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

Henning Arp,[†] Judith Baumgartner,*[,†] Christoph Marschner,*[,†] and Thomas Müller*[,‡]

[†]Institut für Anorganische Chemie, Technische Universität Graz, Stremayrgasse 9, A-8010 Graz, Austria

[‡]Institut für Reine und Angewandte Chemie, Carl von Ossietzky Universität Oldenburg, Carl von Ossietzky Str. 9-11, D-26211 Oldenburg, Federal Republic of Germany

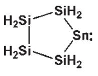
S Supporting Information

ABSTRACT: Reaction of 1,4-dipotassio-1,1,4,4-tetrakis(trimethylsilyl)tetramethyltetrasilane with $[(Me_3Si)_2N]_2Sn$ 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 $B(C_6F_5)_3$ gave rise to the formation of the stannylene $B(C_6F_5)_3$ adduct.

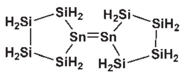
Stannylenes were among the first reported stable group 14 ylenes.[1,2] In contrast to carbenes, they exhibit singlet ground states with a formal $5s^25p^2$ valence electron configuration. Early examples featured heteroatom (group 15 and 16) substituents providing stabilization via interaction of the 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 $[(Me_3Si)_2N]_2Sn$,[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).

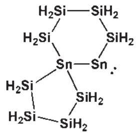
The formation of **3** likely involved the initial formation of the cyclic stannylene **2**. Dimerization of **2** generated an exocyclic distannene **4**, which after two 1,2-silyl shifts via the stannylstannylene **5** formed the endocyclic distannene isomer **3**. Precedent for the formation of stannylstannylenes 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)** → **5(H)** and 30.5 kJ mol^{-1} for **5(H)** → **3(H)** at the MPW1K/Sn(SDD), 6-311+G(d,p) level].



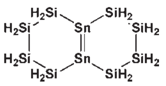
2(H)



4(H)



5(H)



3(H)

As can be expected for the bicyclic structure of **3**, in which the two Sn atoms are held together, a typical distannene ^{119}Sn NMR shift of +544.5 ppm was found; this lies between the value of +630.7 ppm reported for Sekiguchi's compound $(^tBu_2MeSi)_2SnSn(SiMe^tBu_2)_2$ (**6**)[14] and the values of +427.3 ppm for Masmune's tetrakis(2,4,6-triisopropylphenyl)distannene[15] 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 Sn=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 [$\Sigma°(Sn)$ = 354.0(2), 352.2(2), 352.7(2), and 353.7(2)°] and the relatively large trans-bent angles (β = 29.6, 26.5, 25.8, and 28.5°) indicate a significant pyramidalization of the Sn centers. In addition, the Sn=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 $[(Me_3Si)_3Si]_2Sn$ (**7**)[4] and Sekiguchi's compound **6**,[14] reveals an amazing structural diversity of silyl-substituted stannylene dimers [for **6**, $d(Sn{=}Sn)$ = 266.8 pm, β = 1.2°, ε = 44.6°; for **7**, $d(Sn{=}Sn)$ = 282.5 pm, β = 28.6°, ε = 63.2°]. These pronounced differences suggest a high structural flexibility of the $Si_2Sn{=}SnSi_2$ core in distannenes **3**, **6**, and **7**.

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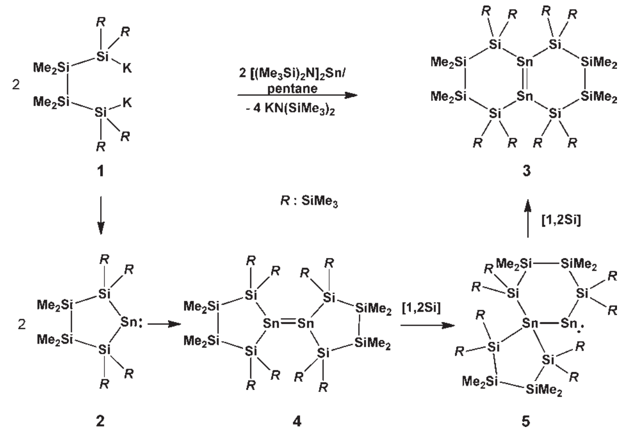
For the model distannene $(H_3Si)_2Sn{=}Sn(SiH_3)_2$ (**8**), DFT calculations[13] predicted a trans-bent ground-state structure having C_{2h} molecular symmetry, in contrast to the results of previous lower-level computations.[17] The folding of the Sn═Sn bond in distannene **8** is in agreement with a significant preference of the singlet state in the constituent stannylene $(H_3Si)_2Sn$: [singlet/triplet energy difference $\Delta E(\mathrm{ST}) = -99.1$ kJ mol^{-1}].

The modulus of $\Delta E(\mathrm{ST})$ 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 ($|^1/_4E(\sigma{+}\pi)| = 89.3$ kJ mol^{-1}).[13] According to the CGMT model,[18,19] this results in a marked trans-bending of the double-bond system. In addition, the computations indicated the flexibility of distannene **8**. That is, variation of the Sn═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., $d(\mathrm{Sn{=}Sn}) = 270.7$ pm, $\Sigma°(\mathrm{Sn}) = 353.2°$, $\beta = 26.5°$, $\varepsilon = 6.0°$). Natural bond order analysis[13] of the DFT density suggested multiple-bond character for the Sn═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)].

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



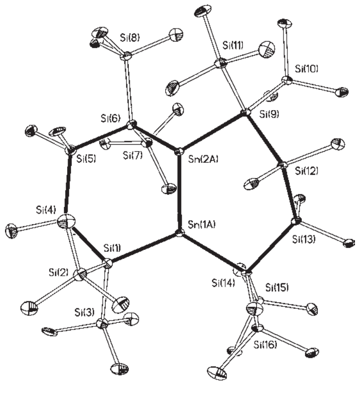
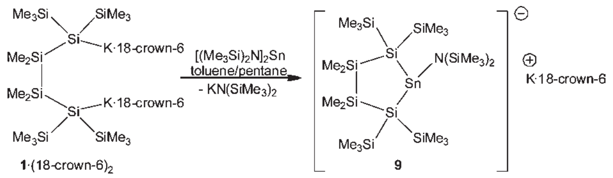


Figure 1. Thermal ellipsoid plot for **3** drawn at the 30% probability level.

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 stannylenoid related to Tamao's amino-substituted silylenoids.[20−22] The formation of **9** is likely associated with the better solubility and nucleophilicity of $KN(SiMe_3)_2$ 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 Si_3SnK[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 $[(Me_3Si)_2N]_2Sn$ was repeated in the presence of triethylphosphane.[26] In the absence of crown ether, PEt_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



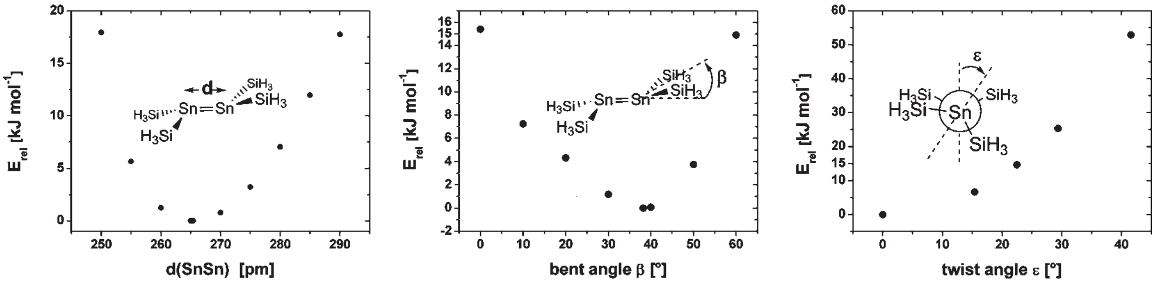
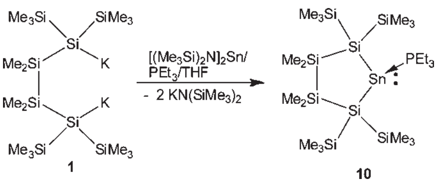


Figure 2. (a) Stretching, (b) bending, and (c) twisting potentials of the Sn═Sn bond in $(H_3Si)_2Sn{=}Sn(SiH_3)_2$ (**8**) calculated at the MPW1K/SDD(Sn), 6-31G(d) level.

Scheme 3. Stannylene Phosphane Adduct Formation



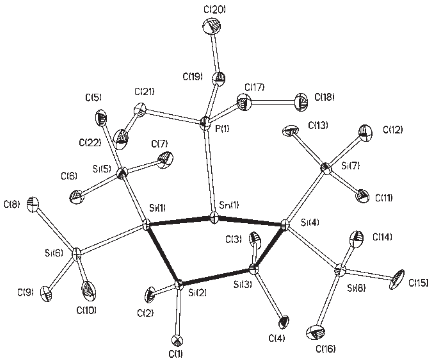


Figure 3. Thermal ellipsoid plot for **10** drawn at the 30% probability level.

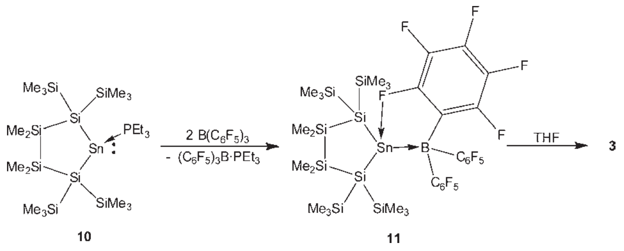
close [−137.9 ppm (**10**) vs −139.6 ppm (**9**)]. A large $^1J_{119\text{SnP}}$ coupling constant of 2200 Hz was observed. Two different resonances for $SiMe_3$ groups were observed for **10** but only one for **9**, indicating configurational stability at Sn for **10**.

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 ∼8° 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 $Si(SiMe_3)_2$ 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)° in the diphenyl compound, decreases to 98.17(9)° 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 $B(C_6F_5)_3$ proceeded smoothly, leading to the corresponding borane stannylene adduct[28,29] **11** accompanied by 1 equiv of the borane−phosphane adduct $(F_5C_6)_3B\cdot PEt_3$[30] (Scheme 4).

It should be noted that in the solid state, $B(C_6F_5)_3$ 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 stannylene[31] (Figure 4). This interaction is also observed in solution in the ^{19}F spectrum, where the ortho-F signal displays $^{117/119}$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. Therefore the coupling to the fluorine atom thus could not be detected. How weak the interaction between $B(C_6F_5)_3$ 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**.

Scheme 4. Stannylene $B(C_6F_5)_3$ Adduct Formation



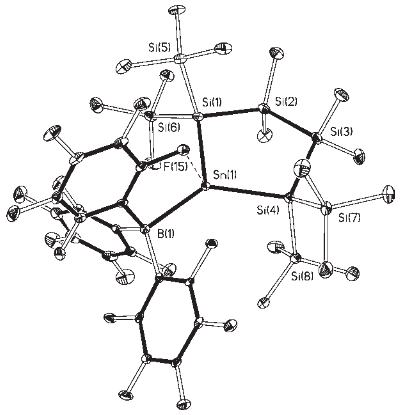


Figure 4. Thermal ellipsoid plot of **11** drawn at the 30% probability level.

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)°. 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

Ⓢ 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.

■ AUTHOR INFORMATION

Corresponding Authors

baumgartner@tugraz.at, christoph.marschner@tugraz.at, thomas.mueller@uni-oldenburg.de

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