The first silastannene >si=sn<: a new doubly-bonded system of heavier group 14 elements.

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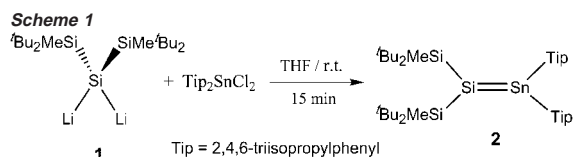# The First Silastannene >Si═Sn<: A New Doubly-Bonded System of Heavier Group 14 Elements

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After the breaking of the so-called "double-bond rule"[1] by the preparation of the first heavy alkene analogues stable both in the solid state and solution, silene >Si═C<[2] and disilene >Si═Si<[3] in 1981, many stable metallenes >E═C< and dimetallenes >E═E< of group 14 elements (E = heavier group 14 element) have been synthesized to date.[4] However, the chemistry of the stable heteronuclear dimetallenes >E═E′< composed of different group 14 elements heavier than carbon is still not very common,[5,6] although the homonuclear dimetallenes (i.e., disilenes, digermenes, distannenes, diplumbenes) are represented by a number of examples reported by several research groups.[4] Recently, we reported the synthesis of a 1,2-disila-3-germacyclopenta-2,4-diene derivative, which has Si═Ge and C═C double bonds with a silole structure, and determined the Si═Ge double bond length for the first time.[7] Very recently, we have also demonstrated the utility of 1,1-dilithiosilanes in the preparation of a variety of doubly bonded derivatives of heavier group 14 elements.[8] We now report on a new application of the dilithiosilane derivative, resulting in the successful isolation of the first *silastannene* with a >Si═Sn< double bond. Compounds of this type, both stable and transient, were completely unknown until our study.[9]

The reaction of bis[di-*tert*-butyl(methyl)silyl]dilithiosilane **1**[8] with dichlorobis(2,4,6-triisopropylphenyl)stannane[10] in dry THF proceeded cleanly to form the corresponding coupling product, 1,1-bis[di-*tert*-butyl(methyl)silyl]-2,2-bis(2,4,6-triisopropylphenyl)-1-sila-2-stannaethene **2**, as deep violet crystals in 50% isolated yield (Scheme 1).[11]

Scheme 1

*Bu$_2$MeSi ... SiMe*Bu$_2$, Si, Li, Li (**1**) + Tip$_2$SnCl$_2$ →[THF / r.t., 15 min] *Bu$_2$MeSi, *Bu$_2$MeSi, Si═Sn, Tip, Tip (**2**)

Tip = 2,4,6-triisopropylphenyl

Silastannene **2**, representing the first example of a compound with a >Si═Sn< double bond, was entirely characterized by a range of spectral data, the most informative being the ^{29}Si and ^{119}Sn NMR spectra. Thus, in the ^{119}Sn NMR spectrum one resonance signal was observed at +516.7 ppm, typical for an sp^2 hybridized Sn atom.[12] In the ^{29}Si NMR spectrum, two resonance signals at 27.4 and 27.6 were observed with an intensity ratio of 1:2, from which it can be deduced that the former belongs to a doubly bonded Si atom and the latter to the two SiMe^{t}Bu$_2$ groups. The resonance of the sp^2 Si atom is greatly shifted upfield compared with the vast majority of other compounds with a doubly bonded Si atom.[13] The same phenomenon has been shown in the case of unsymmetrically substituted disilenes and germasilene: upfield-shifted signals for

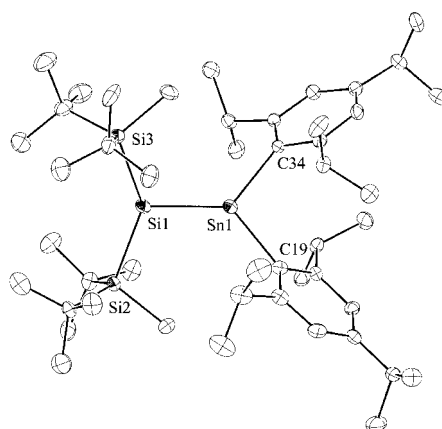*To whom correspondence should be addressed. E-mail: sekiguch@staff.chem.tsukuba.ac.jp.

Figure 1. ORTEP drawing of **2**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Sn(1)−Si(1) = 2.4188(14), Sn(1)−C(19) = 2.190(4), Sn(1)−C(34) = 2.181(4), Si(1)−Si(2) = 2.3647(19), Si(1)−Si(3) = 2.3692(19); Selected bond angles (deg): C(34)−Sn(1)−C(19) = 102.64(17), C(34)−Sn(1)−Si(1) = 126.54(13), C(19)−Sn(1)−Si(1) = 129.55(13), Si(2)−Si(1)−Si(3) = 138.71(8), Si(2)−Si(1)−Sn(1) = 110.61-(6), Si(3)−Si(1)−Sn(1) = 106.27(6).
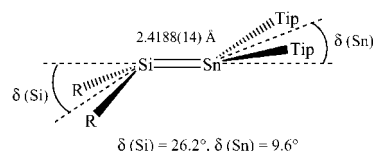

δ (Si) = 26.2°, δ (Sn) = 9.6°

Figure 2. The *trans*-bent angles (δ) around Si and Sn atoms in silastannene **2** (R = SiMe^{t}Bu$_2$, Tip = 2,4,6-triisopropylphenyl).
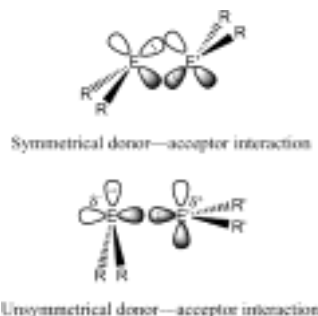
sp^2 Si atoms connected with Si-substituents and downfield-shifted signals for sp^2 Si atoms connected with aryl substituents.[8b]

The crystal structure of **2** was determined by X-ray crystallography (Figure 1).[14] The most important result is the Si═Sn double bond length (2.4188(14) Å), which was determined for the first time. This value is intermediate between the typical Si═Si (2.138−2.289 Å)[15] and Sn═Sn (2.59−3.087 Å)[4e] double bond lengths, being ca. 7% shorter than the usual Si−Sn single bond length of 2.60 Å.[16] The twisting angle is 34.6°, as determined by the angles between the mean plane of Si1−Si2−Si3 and Sn1−C19−C34. As expected, the Si═Sn double bond is *trans*-bent, but the bending angles around the Si and Sn atoms are quite unusual: 26.2° for the Si atom and 9.6° for the Sn atom (Figure 2).

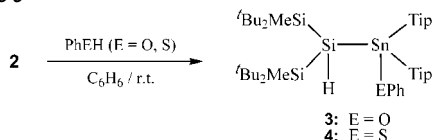It is well-known that disilenes normally prefer to have a planar or near-planar geometry around the Si═Si double bond,[4e] whereas distannenes tend to have a highly pronounced *trans*-bent geometry for the Sn═Sn double bond.[4e] In the case of **2** we have the

Scheme 2

Symmetrical donor—acceptor interaction

Unsymmetrical donor—acceptor interaction

Scheme 3

3: E = O
4: E = S

completely opposite tendency. Such an unusual structural feature can be rationalized by the polar $Si=Sn$ double bond produced by the difference in the substituent electronegativity between the silyl and aryl groups. The electronegativities of Si and Sn atoms are almost equal,[17] but the electropositive silyl groups on the sp^2 Si atom and the electronegative aryl groups on the Sn atom cause the great polarity of the double bond, $Si^{\delta-}=Sn^{\delta+}$. The *trans*-bent structure of dimetallenes of the heavier group 14 elements is well-explained as a dimer of the corresponding divalent species by the donor—acceptor interaction. If an unsymmetrical donor—acceptor interaction operates in the doubly bonded system of heavier group 14 elements, the double bond would be polarized with different bending angles; a negative moiety is more bent than a positive one (Scheme 2).[18] Therefore, the electronegative sp^2 silicon part is more bent than the Sn part in **2**. Indeed, a calculation on the model silastannene $(H_3Si)_2Si=SnPh_2$ (B3LYP/DZd level) revealed that the $Si=Sn$ double bond is highly polarized (NPA analysis): -0.536 for the Si atom and $+1.400$ for the Sn atom.[19] The geometry of the $Si=Sn$ double bond was also well reproduced by the calculations, except for the twisting angle (5°): a $Si=Sn$ double bond length of 2.445 Å with bending angles of 17.8° around the Si atom and 7.2° around the Sn atom.

The $Si=Sn$ double bond in **2** is highly reactive and easily undergoes addition reactions. Thus, **2** reacted with PhOH and PhSH at room temperature to form the corresponding addition products **3** and **4** in 51 and 26% yields, respectively (Scheme 3).[20] The regioselectivity of PhEH (E = O, S) addition corresponds well with the polarity of the $Si=Sn$ double bond in **2**.

Supporting Information Available: Experimental procedures and spectral data of **3** and **4**, tables of crystallographic data including atomic positional and thermal parameters for **2** (PDF/CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Spectral data for **2**: violet crystals; mp 78−79 °C. ^{1}H NMR (C_6D_6, δ) 0.26 (s, 6 H), 1.03 (d, J = 6.6 Hz, 12 H), 1.17 (d, J = 6.6 Hz, 12 H), 1.27 (s, 36 H), 1.41 (d, J = 6.6 Hz, 12 H), 2.73 (sept, J = 6.6 Hz, 2 H), 3.74 (sept, J = 6.6 Hz, 4 H), 7.09 (s, 4 H, ArH); ^{13}C NMR (C_6D_6, δ) −3.0, 22.0, 24.1, 25.8, 30.7, 34.6, 40.4, 122.6, 150.1, 154.2, 154.6; ^{29}Si NMR (C_6D_6, δ) 27.4 ($Si=Sn$), 27.6 ($SiMe^tBu_2$); ^{119}Sn NMR (C_6D_6, δ) 516.7; UV/vis (hexane) λ_{max}/nm (ϵ) 262 (21300), 337sh (2700), 545 (4100). Anal. Calcd for $C_{48}H_{88}Si_3Sn$: C, 66.41; H, 10.22. Found: C, 66.11; H, 10.00.
(12) The typical ^{119}Sn NMR resonances of doubly bonded Sn atoms lie in the region above +400 ppm, see ref 4a.
(13) The typical ^{29}Si NMR resonances for doubly bonded Si atoms lie in the region of +49 to +155 ppm, see ref 4b.
(14) Crystal data for **2** at 120 K: MF = $C_{48}H_{88}Si_3Sn$, MW = 868.14, monoclinic, $P2_1/n$, a = 10.9180(9), b = 18.9170(11) Å, c = 25.0480(18) Å, β = 94.397(4)°, V = 5158.1(6) Å^3, Z = 4, D_{calcd} = 1.118 g·cm^{-3}. The final R factor was 0.0680 for 8168 reflections with $I_o > 2\sigma(I_o)$ (R_w = 0.1630 for all data 12279 reflections), GOF = 1.024.
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(17) The electronegativities of Si and Sn atoms according to the Pauling and the Allred−Rochow electronegativity scales are 1.90 vs 1.96 and 1.90 vs. 1.93, respectively.
(18) The structure on the bottom in Scheme 2 represents an extreme case of such interaction with a planar geometry around a positively polarized Sn atom and 90° bending geometry around a negatively polarized Si atom.
(19) The calculations were carried out using the Gaussian 98 program.
(20) For the experimental procedures and spectral data of **3** and **4**, see the Supporting Information.

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