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

Akira Sekiguchi,* Rika Izumi, Vladimir Ya. Lee, and Masaaki Ichinohe

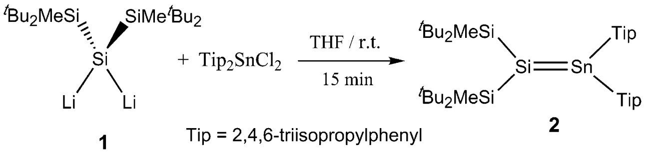
Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan

Received August 12, 2002

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



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 sp^2 Si atoms connected with Si-substituents and downfield-shifted signals for sp^2 Si atoms connected with aryl substituents.[8b]

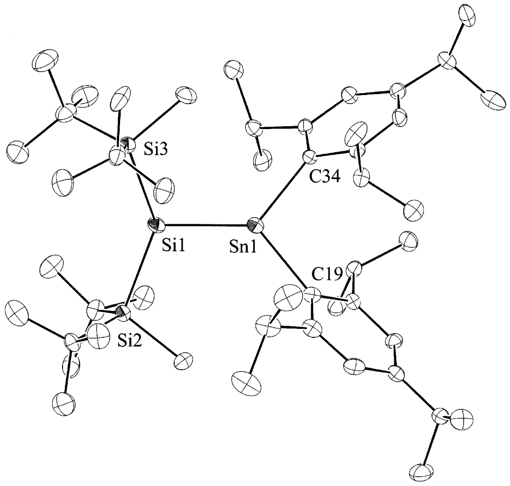


Figure 1. ORTEP drawing of **2**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Sn(1)−Si(1) = 2.4188(14), Sn(1)−C(19) = 2.190(4), Sn(1)−C(34) = 2.181(4), Si(1)−Si(2) = 2.3647(19), Si(1)−Si(3) = 2.3692(19); Selected bond angles (deg): C(34)−Sn(1)−C(19) = 102.64(17), C(34)−Sn(1)−Si(1)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

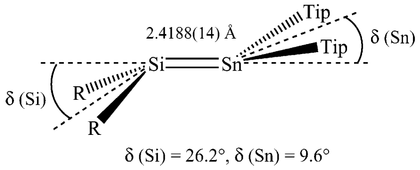


Figure 2. The *trans*-bent angles (δ) around Si and Sn atoms in silastannene **2** (R = SiMe^{t}Bu$_2$, Tip = 2,4,6-triisopropylphenyl).

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

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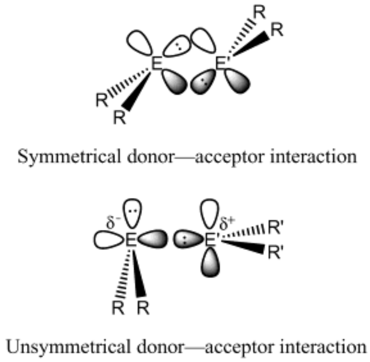
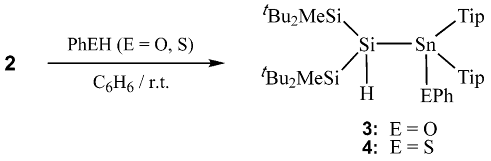
* To whom correspondence should be addressed. E-mail: sekiguch@staff.chem.tsukuba.ac.jp.

10.1021/ja021077l CCC: $22.00 © 2002 American Chemical Society

Scheme 2



Scheme 3



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, $\mathrm{Si}^{\delta-}{=}\mathrm{Sn}^{\delta+}$. 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 (*Si*Me^{t}Bu$_2$); ^{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, $\beta = 94.397(4)°$, $V = 5158.1(6)$ 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.

(15) See ref 4c and also: Schmedake, T. A.; Haaf, M.; Apeloig, Y.; Müller, T.; Bukalov, S.; West, R. *J. Am. Chem. Soc*. **1999**, *121*, 9479.

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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.

JA021077L