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## ARTICLE

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## Stannyl-substituted Disilenes and a Disilastannirane

Kai Abersfelder,<sup>[a]</sup> Thi-loan Nguyen<sup>[a]</sup> and David Scheschkewitz\*<sup>[a]</sup>*Dedicated to Prof. Dr. Michael Veith on the occasion of his 65<sup>th</sup> birthday***Keywords:** Group 14 elements; Metallacycles; Multiple bonds; Silicon; Stannanes

**Abstract.** The reaction of disilenide  $\text{Tip}_2\text{Si}=\text{Si}(\text{Tip})\text{Li}$  (**1**, Tip = 2,4,6-*t*-Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) with chlorostannanes  $\text{R}_3\text{SnCl}$  quantitatively affords the first stannyl substituted disilenes  $\text{Tip}_2\text{Si}=\text{Si}(\text{Tip})\text{SnR}_3$  (**2a**: R = Me, **2b**: R = Bu, **2c**: R = Ph). The *Sn*-functional derivative  $\text{Tip}_2\text{Si}=\text{Si}(\text{Tip})\text{Sn}^t\text{Bu}_2\text{Cl}$  (**3**) is accessible in good yield from **1** and  $^t\text{Bu}_2\text{SnCl}_2$ .

Additionally, the first heavy analogue of cyclopropanes containing two endocyclic silicon and one tin atom was prepared from **1** and  $\text{Me}_2\text{SnCl}_2$ . All new compounds were characterised by multinuclear NMR spectroscopy and the thus deduced structural assignments corroborated by single crystal X-ray diffraction.

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multinuclear NMR spectroscopy. Single crystals of **2a** and **3** were analysed by X-ray diffraction.

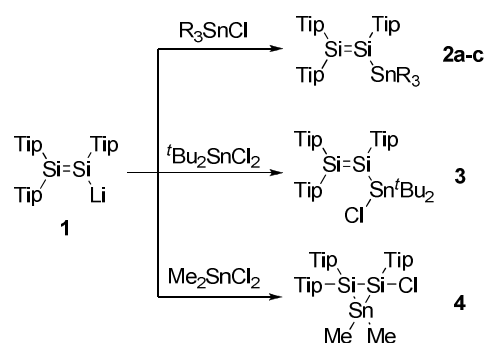
## Introduction

Organotin compounds are widely applied in synthetic organic chemistry. The palladium-catalysed coupling of organotin reagents with a variety of organic substrates (Stille coupling) allows for the generation of  $\text{sp}^2\text{-sp}^2$  carbon-carbon linkages under mild and neutral conditions; a broad variety of unprotected functional groups on both coupling partners are tolerated.[1] The transmetalation of tin organyls is a useful tool for the preparation of organo lithium species, *e.g.* vinyl lithiums[2] or allyl lithiums.[3]

During the last five years we and others have reported a variety of disilenes, disila analogues of vinyl anions.[4,5] The rising interest in this class of compounds stems from their ability to transfer the Si=Si double bond to organic and inorganic substrates.[5a,5d,5g;6] In order to broaden the scope of the Si=Si transfer, the preparation of a range of hitherto unknown stannyl substituted disilenes appeared desirable and will be reported here. Additionally, we discuss the preparation of an *Sn*-chlorinated derivative, a chlorostannyl disilene, as well as that of a related saturated cyclic compound, a disilastannirane.

## Results and Discussion

The reactions of disilenide **1** with  $\text{R}_3\text{SnCl}$  or  $^t\text{Bu}_2\text{SnCl}_2$  in hexane or toluene lead to stannyl substituted disilenes **2a-c** (**a**: R = Me, **b**: R = Bu, **c**: R = Ph) and **3** (Scheme 1). The products were isolated in yields between 59% and 95% after crystallisation from hexane and characterised by



**Scheme 1.** Syntheses of stannyl disilenes **2a-c** (**a**: R = Me, **b**: R = Bu, **c**: R = Ph) and **3** as well as disilastannirane **4** (Tip = 2,4,6-*t*-Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>).

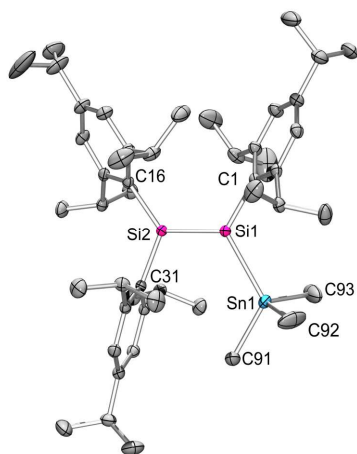
The <sup>119</sup>Sn NMR resonances of **2a-c** from  $\delta = -52.9$  to  $-108.9$  ppm are found in the expected range for tetra-coordinated tin atoms (Table 1). The chemical shifts in the <sup>29</sup>Si NMR chemical shifts of the stannyl disilenes **2a-c** between  $\delta = 113.3$  and 103.4 ppm for the SiTip<sub>2</sub> moiety and  $\delta = 38.9$  and 30.4 ppm for the tin-bonded silicon atom are similar to those of the monosilyl disilenes we had reported earlier.[5a,6e] All signals were unambiguously assigned with the help of <sup>29</sup>Si,<sup>1</sup>H 2D-NMR spectra and show well resolved <sup>119</sup>Sn-<sup>29</sup>Si coupling patterns. For all stannyl disilenes **2a-c** the <sup>1</sup>J(<sup>119</sup>Sn/<sup>29</sup>Si) coupling constants are between 3.5 and 4.0 times larger than the corresponding <sup>2</sup>J values.

The UV/vis spectra of **2a-c** are very similar to that of the monosilyl substituted disilenes as well (Table 1). The extinction coefficients range from  $\epsilon = 8300$  to 10000.

**Table 1.** Comparison of  $^{29}\text{Si}$  NMR and UV-Vis Data of Stannyl Disilenes **2a**, **2b**, **2c** and **3**.

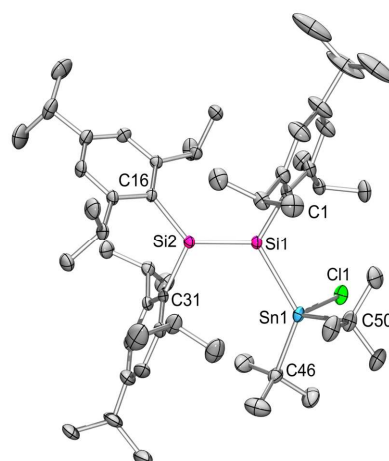
	<b>2a</b>	<b>2b</b>	<b>2c</b>	<b>3</b>
$\delta^{29}\text{Si1}$ , ppm	38.9	36.8	30.4	40.9
$\delta^{29}\text{Si2}$ , ppm	103.4	105.3	113.3	114.5
$\delta^{119}\text{Sn}$ , ppm	-68.3	-52.9	-108.9	109.5
$^1J_{\text{Sn,Si}}$ , Hz	474.2	353.6	480.7	88.4
$^2J_{\text{Sn,Si}}$ , Hz	122.9	98.8	119.7	106.9
$\lambda_{\text{max}}$ , nm	441	430	417	431
$\epsilon$ , $10^3\text{M}^{-1}\text{cm}^{-1}$	8.3	9.6	10	10

Single crystals of **2a** were investigated by X-ray diffraction to confirm the structure deduced from the spectroscopic data (Figure 1). Stannyl disilene **2a** crystallised with two independent molecules plus half a molecule of hexane in the asymmetric unit. Both molecules differ slightly in the Si=Si bond length (**2a**: Si1-Si2: 216.18(8); Si3-Si4 217.18(9) pm). A similar observation had been made in case of  $\text{Tip}_2\text{Si}=\text{Si}(\text{Tip})\text{SiPh}_2\text{Cl}$ , which exhibits four different Si=Si bond lengths in the asymmetric unit.[6e] Similarly, in case of **2a** the variability of the Si=Si bond length can be rationalised with the conformational flexibility of the Si=Si double bond: the relatively weak crystal packing forces account for a substantial variations in *trans*-bending of the disilene molecules, which in turn are closely related to the Si=Si bond length. In case of **2a** the smaller *trans*-bent angles  $\theta$  are found in the molecule with the shorter Si=Si distance (**2a**:  $\theta_{\text{Si1}} = 10.85^\circ$ ,  $\theta_{\text{Si2}} = 14.74^\circ$ ,  $\theta_{\text{Si3}} = 18.82^\circ$ ,  $\theta_{\text{Si4}} = 17.87^\circ$ ;  $\theta$  is the angle between the Si=Si bond vector and the normal of the plane defined by a Si atom and the *ipso* atoms of the pendant groups). The Sn-Si distances of the two molecules of **2a** are virtually identical (256.75(6) pm to 256.23(6) pm) and in the expected range for Sn-Si single bonds from 252 pm to 261 pm.[7]

**Figure 1.** Structure of **2a** in the solid state. Thermal ellipsoids at the 30% probability level. Only one of the two independent molecules shown. Disordered  $^i\text{Pr}$  groups and protons omitted for clarity. Selected bond lengths [pm] and angles [ $^\circ$ ] (for the depicted molecule only): Si1-Si2 216.18(8), Si1-Sn1 256.75(6), Si1-C1 189.6(2), Si2-C16 190.9(2), Si2-C31 189.3(2), Si2-Si1-Sn1 120.57(3), Sn1-Si1-C1 117.79(7), C1-Si1-Si2 121.56(7), C16-Si2-Si1 125.40(7), C16-Si2-C31 122.17(10), C31-Si2-Si1 111.69(7).

Like in the case of **2a**, the structure of chlorostannyl substituted disilene **3** in the solid state as determined by X-ray diffraction on single crystals shows two independent

molecules in the asymmetric unit (Figure 2). The Si=Si bonds of **3** are slightly longer than those of **2a** (**3**: Si1-Si2: 218.82(12) pm, Si3-Si4: 217.67(11) pm). The same holds true for the Sn-Si bonds (**3**: Si1-Sn1 259.74(9) pm, Si3-Sn2 258.97(9) pm), which suggests that all elongations relative to **2a** are mainly due to the increased steric demand of the substitution pattern in **3** rather than to any  $\sigma^*$ -conjugative effects. Similarly as in **2a** the shorter Si=Si bond correlate to smaller *trans*-bent angles (**3**:  $\theta_{\text{Si1}} = 22.42^\circ$ ,  $\theta_{\text{Si2}} = 17.95^\circ$ ,  $\theta_{\text{Si3}} = 15.36^\circ$ ,  $\theta_{\text{Si4}} = 10.53^\circ$ ). It is noteworthy that the tin coordination environments are considerably distorted from the ideal tetrahedral one. The sums of bonds angles at the tin atoms disregarding the angles involving chlorine is close to  $360^\circ$ , which indicates an almost triangular pyramidal coordination sphere (Sn1  $354.6^\circ$ , Sn2  $351.7^\circ$ ). The tin-chlorine distance is inconspicuous (Sn1-Cl1 239.63(9) pm, Sn2-Cl2 240.70(10) pm) and therefore the described distortion could well be attributed to steric congestion. In fact, similar structural parameters at the tin atom have been reported for the simple monostannane  $\text{Mes}^*\text{Sn}(\text{Cl})^i\text{Bu}_2$  ( $\text{Mes}^* = 2,4,6\text{-}^i\text{Bu}_3\text{C}_6\text{H}_2$ ).[8] Although not manifested in the observed intramolecular Sn1-Si2 distances (419.92(10) and 418.56(10) pm), a weak through space interaction and thus a certain degree of coordination sphere expansion of tin from 4 to 5 cannot be excluded.

**Figure 2.** Structure of **3** in the solid state. Thermal ellipsoids at the 30% probability level. Only one of the two independent molecules shown. Co-crystallised hexane, disordered  $^i\text{Pr}$  groups and protons omitted for clarity. Selected bond lengths [pm] and angles [ $^\circ$ ] (for the depicted molecule only): Si1-Si2 218.82(12), Si1-Sn1 259.74(9), Si1-C1 189.8(3), Si2-C16 189.9(3), Si2-C31 188.6(3), Sn1-Cl1 239.63(9), Si2-Si1-Sn1 122.44(4), Sn1-Si1-C1 115.62(9), C1-Si1-Si2 117.86(10), C16-Si2-Si1 130.05(9), C16-Si2-C31 111.34(12), C31-Si2-Si1 115.39(9), Si1-Sn1-Cl1 99.91(3), Si1-Sn1-C46 125.06(9), Si1-Sn1-C50 112.87(9).

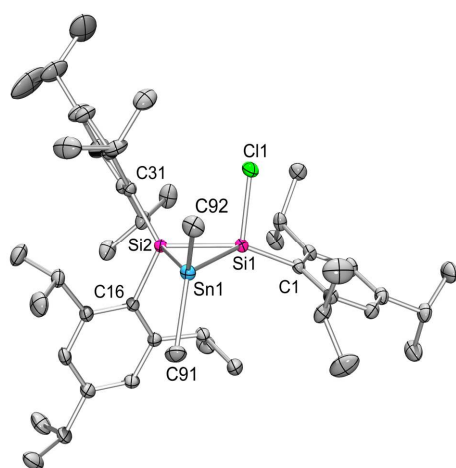
At least in solution, the NMR spectroscopic analysis of **3** indeed suggests the presence of a through space interaction between Sn1 and Si2, the silicon atom in  $\beta$ -position to the stannyl group. The  $^{119}\text{Sn}$  signal of **3** is considerably shifted to low field by the presence of the electronegative chlorine atom. Additionally, an electronegative substituent such as chlorine is expected to lower the  $\sigma^*$  orbitals at tin and thus facilitate any through space interaction. Indeed, the chlorostannyl substituted disilene **3** exhibits a rather small one-bond coupling constant of  $^1J(^{119}\text{Sn}/^{29}\text{Si}) = 88.4$  Hz, which is in fact smaller than the two-bond coupling of

$^2J(^{119}\text{Sn}/^{29}\text{Si}) = 106.9$  Hz. This would be nicely explained by a second coupling pathway with reversed sign attenuating the  $^1J$  coupling constant.

As mentioned before, however, no corroborating evidence for such an interaction could be obtained from neither spectroscopic nor crystallographic data. It is known that tin coupling constants are very sensitive to small variations in structural parameters even though there are only few examples of clear-cut correlations between  $^1J(^{119}\text{Sn}/^{13}\text{C})$  and  $^2J(^{119}\text{Sn}/^1\text{H})$  coupling constants and bond angles or distances.[9] Likewise the prediction of  $^{119}\text{Sn}$ -coupling constants by quantum chemical methods is still in its infancy and a matter of current research.[10]

In order to probe whether the steric demand of the *tert*-butyl groups at tin might prevent a more tangible 1,3- interaction between Sn1 and Si2, we investigated the reaction of **1** with  $\text{Me}_2\text{SnCl}_2$ . The treatment of disilenide **1** with a 1.2fold excess of  $\text{Me}_2\text{SnCl}_2$  indeed results among other unidentified products in the formation of a three-membered ring compound (Scheme 1), albeit one where the chlorine atom has shifted from Sn1 to Si1 in what resembles the isomerisation of chlorosilyl substituted disilenes to cyclotrisilanes.[6e]

The first disilastannirane **4** was isolated in 21% yield by crystallisation at  $0^\circ\text{C}$  from hexane and characterised by multinuclear NMR spectroscopy and X-ray diffraction of a single crystal. The  $^{29}\text{Si}$  NMR spectrum shows two signals at  $-28.3$  ppm and  $-57.3$  ppm in the typical region for heavier cyclopropanes.[11] The  $^{119}\text{Sn}$  NMR signal is observed at  $-252.4$  ppm. Due to the relatively broad signals the tin-silicon coupling constants could not be resolved in case of **4**. Unlike the open-chained derivatives **2a-c** and **3**, cyclic **4** is sensitive to light. When a solution of **4** in benzene is exposed to ambient light, complete conversion to an as yet unidentified product is attained after one week.



**Figure 3.** Structure of **4** in the solid state. Thermal ellipsoids at the 30% probability level. Only one of the two independent molecules is displayed and hydrogen atoms are omitted for clarity. Selected bond lengths [pm] and angles [ $^\circ$ ] (for the depicted molecule only): Si1-Si2 237.66(9), Si1-Sn1 254.22(6), Si2-Sn1 261.26(7), Si1-Cl1 210.45(9), Si1-C1 189.8(2), Si2-C16 190.5(2), Si2-C31 191.2(2), C1-Si1-Si2 141.59(7), C1-Si1-Sn1 135.91(8), Si2-Si1-Sn1 64.06(2), Si1-Si2-Sn1 61.05(2), Si1-Sn1-Si2 54.89(2), Si2-Si1-Sn1-C91 97.33(10), Si2-Si1-Sn1-C91  $-121.61(10)$ .

Disilastannirane **4** crystallises with two independent molecules in the asymmetric unit (Figure 3). The Si-Si bond lengths are determined to 237.66(9) pm and 237.99(9) pm, which is significantly longer than the corresponding Si-Si bond of the related cyclotrisilane **5** (235.8(1) pm).[6e] Given the unavailability of data on disilastannirane comparison with the known disilagermiranes seems appropriate. Derivative **6** was reported by Watanabe, Goto et al. in 1996,[12] **7** by Sekiguchi et al. in 2003 (Chart 1).[13]



**Chart 1.** Heavy cyclopropane analogues **5**,[6e] **6**,[12] and **7** (Tip = 2,4,6- $^i\text{Pr}_3\text{C}_6\text{H}_2$ , R =  $^t\text{Bu}$ ).[13]

One of the Si-Si-Sn angles of each molecule of **4** is considerably wider than the other (Si2-Si1-Sn1  $64.06(2)^\circ$ , Si4-Si3-Sn2  $63.67(2)^\circ$ ; Si1-Si2-Sn1  $61.05(2)^\circ$ , Si3-Si4-Sn2  $61.38(2)^\circ$ ), which avoids the steric congestion around Si2 to some extent. In accord with the larger covalent radius, the endocyclic angle of **4** at tin (Si1-Sn1-Si2  $54.89(2)^\circ$ ; Si3-Sn2-Si4  $54.94(2)^\circ$ ) is significantly smaller than the corresponding angles of **6** and **7** at germanium (**6**:  $58.6^\circ$ ; **7**:  $57.19^\circ$ ).[12,13] The resulting higher ring strain should favour any ring opening or expansion reaction, which could explain the relatively high sensitivity of **4** towards light. Additionally, unlike the corresponding cyclotrisilane **5** the tin derivative **4** is sensitive towards oxygen and moisture. This increased reactivity of **4** might well be of preparative use in future studies.

## Conclusion

The first stannyl substituted disilenes **2a-c** were synthesised from disilenide **1** and the appropriate chlorostannanes. While the reaction of **1** and  $^t\text{Bu}_2\text{SnCl}_2$  yields *Sn*-functional stannyl disilene **3**, treatment of **1** with  $\text{Me}_2\text{SnCl}_2$  affords the first disilastannirane **4**. All new compounds were characterised by multinuclear NMR spectroscopy and the derived structures were confirmed by single crystal X-ray diffraction for each class of compounds. Studies concerning the reactivity of stannyl disilenes **2a-c** are currently in progress.

## Experimental Section

All manipulations were carried out under a protective atmosphere of argon or nitrogen using standard Schlenk techniques and a glovebox. Etheral solvents were refluxed over sodium/benzophenone; hexane over sodium and deuterated benzene over potassium. All solvents were stored under argon and degassed prior to use. NMR spectra were recorded on a Bruker DRX400 NMR spectrometer ( $^{119}\text{Sn}$ , 149.21 MHz) FT-NMR spectrometer or a Bruker Avance 500 NMR spectrometer ( $^1\text{H}$ , 500.13 MHz,  $^{13}\text{C}$ , 125.76 MHz,  $^{29}\text{Si}$ , 99.36 MHz) FT-NMR spectrometer.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were referenced to the peaks of residual protons of deuterated solvents ( $^1\text{H}$ ) or the deuterated solvent itself ( $^{13}\text{C}$ ).  $^{29}\text{Si}$  NMR spectra were referenced

to external TMS and  $^{119}\text{Sn}$  NMR spectra were referenced to external  $\text{Bu}_4\text{Sn}$  in  $\text{C}_6\text{D}_6$  ( $-11.7$  ppm). All chemical shifts are reported in ppm. Elemental analyses (C, H) were performed on a Leco Instruments Elemental Analyzer, type CHNS 932. UV-Vis spectra were recorded on a Perkin Elmer Lambda 20 UV/Vis Spectrometer. Melting points were determined under argon or nitrogen in closed NMR tubes and are uncorrected.  $\text{Tip}_2\text{Si}=\text{Si}(\text{Tip})\text{Li}$  (**1**) was prepared according to our published procedure.[5a] Chlorostannanes were purchased from Sigma-Aldrich and used as received.

#### 1-Trimethylstannyl-1,2,2-tris(2',4',6'-triisopropylphenyl)-

**disilene (2a):** Via cannula 40 mL of hexane are added to a mixture of 1.69 g (1.980 mmol) disilenide **1** and 0.39 g (1.957 mmol)  $\text{Me}_3\text{SnCl}$ . The resulting orange suspension is stirred overnight at r.t. Precipitated solids are filtered off and solvents are evaporated to yield a red oil. After a few days 1.56 g (95%) **2a** are obtained as red crystals (mp. 141 °C, dec) from a minimum amount of pentane.  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ , r.t.):  $\delta = 7.10, 7.08, 7.01$  (each s, each 2H, Tip-H), 4.35, 4.10, 3.90 (each hept., each 2H, iPr-CH), 2.82 (m, 2H, iPr-CH), 2.72 (hept., 1H, iPr-CH), 1.33, 1.26, 1.24, 1.14, 0.99 (each d, altogether 54H, iPr-CH<sub>3</sub>), 0.19 (Sn-CH<sub>3</sub>).  $^{13}\text{C}$  NMR (125 MHz,  $\text{C}_6\text{D}_6$ , r.t.):  $\delta = 155.96, 155.38, 155.15$  (Tip-C<sub>o</sub>), 151.32, 150.92, 150.15 (Tip-C<sub>i</sub>), 135.14, 134.61, 132.18 (Tip-C<sub>p</sub>), 122.24, 122.01, 121.56 (Tip-CH), 38.41, 37.53, 36.39, 34.94, 34.88, 34.54 (iPr-CH), 25.16 (br.), 24.68, 24.29, 24.26, 24.03 (iPr-CH<sub>3</sub>),  $-5.17$  ( $^1\text{J}(\text{Sn},\text{C}) = 283.7$  Hz, Sn-CH<sub>3</sub>).  $^{29}\text{Si}$  NMR (99.36 MHz,  $\text{C}_6\text{D}_6$ , r.t.):  $\delta = 103.4$  ( $^2\text{J}(\text{Sn},\text{Si}) = 122.9$  Hz, SiTip<sub>2</sub>), 38.9 ( $^1\text{J}(\text{Sn},\text{Si}) = 474.2$  Hz, SiTip).  $^{119}\text{Sn}$  NMR (186.46 MHz,  $\text{C}_6\text{D}_6$ , r.t.):  $\delta = -68.3$  ( $^1\text{J}(\text{Sn},\text{Si}) = 474.2$  Hz,  $^2\text{J}(\text{Sn},\text{Si}) = 122.9$  Hz, und  $^1\text{J}(\text{Sn},\text{C}) = 283.7$  Hz, SnMe<sub>3</sub>). UV/Vis (hexane):  $\lambda_{\text{max}}$  ( $\epsilon$ ) 441 nm (8300  $\text{Lmol}^{-1}\text{cm}^{-1}$ ). **Element. anal.:** Calcd. for  $\text{C}_{48}\text{H}_{78}\text{Si}_2\text{Sn}$ : C, 69.46; H, 9.47. Found: C, 68.70; H, 9.37. **Exact Mass (ESI-MS)** Calcd.  $m/z$  for  $\text{C}_{48}\text{H}_{78}\text{Si}_2\text{Sn}^+$  ( $\text{M}^+$ ): 830.4664. Found: 830.4662. **MS** (CI, isobutane)  $m/z = 830$  ( $\text{M}^+$ ), 697 ( $\text{M}^+ + \text{O}_2 - \text{SnMe}_3$ ), 665 ( $\text{M}^+ - \text{SnMe}_3$ ), 449 (Tip<sub>2</sub>SiMe<sup>+</sup>), 433, 321, 261, 245, 231, 203, 189, 43 ( $\text{C}_3\text{H}_7^+$ ).

#### 1-Tributylstannyl-1,2,2-tris(2',4',6'-triisopropylphenyl)disilene

**(2b):** Via cannula 30 mL of toluene are added to 5.14 g (6.023 mmol) disilenide **1**. The orange solution is cooled to 0 °C and 1.96 g (6.021 mmol)  $\text{Bu}_3\text{SnCl}$  are added via syringe. After stirring for 16 h the precipitated LiCl is removed by filtration. All volatiles are removed in vacuum and the solid residue is dissolved in approx. 5 mL of pentane. After 5 days at 0 °C 4.97 g (86%) **2b** are separated from the mother liquor as red crystals (mp. 64 - 67 °C).  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ , r.t.):  $\delta = 7.072, 7.070, 6.99$  (each s, each 2H, Tip-H), 4.36, 4.12, 3.86 (each hept., each 2H, iPr-CH), 2.79, 2.75, 2.66 (each hept., each 1H, iPr-CH), 1.57 (m, 6H, Bu-C <sub>$\gamma$</sub> H<sub>2</sub>), 1.38 (d, 12H, iPr-CH<sub>3</sub>), 1.32 (q, 6H, Bu-C <sub>$\alpha$</sub> H<sub>2</sub>), 1.24, 1.19, 1.10 (each d, altogether 36H, iPr-CH<sub>3</sub>), 0.98 (m, 6H, Bu-C <sub>$\beta$</sub> H<sub>2</sub>), 0.96 (d, 6H, iPr-CH<sub>3</sub>), 0.88 (t, 9H, Bu-C <sub>$\delta$</sub> H<sub>3</sub>).  $^{13}\text{C}$  NMR (125 MHz,  $\text{C}_6\text{D}_6$ , r.t.):  $\delta = 155.84, 155.24, 154.99$  (Tip-C<sub>o</sub>), 151.13, 150.85, 150.13 (Tip-C<sub>p</sub>), 135.65, 135.47, 132.92 (Tip-C<sub>i</sub>), 122.33, 121.97, 121.66 (Tip-CH), 38.34, 37.41, 36.54, 34.84, 34.77, 34.49 (iPr-CH), 30.45, 27.94 ( $^1\text{J}(\text{Sn},\text{C}) = 63.4$  Hz, Bu-C <sub>$\gamma$</sub> H<sub>2</sub>), 24.60, 24.17, 23.94 (iPr-CH<sub>3</sub>), 13.98, 12.44 ( $^2\text{J}(\text{Sn},\text{C}) = 280.1$  Hz, Bu-C <sub>$\delta$</sub> H<sub>3</sub>).  $^{29}\text{Si}$  NMR (99.36 MHz,  $\text{C}_6\text{D}_6$ , r.t.):  $\delta = 105.3$  ( $^2\text{J}(\text{Sn},\text{Si}) = 98.8$  Hz, SiTip<sub>2</sub>), 36.8 ( $^1\text{J}(\text{Sn},\text{Si}) = 353.6$  Hz, SiTip) ppm.  $^{119}\text{Sn}$  NMR (186.46 MHz,  $\text{C}_6\text{D}_6$ , r.t.):  $\delta = -52.9$  ( $^1\text{J}(\text{Sn},\text{Si}) = 353.6$  Hz,  $^2\text{J}(\text{Sn},\text{Si}) = 98.8$  Hz,  $^2\text{J}(\text{Sn},\text{C}) = 280.1$  Hz und  $^1\text{J}(\text{Sn},\text{C}) = 63.4$  Hz, SnBu<sub>3</sub>). UV/Vis (hexane):  $\lambda_{\text{max}}$  ( $\epsilon$ ) 430 nm (9620  $\text{Lmol}^{-1}\text{cm}^{-1}$ ).

**Element. anal.:** Calcd. for  $\text{C}_{57}\text{H}_{96}\text{Si}_2\text{Sn}$ : C, 71.59; H, 10.12. Found: C, 71.55; H, 9.96. **MS** (CI, isobutane)  $m/z = 956$  ( $\text{M}^+$ ), 931 ( $\text{M}^+ + \text{O}_2 - \text{C}_4\text{H}_9$ ), 899 ( $\text{M}^+ - \text{C}_4\text{H}_9$ ), 697 ( $\text{M}^+ + \text{O}_2 - \text{SnBu}_3$ ), 665 ( $\text{M}^+ - \text{SnBu}_3$ ), 491 (Tip<sub>2</sub>SiBu<sup>+</sup>), 433, 345, 323 (SnBu<sub>3</sub><sup>+</sup> + O<sub>2</sub>), 289, 231, 203, 189, 43 ( $\text{C}_3\text{H}_7^+$ ).

#### 1-Triphenylstannyl-1,2,2-tris(2',4',6'-triisopropylphenyl)-

**disilene (2c):** Via cannula 25 mL of toluene are added to a mixture of 2.54 g (2.976 mmol) disilenide **1** and 1.15 g (2.983 mmol)  $\text{Ph}_3\text{SnCl}$  at 0 °C. The resulting orange suspension is stirred overnight at r.t. Precipitated solids are filtered off and volatiles are removed from the filtrate in vacuum. The remaining solid is dissolved in 5 mL of hot hexane. After 16 h at r.t. 2.21 g (73%) **2c** are isolated as red crystals (mp. 170 °C, dec).

$^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ , r.t.):  $\delta = 7.74-7.60$  (m, 6H, Ph-H), 7.09-7.03 (m, 9H, Ph-H), 7.02, 6.99, 6.91 (each s, each 2H, Tip-H), 4.42, 4.06, 3.88 (each hept., each 2H, iPr-CH), 2.68 (m, 3H, iPr-CH), 1.25 (br., 6H, iPr-CH<sub>3</sub>), 1.144, 1.137, 1.12 (each d, each 6H, iPr-CH<sub>3</sub>), 1.05, 0.98 (each d, each 12H, iPr-CH<sub>3</sub>).  $^{13}\text{C}$  NMR (125 MHz,  $\text{C}_6\text{D}_6$ , r.t.):  $\delta = 155.96, 155.13, 154.56$  (Tip-C<sub>o</sub>), 151.25, 151.09, 150.77 (Tip-C<sub>p</sub>), 142.35 ( $^1\text{J}(\text{Sn},\text{C}) = 434.5$  Hz, Ph-C<sub>i</sub>), 137.85 ( $^2\text{J}(\text{Sn},\text{C}) = 40.8$  Hz, Ph-C<sub>o</sub>), 135.71, 134.34, 130.97 (Tip-C<sub>i</sub>), 128.59 (Ph-C <sub>$m/p$</sub> ), 122.51, 122.31, 122.00 (Tip-CH), 38.15, 38.04, 37.54, 34.77, 34.58, 34.50 (iPr-CH), 24.86, 24.55, 24.10, 24.04, 23.96 (iPr-CH<sub>3</sub>).  $^{29}\text{Si}$  NMR (99.36 MHz,  $\text{C}_6\text{D}_6$ , r.t.):  $\delta = 113.3$  ( $^2\text{J}(\text{Sn},\text{Si}) = 119.7$  Hz, SiTip<sub>2</sub>), 30.4 ( $^1\text{J}(\text{Sn},\text{Si}) = 480.7$  Hz, SiTip) ppm.  $^{119}\text{Sn}$  NMR (186.46 MHz,  $\text{C}_6\text{D}_6$ , r.t.):  $\delta = -108.9$  ( $^1\text{J}(\text{Sn},\text{Si}) = 480.7$  Hz,  $^2\text{J}(\text{Sn},\text{Si}) = 119.7$  Hz,  $^1\text{J}(\text{Sn},\text{C}) = 434.5$  Hz und  $^2\text{J}(\text{Sn},\text{C}) = 40.8$  Hz, SnPh<sub>3</sub>). UV/Vis (hexane):  $\lambda_{\text{max}}$  ( $\epsilon$ ) 417 nm (10050  $\text{Lmol}^{-1}\text{cm}^{-1}$ ). **Element. anal.:** Calcd. for  $\text{C}_{63}\text{H}_{84}\text{Si}_2\text{Sn}$ : C, 74.46; H, 8.33. Found: C, 74.00; H, 8.36. **MS** (CI, isobutane)  $m/z = 1048$  ( $\text{M}^+ + \text{O}_2$ ), 1016 ( $\text{M}^+$ ), 971 ( $\text{M}^+ + \text{O}_2 - \text{C}_6\text{H}_5$ ), 767 (11), 742 ( $\text{M}^+ - \text{SnPh}_2$ ), 697 ( $\text{M}^+ + \text{O}_2 - \text{SnPh}_3$ ), 511 (Tip<sub>2</sub>SiPh<sup>+</sup>), 494, 433, 351 (SnPh<sub>3</sub><sup>+</sup>), 273, 231, 204, 189, 43 ( $\text{C}_3\text{H}_7^+$ ).

#### 1-(Chlorodi-tert.-butylstannyl)-1,2,2-tris(2',4',6'-

**triisopropylphenyl)disilene (3):** Via cannula 25 mL of hexane are added to a mixture of 1.40 g (1.640 mmol) disilenide **1** and 0.50 g (1.646 mmol)  $\text{tBu}_2\text{SnCl}_2$  at r.t. The colour of the mixture turns to dark red. After stirring overnight, all insoluble parts are removed by filtration. The filtrate is reduced until the product starts to precipitate, which is re-dissolved by gentle heating to 35 °C. After keeping at r.t. overnight 0.91 g (59%) **3** are obtained as deep red crystals (mp. 155 °C dec.).

$^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ , r.t.):  $\delta = 7.07, 7.03, 6.98$  (each s, each 2H, Tip-H), 4.39, 3.97, 3.65 (each hept., each 2H, iPr-CH), 2.72 (m, 2H, iPr-CH), 2.63 (hept., 1H, iPr-CH), 1.43 (d, 12H, iPr-CH<sub>3</sub>), 1.27 (s, 18H, tBu-CH<sub>3</sub>), 1.18, 1.14, 1.07, 0.92 (each d, altogether 42H, iPr-CH<sub>3</sub>).  $^{13}\text{C}$  NMR (125 MHz,  $\text{C}_6\text{D}_6$ , r.t.):  $\delta = 156.36, 155.17, 155.06$  (Tip-C<sub>o</sub>), 151.77, 151.24, 150.78 (Tip-C<sub>i</sub>), 135.27, 134.88, 132.80 (Tip-C<sub>p</sub>), 122.81, 122.38, 122.32 (Tip-CH), 40.88 ( $^1\text{J}(\text{Sn},\text{C}) = 302.1$  Hz, tBu-CMe<sub>3</sub>), 38.47, 38.02, 36.85, 34.85, 34.72, 34.38 (iPr-CH), 31.82 (tBu-CH<sub>3</sub>), 25.69 (br.), 24.70, 24.19, 24.02, 23.86 (iPr-CH<sub>3</sub>).  $^{29}\text{Si}$  NMR (99.36 MHz,  $\text{C}_6\text{D}_6$ , r.t.):  $\delta = 114.5$  ( $^2\text{J}(\text{Sn},\text{Si}) = 106.9$  Hz, SiTip<sub>2</sub>), 40.9 ( $^1\text{J}(\text{Sn},\text{Si}) = 88.4$  Hz, SiTip).  $^{119}\text{Sn}$  NMR (186.46 MHz,  $\text{C}_6\text{D}_6$ , r.t.):  $\delta = 109.5$ . UV/Vis (hexane):  $\lambda_{\text{max}}$  ( $\epsilon$ ) 431 nm (10000  $\text{Lmol}^{-1}\text{cm}^{-1}$ ). **Element. anal.:** Calcd for  $\text{C}_{53}\text{H}_{87}\text{Si}_2\text{SnCl}$ : C, 68.11; H, 9.38. Found: C, 67.22; H, 9.30. **MS** (CI, isobutane)  $m/z = 935$  ( $\text{M}^+$ ), 909 ( $\text{M}^+ + \text{O}_2 - \text{C}_4\text{H}_9$ ), 877 ( $\text{M}^+ - \text{C}_4\text{H}_9$ ), 853, 671, 665 ( $\text{M}^+ - \text{tBu}_2\text{SnCl}$ ), 469 (Tip<sub>2</sub>SiCl<sup>+</sup>), 435, 265, 230, 204, 189, 57 ( $\text{C}_4\text{H}_9^+$ ), 43 ( $\text{C}_3\text{H}_7^+$ ).

**1,1-Dimethyl-2-chloro-2,3,3-tris(2',4',6'-triisopropylphenyl)-disilastannirane (4):** At r.t. a solution of 2.04 g (2.390 mmol) disilenide **1** in 20 mL of toluene is added dropwise to a solution of 0.85 g (3.869 mmol) Me<sub>2</sub>SnCl<sub>2</sub> over a period of 15 min. The resulting orange suspension is stirred overnight at r.t. All precipitates are filtered off and the filtrate is distilled off to give 2.25 g of a yellow solid. Crystallisation from 10 mL of hexane at 0°C yields 0.43 g (21%) of **4** as colourless blocks (mp. 168 °C, dec).

<sup>1</sup>H NMR (500 MHz, toluene-d<sub>8</sub>, r.t.): δ = 7.10, 7.09, 7.07 (each s, each 1H, Tip-H), 6.92 (s, 2H, Tip-H), 6.86 (s, 1H, Tip-H), 4.45 - 4.32 (m, 2H, iPr-CH), 3.86 (hept., 1H, iPr-CH), 3.60, 3.51, 3.18 (each br., each 1H, iPr-CH), 2.71 (m, 2H, iPr-CH), 2.63 (hept., 1H, iPr-CH), 1.42 (d, 6H, iPr-CH<sub>3</sub>), 1.33 (br., 3H, iPr-CH<sub>3</sub>), 1.30, 1.27, 1.17, 1.16, 1.14, 1.13, 1.082, 1.077 (each d, altogether 36H, iPr-CH<sub>3</sub>), 0.81 (Sn-CH<sub>3</sub>), 0.64, 0.44 (each br., altogether 9H, iPr-CH<sub>3</sub>), 0.16 (Sn-CH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, toluene-d<sub>8</sub>, r.t.): δ = 156.25, 156.18, 156.06, 156.01, 153.91 (Tip-C<sub>o</sub>), 152.08, 150.80, 150.31 (Tip-C<sub>i</sub>), 133.37, 130.42, 130.01 (Tip-C<sub>p</sub>), 122.66, 122.12, 121.97, 121.71, 121.27, 121.23 (Tip-CH), 38.17, 37.29, 37.14, 36.00, 35.68, 34.87, 34.66, 34.53, 34.29 (iPr-CH), 28.49 (br.), 27.94, 27.45, 27.11, 26.23, 24.59, 24.38, 24.05, 23.99, 23.62, 23.00, 22.45 (iPr-CH<sub>3</sub>), -8.72, -10.81 (Sn-CH<sub>3</sub>). <sup>29</sup>Si NMR (99.36 MHz, toluene-d<sub>8</sub>, r.t.): δ = -28.3, -57.3. <sup>119</sup>Sn NMR (186.46 MHz, toluene-d<sub>8</sub>, r.t.): δ = -252.4. **Exact Mass** (ESI-MS) Calcd. *m/z* for C<sub>47</sub>H<sub>75</sub>Si<sub>2</sub>SnCl<sup>+</sup> (M<sup>+</sup>): 850.4118. Found: 850.4121. **MS** (CI, isobutane) *m/z* = 850 (M<sup>+</sup>), 665 (M<sup>+</sup>-Me<sub>2</sub>SnCl), 469 (Tip<sub>2</sub>SiCl<sup>+</sup>), 449 (Tip<sub>2</sub>SiMe<sup>+</sup>), 435, 323, 265, 245, 231, 204, 189, 57, 43 (C<sub>3</sub>H<sub>7</sub><sup>+</sup>).

**Crystallography:** Single crystals of **2a**, **3**, and **4** were coated with perfluorinated polyether and quickly transferred to the cold nitrogen stream at the goniometer. The accumulation of data sets was carried out using a Bruker SMART CCD area-detector diffractometer with Mo-K<sub>α</sub> radiation (λ = 0.71073 Å).[14] Unit cells were determined using a number of representative frames. Intensities were determined from several series of frames, each covering 0.3° in ω of an entire sphere. Numerical absorption corrections were applied using SADABS. The structures were solved by direct methods or with a Patterson map and refined by least squares on weighted *F*<sup>2</sup> values for all reflections. Refinements (ShelXL-97) yielded the crystallographic parameters summarized in Table 2. Crystallographic data (excluding structure factors) for the structural analyses of **2a**, **3**, and **4** have been deposited with the Cambridge Crystallographic Data Centre as CCDC-728277 to 728279 Copies of this information may be obtained free of charge from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; E-Mail: deposit@ccdc.cam.ac.uk) or under <http://www.ccdc.cam.ac.uk>

**Table 2.** Selected Crystallographic Details for Compounds **2a**, **3**, and **4**.

	<b>2a</b>	<b>3</b>	<b>4</b>
Formula	C <sub>99</sub> H <sub>163</sub> Si <sub>4</sub> Sn <sub>2</sub>	C <sub>53</sub> H <sub>87</sub> ClSi <sub>2</sub> Sn	C <sub>47</sub> H <sub>75</sub> ClSi <sub>2</sub> Sn
<i>T</i> , K	173(2)	173(2)	173(2)
System	triclinic	orthorhombic	triclinic
Space group	P <sup>-</sup> 1	Pca2(1)	P <sup>-</sup> 1
<i>a</i> , Å	11.5193(6)	22.389(5)	14.1341(9)
<i>b</i> , Å	17.6904(10)	19.011(4)	17.9108(11)
<i>c</i> , Å	25.5702(14)	25.944(5)	20.6439(13)
α	96.7910(10)°	90°	69.9390(10)°
β	101.0180(10)°	90°	77.0990(10)°

γ	92.0510(10)°	90°	89.8660(10)°
<i>V</i> , Å <sup>3</sup>	5069.7(5)	11043(4)	4769.3(5)
<i>Z</i>	2	8	4
<i>d</i> , g cm <sup>-3</sup>	1.116	1.124	1.184
μ, mm <sup>-1</sup>	0.580	0.585	0.671
<i>F</i> (000)	1826	4000	1808
θ <sub>max</sub>	26.08°	26.02°	26.37°
Refl. <sub>total</sub>	73180	92746	85064
Refl. <sub>unique</sub>	20064	21703	19517
<i>S</i>	1.063	1.066	1.026
<i>R</i> <sub>i</sub> ( <i>I</i> > 2σ)	0.0393	0.0344	0.0353
<i>wR</i> <sub>2</sub> (all data)	0.1080	0.0827	0.0898

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