indicate a significant pyramidalization of the Sn centers. In addition, the $\text{Sn}=\text{Sn}$ bonds in **3** are twisted by angles ϵ of 27.0 and 28.6° . Comparison with the structural parameters of two closely related compounds, namely, the dimeric structure $[(\text{Me}_3\text{Si})_3\text{Si}]_2\text{Sn}$ (**7**)⁴ and Sekiguchi's compound **6**,¹⁴ reveals an amazing structural diversity of silyl-substituted stannylene dimers [for **6**, $d(\text{Sn}=\text{Sn}) = 266.8 \text{ pm}$, $\beta = 1.2^\circ$, $\epsilon = 44.6^\circ$; for **7**, $d(\text{Sn}=\text{Sn}) = 282.5 \text{ pm}$, $\beta = 28.6^\circ$, $\epsilon = 63.2^\circ$]. These pronounced differences suggest a high structural flexibility of the $\text{Si}_2\text{Sn}=\text{SnSi}_2$ core in distannenes **3**, **6**, and **7**.

Received: November 10, 2010

Published: March 25, 2011

For the model distannene ($\text{H}_3\text{Si})_2\text{Sn}=\text{Sn}(\text{SiH}_3)_2$ (**8**), DFT calculations¹³ predicted a trans-bent ground-state structure having C_{2h} molecular symmetry, in contrast to the results of previous lower-level computations.¹⁷ The folding of the $\text{Sn}=\text{Sn}$ bond in distannene **8** is in agreement with a significant preference of the singlet state in the constituent stannylene ($\text{H}_3\text{Si})_2\text{Sn}$: [singlet/triplet energy difference $\Delta E(\text{ST}) = -99.1 \text{ kJ mol}^{-1}$].

The modulus of $\Delta E(\text{ST})$ is larger than a quarter of the modulus of the σ and π bond energy $E(\sigma+\pi)$ of distannene **8** in its planar D_{2h} form ($|1/4 E(\sigma+\pi)| = 89.3 \text{ kJ mol}^{-1}$).¹³ According to the CGMT model,^{18,19} this results in a marked

Scheme 1. Formation of $\Delta^{9,10}$ -Octalin-Type Distannene **3**

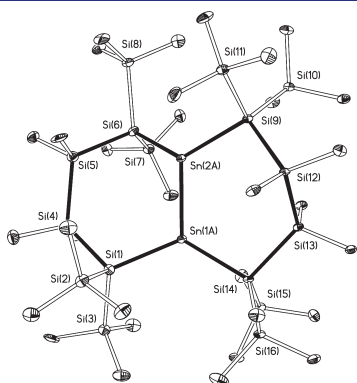
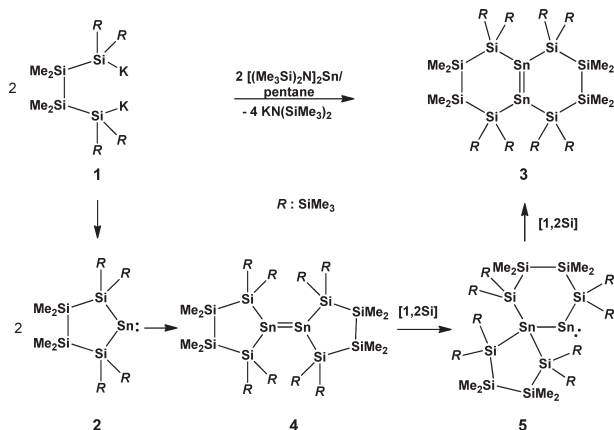


Figure 1. Thermal ellipsoid plot for **3** drawn at the 30% probability level.

trans-bending of the double-bond system. In addition, the computations indicated the flexibility of distannene **8**. That is, variation of the $\text{Sn}=\text{Sn}$ bond length from 250 to 290 pm, the bending angle β from 0 to 60° , and the twisting angle ε from 0 to 22.5° all required less than 15 kJ mol^{-1} (Figure 2). For distannene **3**, the computations predicted a molecular structure having C_2 symmetry that closely resembles in all significant parameters the experimental structure [i.e., $d(\text{Sn}=\text{Sn}) = 270.7 \text{ pm}$, $\Sigma^\circ(\text{Sn}) = 353.2^\circ$, $\beta = 26.5^\circ$, $\varepsilon = 6.0^\circ$]. Natural bond order analysis¹³ of the DFT density suggested multiple-bond character for the $\text{Sn}=\text{Sn}$ bond in compound **3** on the basis of a Wiberg bond index (WBI) of 1.66. This value should be compared with the WBI values computed for **8** and the parent Sn_2H_4 in both their planar configurations of D_{2h} symmetry and their trans-bent minimum structures of C_{2h} symmetry [for D_{2h} symmetry, WBI = 1.84 (**8**), 1.94 (Sn_2H_4); for C_{2h} symmetry, WBI = 1.68 (**8**), 1.55 (Sn_2H_4)].

When the reaction was repeated using the 18-crown-6 adduct of **1**⁸ instead of the product generated in THF, the course of the reaction was altered, and compound **9** was obtained as the main product (Scheme 2). This compound can be regarded as either the amide adduct of **2** or a stannyleneid related to Tamao's amino-substituted silylenoids.^{20–22} The formation of **9** is likely associated with the better solubility and nucleophilicity of $\text{KN}(\text{SiMe}_3)_2$ in the presence of the crown ether.²³ Relative to that of **3**, the ^{119}Sn NMR resonance of **9** was shifted markedly to higher field (-256.6 ppm), indicating sp^3 hybridization. While compounds of the type $\text{Si}_3\text{SnK}^{24}$ usually resonate at around -880 ppm , the signal of **9** resembles the downfield-shifted behavior typically found for ^{29}Si NMR chemical shifts of amino-substituted silylenoids.^{20–22,25} A crystal structure obtained from **9** (Figure S-2 in the Supporting Information) was of poor quality ($R_1 = 15.6$) but nevertheless provided unambiguous proof of the assigned structure.

To obtain a neutral stannylene base adduct, the reaction of **1** with $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Sn}$ was repeated in the presence of triethylphosphane.²⁶ In the absence of crown ether, $\text{P}(\text{Et}_3)$ added to stannylene **2**, affording stannylene adduct **10** (Scheme 3). The NMR spectra of **10** showed its electronic similarity to **9**: the ^{119}Sn NMR resonance of -224.4 ppm was in the same region, and the ^{29}Si signals for the attached silicon atoms were also very

Scheme 2. Stannylene Amide Adduct Formation

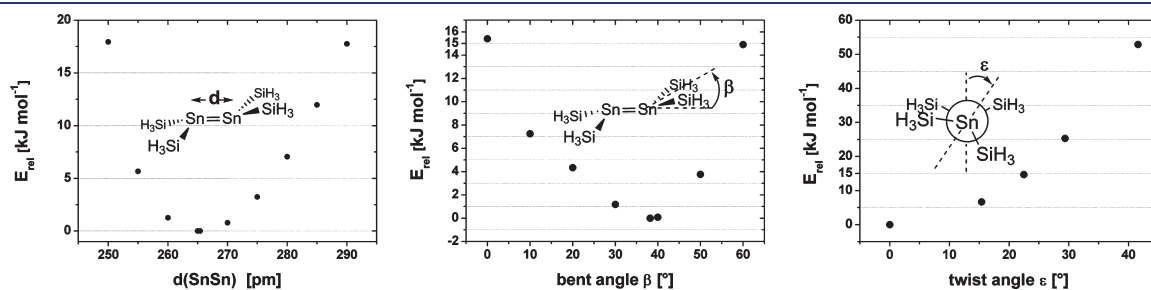
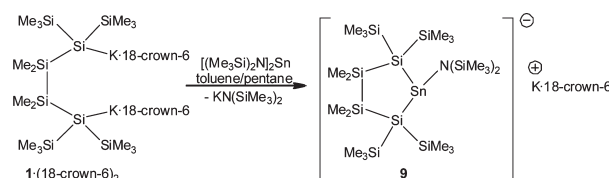


Figure 2. (a) Stretching, (b) bending, and (c) twisting potentials of the $\text{Sn}=\text{Sn}$ bond in $(\text{H}_3\text{Si})_2\text{Sn}=\text{Sn}(\text{SiH}_3)_2$ (**8**) calculated at the MPW1K/SDD(Sn), 6-31G(d) level.

Scheme 3. Stannylene Phosphane Adduct Formation

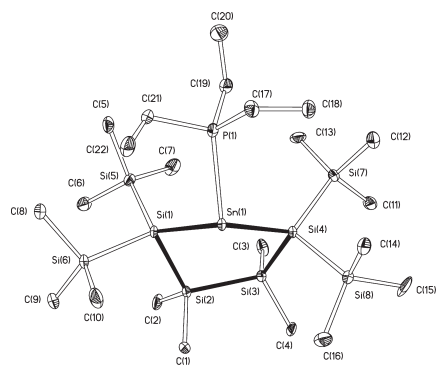
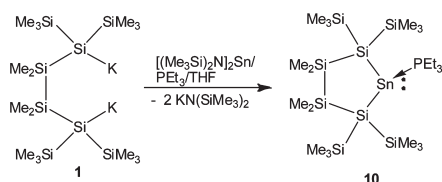


Figure 3. Thermal ellipsoid plot for **10** drawn at the 30% probability level.

close [-137.9 ppm (**10**) vs -139.6 ppm (**9**)]. A large $^1J_{119\text{SnP}}$ coupling constant of 2200 Hz was observed. Two different resonances for SiMe_3 groups were observed for **10** but only one for **9**, indicating configurational stability at Sn for **10**.

The only structurally characterized compound containing a 1-stannacyclopentasilane unit known to date is 3,3,4,4-tetramethyl-1,1-diphenyl-2,2,5,5-tetrakis(trimethylsilyl)-1-stannacyclopentasilane,⁸ which was obtained from the reaction of **1** with dichlorodiphenylstannane. The Si–Sn bond lengths in this compound are 262.0(4) and 259.4(4) pm, and the five-membered ring shows a twisted half-chair conformation in which the two SiMe_2 groups lie $\sim 8^\circ$ below or above the ring plane. In comparison with this, the picture is different for **10** (Figure 3), where the ring adopts an envelope conformation with one of the $\text{Si}(\text{SiMe}_3)_2$ groups on the flap. The Si–Sn bond lengths are elongated to 264.8(3) and 265.3(3) pm, and the Si–Sn–Si bond angle, which has a value of $105.2(1)^\circ$ in the diphenyl compound, decreases to $98.17(9)^\circ$ in **10**. The Sn–P bond distance of 260.8(3) pm is slightly shorter than in a comparable stannylene [266.3(2) pm].²⁷

With **10** in hand, it was possible to test the Lewis base properties of **2**. Reaction of **10** with 2 equiv of the strong Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$ proceeded smoothly, leading to the corresponding borane stannylene adduct^{28,29} **11** accompanied by 1 equiv of the borane–phosphane adduct $(\text{F}_5\text{C}_6)_3\text{B} \cdot \text{PEt}_3$ ³⁰ (Scheme 4).

It should be noted that in the solid state, $\text{B}(\text{C}_6\text{F}_5)_3$ serves not only as a Lewis acid but also as a Lewis base. A fluorine atom in the ortho position of one of the C_6F_5 groups donates electron density into the empty p orbital of the stannylene³¹ (Figure 4). This interaction is also observed in solution in the ^{19}F spectrum, where the ortho-F signal displays $^{117/119}\text{Sn}$ satellites with coupling constants of 113/123 Hz. As only three signals for the respective ortho, meta, and para positions were observed in the ^{19}F and ^{13}C NMR spectra, rotation around the Sn–B and B–C bonds is fast at ambient temperature. The ^{119}Sn resonance of **11**, which was downfield-shifted to +68.1 ppm was very broad, as a result of the interaction with the quadrupole boron nuclei.

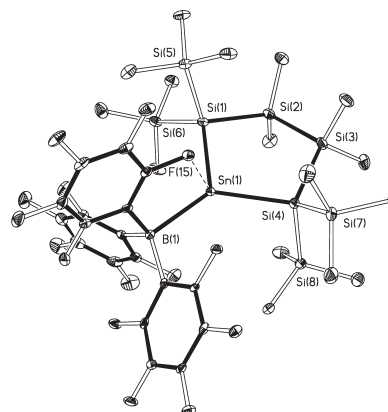
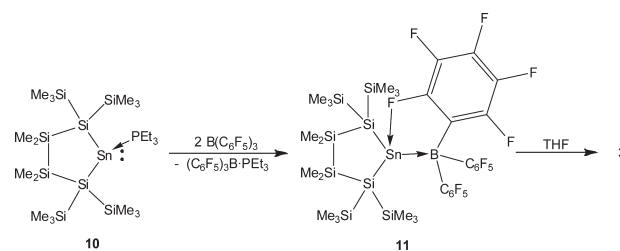
Scheme 4. Stannylene $\text{B}(\text{C}_6\text{F}_5)_3$ Adduct Formation

Figure 4. Thermal ellipsoid plot of **11** drawn at the 30% probability level.

Therefore the coupling to the fluorine atom thus could not be detected. How weak the interaction between $\text{B}(\text{C}_6\text{F}_5)_3$ and the stannylene is can be estimated from the fact that a change of solvent from benzene to THF led to the fast formation of **3**.

Similar to **9**, compound **11** (Figure 4) exhibits an envelope ring conformation with a SiMe_2 group on the flap. The Si–Sn bond lengths of 259.7(1) and 260.9(1) pm are close to those in the published stannacyclopentasilane,⁸ as is the Si–Sn–Si bond angle of $104.10(4)^\circ$. The Sn–B bond length of 235.9(5) pm is in the normal range, and the dative character of the Sn–F interaction is clearly shown by the elongation to 248.7(2) pm from a typical Sn–F value of 208 pm.

■ ASSOCIATED CONTENT

S Supporting Information. Experimental and theoretical characterization, including preparation of **3**, **9**, **10**, and **11**; crystal structure analysis data (CIF); computational details; and complete ref 13 (as SI ref 13). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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■ ACKNOWLEDGMENT

This study was supported by the Austrian Science Fund (FWF) via Project P-21346. Dr. Jörg Albring (TU Graz) provided assistance with the crystal structure determination of **3**.

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