

Stannyl-substituted Disilenes and a Disilastannirane

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Dedicated to Professor Michael Veith on the Occasion of His 65th 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**, $\text{Tip} = 2,4,6\text{-}i\text{Pr}_3\text{C}_6\text{H}_2$) with chlorostannanes R_3SnCl quantitatively affords the first stannyl-substituted disilenes $\text{Tip}_2\text{Si}=\text{Si}(\text{Tip})\text{SnR}_3$ (**2a**: $\text{R} = \text{Me}$, **2b**: $\text{R} = \text{Bu}$, **2c**: $\text{R} = \text{Ph}$). 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 Me_2SnCl_2 . All new compounds were characterised by multinuclear NMR spectroscopy and the thus deduced structural assignments corroborated by single-crystal X-ray diffraction.

Introduction

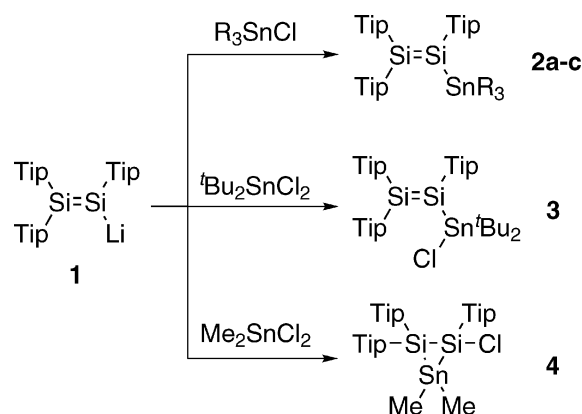
Organotin compounds are widely applied in synthetic organic chemistry. The palladium-catalysed coupling of organotin reagents with a variety of organic substrates (Stille coupling) allows for the generation of $\text{sp}^2\text{-sp}^2$ carbon-carbon linkages under mild and neutral conditions; a broad 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-lithium[2] or allyllithium [3] compounds.

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 $\text{Si}=\text{Si}$ double bond to organic and inorganic substrates [5a, 5d, 5g, 6]. In order to broaden the scope of the $\text{Si}=\text{Si}$ 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 a *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 R_3SnCl or $t\text{Bu}_2\text{SnCl}_2$ in hexane or toluene lead to stannyl-substituted disilenes **2a–c** (**a**: $\text{R} = \text{Me}$, **b**: $\text{R} = \text{Bu}$, **c**: $\text{R} = \text{Ph}$) and **3** (Scheme 1). The products

were isolated in yields between 59 % and 95 % after crystallisation from hexane and characterised by multinuclear NMR spectroscopy. Single crystals of **2a** and **3** were analysed by X-ray diffraction.



Scheme 1. Syntheses of stannyl disilenes **2a–c** (**a**: $\text{R} = \text{Me}$, **b**: $\text{R} = \text{Bu}$, **c**: $\text{R} = \text{Ph}$) and **3** as well as disilastannirane **4** ($\text{Tip} = 2,4,6\text{-}i\text{Pr}_3\text{C}_6\text{H}_2$).

The ^{119}Sn NMR resonances of **2a–c** from -52.9 to -108.9 ppm are found in the expected range for tetracoordinated tin atoms (Table 1). The chemical shifts in the ^{29}Si NMR chemical shifts of the stannyl disilenes **2a–c** between 113.3 and 103.4 ppm for the SiTip_2 moiety and 38.9 and 30.4 ppm for the tin-bonded silicon atom are similar to those of the monosilyl disilenes were reported earlier [5a, 6e]. All signals were unambiguously assigned with the help of $^{29}\text{Si}, ^1\text{H}$ 2D-NMR spectra and show well resolved $^{119}\text{Sn}\text{-}^{29}\text{Si}$ coupling patterns. For all stannyl disilenes **2a–c** the $^1J(^{119}\text{Sn}/^{29}\text{Si})$ coupling constants are between 3.5 and 4.0 times larger than the corresponding 2J values.

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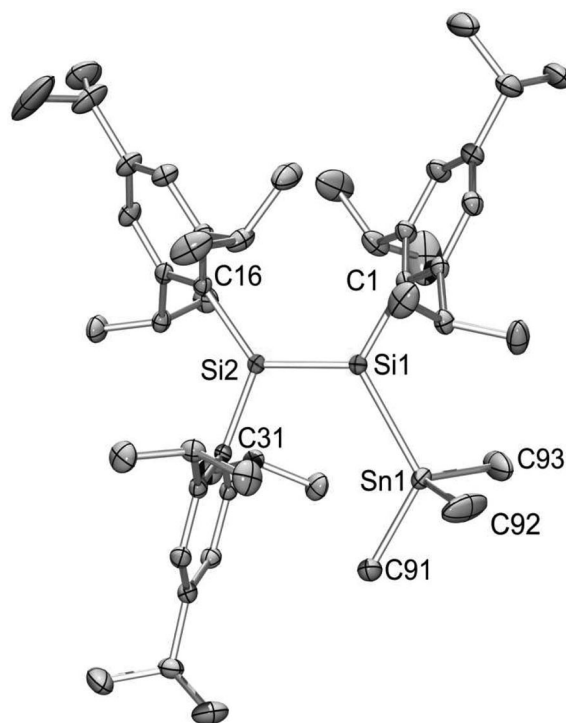
Table 1. Comparison of ^{29}Si NMR and UV/Vis Data of Stannyl Disilenes **2a**, **2b**, **2c** and **3**.

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

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.

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 θ are found in the molecule with the shorter Si=Si distance (**2a**: $\theta_{\text{Si1}} = 10.85^\circ$, $\theta_{\text{Si2}} = 14.74^\circ$, $\theta_{\text{Si3}} = 18.82^\circ$, $\theta_{\text{Si4}} = 17.87^\circ$; θ is the angle between the Si=Si bond vector and the normal of the plane defined by a silicon 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) to 256.23(6) pm] and in the expected range for Sn–Si single bonds from 252 to 261 pm [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), Si3–Si4: 217.67(11) pm]. The same holds true for the Sn–Si bonds [**3**: Si1–Sn1 259.74(9), Si3–Sn2 258.97(9) pm], which suggests that all elongations relative to **2a** are mainly because of the increased steric demand of the substitution pattern in **3** rather than to any σ^* -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° , which indicates an almost triangular pyramidal coordination sphere (Sn1 354.6° , Sn2 351.7°). The tin–chlorine distance is inconspicuous [Sn1–Cl1 239.63(9), Sn2–Cl2 240.70(10) pm] and therefore the described distortion could well be attributed to steric congestion. In fact, similar

**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*Pr groups and protons omitted for clarity. Selected bond lengths /pm and angles /° (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).

structural parameters at the tin atom have been reported for the simple monostannane $\text{Mes}^*\text{Sn}(\text{Cl})\text{tBu}_2$ ($\text{Mes}^* = 2,4,6\text{-tBu}_3\text{C}_6\text{H}_2$) [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 four to five cannot be excluded.

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 β -position to the stannyl group. The ^{119}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 σ^* 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 $^1J(^{119}\text{Sn}/^{29}\text{Si}) = 88.4 \text{ Hz}$, which is in fact smaller than the two-bond coupling of $^2J(^{119}\text{Sn}/^{29}\text{Si}) = 106.9 \text{ Hz}$. 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-

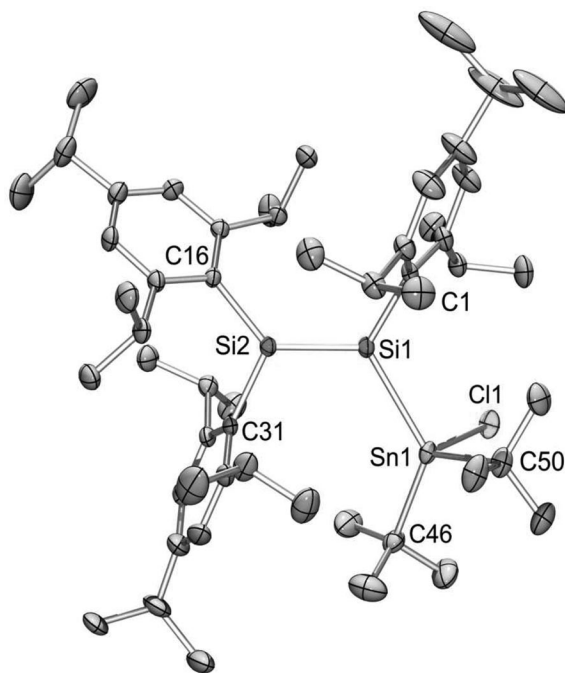


Figure 2. Structure of **3** in the solid state. Thermal ellipsoids at the 30 % probability level. Only one of the two independent molecules shown. Co-crystallised hexane, disordered *i*Pr groups and protons omitted for clarity. Selected bond lengths /pm and angles /° (for the depicted molecule only): 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–C11 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–C11 99.91(3), Si1–Sn1–C46 125.06(9), Si1–Sn1–C50 112.87(9).

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}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 Me_2SnCl_2 . The treatment of disilenide **1** with a 1.2-fold excess of Me_2SnCl_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 °C from hexane and was characterised by multinuclear NMR spectroscopy and single-crystal X-ray diffraction. The ^{29}Si NMR spectrum shows two signals at –28.3 ppm and –57.3 ppm in the typical region for heavier cyclopropanes [11]. The ^{119}Sn NMR signal is observed at –252.4 ppm. Because of 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**, the cyclic compound **4** is sensitive to light. When a solution of **4** in ben-

zene is exposed to ambient light, complete conversion to an as yet unidentified product is attained after one week.

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 (Scheme 2) [13].

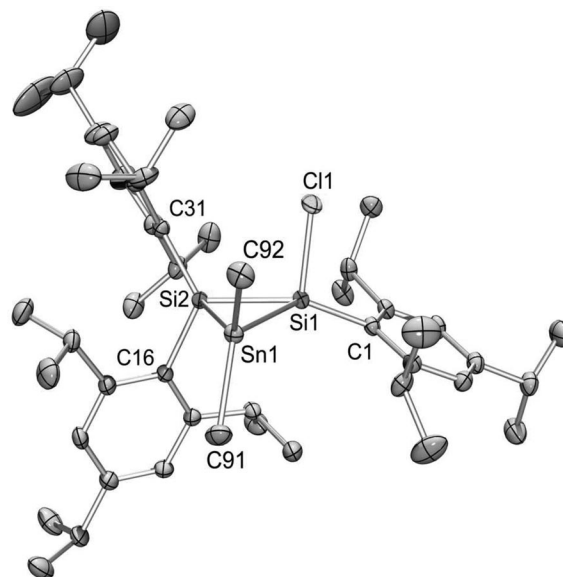
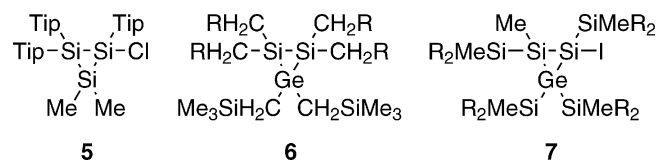


Figure 3. Structure of **4** in the solid state. Thermal ellipsoids at the 30 % probability level. Only one of the two independent molecules is displayed and hydrogen atoms are omitted for clarity. Selected bond lengths /pm and angles /° (for the depicted molecule only): Si1–Si2 237.66(9), Si1–Sn1 254.22(6), Si2–Sn1 261.26(7), Si1–C11 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–C92 121.61(10).



Scheme 2. Heavy cyclopropane analogues **5** [6e, 6 12], and **7** (Tip = 2,4,6-*i*Pr₃C₆H₂, R = *t*Bu) [13].

One of the Si–Si–Sn angles of each molecule of **4** is considerably wider than the others [Si2–Si1–Sn1 64.06(2)°, Si4–Si3–Sn2 63.67(2)°; Si1–Si2–Sn1 61.05(2)°, Si3–Si4–Sn2 61.38(2)°], 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)°; Si3–Sn2–Si4 54.94(2)°] is significantly smaller than the corresponding angles of **6** and **7** at germanium (**6**: 58.6°; **7**: 57.19°) [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.

Conclusions

The first stannyl-substituted disilenes **2a–c** were synthesised from disilenide **1** and the appropriate chlorostannanes. While the reaction of **1** and *t*Bu₂SnCl₂ yields *Sn*-functional stannyl disilene **3**, treatment of **1** with Me₂SnCl₂ 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. Ethereal solvents were heated under reflux 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 with a Bruker DRX-400 FT-NMR spectrometer (¹¹⁹Sn, 149.21 MHz) or a Bruker Avance 500 FT-NMR spectrometer (¹H, 500.13 MHz, ¹³C, 125.76 MHz, ²⁹Si, 99.36 MHz). ¹H and ¹³C{¹H} NMR spectra were referenced to the peaks of residual protons of deuterated solvents (¹H) or the deuterated solvent itself (¹³C). ²⁹Si NMR spectra were referenced to external TMS and ¹¹⁹Sn NMR spectra were referenced to external Bu₄Sn in C₆D₆ (−11.7 ppm). All chemical shifts are reported in ppm. Elemental analyses (C, H) were performed with a Leco Instruments Elemental Analyzer, type CHNS 932. UV/Vis spectra were recorded with a Perkin–Elmer Lambda 20 UV/Vis Spectrometer. Melting points were determined under argon or nitrogen in closed NMR tubes and are uncorrected. Tip₂Si = Si(Tip)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): Hexane (40 mL) was added to a mixture of disilenide **1** (1.69 g, 1.980 mmol) and Me₃SnCl (0.39 g, 1.957 mmol) through a cannula. The resulting orange suspension was stirred overnight at room temperature. Precipitated solids were filtered off and the solvents were evaporated to yield red oil. After a few days, 1.56 g (95 %) **2a** were obtained as red crystals (mp. 141 °C, dec) from a minimum amount of pentane. Elemental analysis: calcd. for C₄₈H₇₈Si₂Sn: C, 69.46; H, 9.47. Found: C, 68.70; H, 9.37.

¹H NMR (500 MHz, C₆D₆, room temp.): δ = 7.10, 7.08, 7.01 (each s, each 2 H, Tip-*H*), 4.35, 4.10, 3.90 (each hept., each 2 H, *i*Pr-*CH*), 2.82 (m, 2 H, *i*Pr-*CH*), 2.72 (hept., 1 H, *i*Pr-*CH*), 1.33, 1.26, 1.24, 1.14, 0.99 (each d, altogether 54 H, *i*Pr-*CH*₃), 0.19 (Sn-*CH*₃). ¹³C NMR (125 MHz, C₆D₆, room temp.): δ = 155.96, 155.38, 155.15 (Tip-C_o), 151.32, 150.92, 150.15 (Tip-C_i), 135.14, 134.61, 132.18 (Tip-C_p), 122.24, 122.01, 121.56 (Tip-*CH*), 38.41, 37.53, 36.39, 34.94, 34.88, 34.54 (*i*Pr-*CH*), 25.16 (br.), 24.68, 24.29, 24.26, 24.03 (*i*Pr-*CH*₃), −5.17 (¹J(Sn,C) = 283.7 Hz, Sn-*CH*₃). ²⁹Si NMR (99.36 MHz, C₆D₆, room temp.): δ = 103.4 (²J(Sn,Si) = 122.9 Hz, *Si*Tip₂), 38.9 (¹J(Sn,Si) = 474.2 Hz, *Si*Tip). ¹¹⁹Sn NMR (186.46 MHz, C₆D₆, room

temp.): δ = −68.3 (¹J(Sn,Si) = 474.2, ²J(Sn,Si) = 122.9, ¹J(Sn,C) = 283.7 Hz, SnMe₃). UV/Vis (hexane): λ_{max} (ε) 441 nm (8300 L·mol^{−1}·cm^{−1}). Exact Mass (ESI-MS) Calcd. *m/z* for C₄₈H₇₈Si₂Sn⁺ (M⁺): 830.4664. Found: 830.4662. MS (CI, isobutane) *m/z* = 830 (M⁺), 697 (M⁺+O₂−SnMe₃), 665 (M⁺−SnMe₃), 449 (Tip₂SiMe⁺), 433, 321, 261, 245, 231, 203, 189, 43 (C₃H₇⁺).

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

(2b): Toluene (30 mL) was added to disilenide **1** (5.14 g, 6.023 mmol) through a cannula. The orange solution was cooled to 0 °C and Bu₃SnCl (1.96 g, 6.021 mmol) was added through a syringe. After stirring for 16 h, the precipitated LiCl was removed by filtration. All volatiles were removed in vacuo and the solid residue was dissolved in pentane (approx. 5 mL). After 5 days at 0 °C, 4.97 g (86 %) **2b** were separated from the mother liquor as red crystals (mp. 64–67 °C). Elemental analysis: calcd. for C₅₇H₉₆Si₂Sn: C, 71.59; H, 10.12. Found: C, 71.55; H, 9.96.

¹H NMR (500 MHz, C₆D₆, room temp.): δ = 7.072, 7.070, 6.99 (each s, each 2 H, Tip-*H*), 4.36, 4.12, 3.86 (each hept., each 2 H, *i*Pr-*CH*), 2.79, 2.75, 2.66 (each hept., each 1 H, *i*Pr-*CH*), 1.57 (m, 6 H, Bu-C_γH₂), 1.38 (d, 12 H, *i*Pr-*CH*₃), 1.32 (q, 6 H, Bu-C_αH₂), 1.24, 1.19, 1.10 (each d, altogether 36 H, *i*Pr-*CH*₃), 0.98 (m, 6 H, Bu-C_βH₂), 0.96 (d, 6 H, *i*Pr-*CH*₃), 0.88 (t, 9 H, Bu-C_δH₃). ¹³C NMR (125 MHz, C₆D₆, room temp.): δ = 155.84, 155.24, 154.99 (Tip-C_o), 151.13, 150.85, 150.13 (Tip-C_p), 135.65, 135.47, 132.92 (Tip-C_i), 122.33, 121.97, 121.66 (Tip-*CH*), 38.34, 37.41, 36.54, 34.84, 34.77, 34.49 (*i*Pr-*CH*), 30.45, 27.94 (¹J(Sn,C) = 63.4 Hz, Bu-C_{γ/a}), 24.60, 24.17, 23.94 (*i*Pr-*CH*₃), 13.98, 12.44 (²J(Sn,C) = 280.1 Hz, Bu-C_{δ/β}). ²⁹Si NMR (99.36 MHz, C₆D₆, room temp.): δ = 105.3 (²J(Sn,Si) = 98.8 Hz, *Si*Tip₂), 36.8 (¹J(Sn,Si) = 353.6 Hz, *Si*Tip). ¹¹⁹Sn NMR (186.46 MHz, C₆D₆, room temp.): δ = −52.9 (¹J(Sn,Si) = 353.6, ²J(Sn,Si) = 98.8, ²J(Sn,C) = 280.1, ¹J(Sn,C) = 63.4 Hz, SnBu₃). UV/Vis (hexane): λ_{max} (ε) 430 nm (9620 L·mol^{−1}·cm^{−1}). MS (CI, isobutane) *m/z* = 956 (M⁺), 931 (M⁺+O₂−C₄H₉), 899 (M⁺−C₄H₉), 697 (M⁺+O₂−SnBu₃), 665 (M⁺−SnBu₃), 491 (Tip₂SiBu⁺), 433, 345, 323 (SnBu₃⁺+O₂), 289, 231, 203, 189, 43 (C₃H₇⁺).

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

(2c): Toluene (25 mL) was added to a mixture of disilenide **1** (2.54 g, 2.976 mmol) and Ph₃SnCl (1.15 g, 2.983 mmol) through a cannula at 0 °C. The resulting orange suspension was stirred overnight at room temperature. Precipitated solids were filtered off and volatiles were removed from the filtrate in vacuo. The remaining solid was dissolved in hot hexane (5 mL). After 16 h at room temperature, 2.21 g (73 %) **2c** were isolated as red crystals (mp. 170 °C, dec). Elemental analysis: Calcd. for C₆₃H₈₄Si₂Sn: C, 74.46; H, 8.33. Found: C, 74.00; H, 8.36.

¹H NMR (500 MHz, C₆D₆, room temp.): δ = 7.74–7.60 (m, 6 H, Ph-*H*), 7.09–7.03 (m, 9 H, Ph-*H*), 7.02, 6.99, 6.91 (each s, each 2 H, Tip-*H*), 4.42, 4.06, 3.88 (each hept., each 2 H, *i*Pr-*CH*), 2.68 (m, 3 H, *i*Pr-*CH*), 1.25 (br., 6 H, *i*Pr-*CH*₃), 1.144, 1.137, 1.12 (each d, each 6 H, *i*Pr-*CH*₃), 1.05, 0.98 (each d, each 12 H, *i*Pr-*CH*₃). ¹³C NMR (125 MHz, C₆D₆, room temp.): δ = 155.96, 155.13, 154.56 (Tip-C_o), 151.25, 151.09, 150.77 (Tip-C_p), 142.35 (¹J(Sn,C) = 434.5 Hz, Ph-C_i), 137.85 (²J(Sn,C) = 40.8 Hz, Ph-C_o), 135.71, 134.34, 130.97 (Tip-C_i), 128.59 (Ph-C_{m/p}), 122.51, 122.31, 122.00 (Tip-*CH*), 38.15, 38.04, 37.54, 34.77, 34.58, 34.50 (*i*Pr-*CH*), 24.86, 24.55, 24.10, 24.04, 23.96 (*i*Pr-*CH*₃). ²⁹Si NMR (99.36 MHz, C₆D₆, room temp.): δ = 113.3 (²J(Sn,Si) = 119.7 Hz, *Si*Tip₂), 30.4 (¹J(Sn,Si) = 480.7 Hz, *Si*Tip). ¹¹⁹Sn NMR (186.46 MHz, C₆D₆, room temp.): δ = −108.9 (¹J(Sn,Si) = 480.7, ²J(Sn,Si) = 119.7, ¹J(Sn,C) = 434.5, ²J(Sn,C) = 40.8 Hz, SnPh₃). UV/Vis (hexane): λ_{max} (ε) 417 nm (10050 L·mol^{−1}·cm^{−1}). MS (CI, isobutane) *m/z* = 1048 (M⁺+O₂), 1016 (M⁺), 971 (M⁺+O₂−C₆H₅), 767

(11), 742 (M^+-SnPh_2), 697 ($M^+-O_2-SnPh_3$), 511 (Tip_2SiPh^+), 494, 433, 351 ($SnPh_3^+$), 273, 231, 204, 189, 43 ($C_3H_7^+$).

1-(Chlorodi-tert-butylstannyl)-1,2,2-tris(2',4',6'-triisopropylphenyl)disilene (3): Hexane (25 mL) was added to a mixture of disilene **1** (1.40 g, 1.640 mmol) and tBu_2SnCl_2 (0.50 g, 1.646 mmol) through a cannula at room temperature. The colour of the mixture turned to dark red. After stirring overnight, all insoluble parts were removed by filtration. The filtrate was reduced until the product started to precipitate, which was redissolved by gentle heating to 35 °C. After keeping at room temperature overnight, compound **3** (0.91 g, 59 %) was obtained as deep red crystals (mp. 155 °C dec.). Elemental analysis: calcd. for $C_{53}H_{87}Si_2SnCl$: C, 68.11; H, 9.38. Found: C, 67.22; H, 9.30.

1H NMR (500 MHz, C_6D_6 , room temp.): δ = 7.07, 7.03, 6.98 (each s, each 2 H, $Tip-H$), 4.39, 3.97, 3.65 (each hept., each 2 H, $iPr-CH$), 2.72 (m, 2 H, $iPr-CH$), 2.63 (hept., 1 H, $iPr-CH$), 1.43 (d, 12 H, $iPr-CH_3$), 1.27 (s, 18 H, $tBu-CH_3$), 1.18, 1.14, 1.07, 0.92 (each d, altogether 42 H, $iPr-CH_3$). **^{13}C NMR** (125 MHz, C_6D_6 , room temp.): δ = 156.36, 155.17, 155.06 ($Tip-C_0$), 151.77, 151.24, 150.78 ($Tip-C_i$), 135.27, 134.88, 132.80 ($Tip-C_p$), 122.81, 122.38, 122.32 ($Tip-CH$), 40.88 ($^1J(Sn,C)$ = 302.1 Hz, $tBu-CMe_3$), 38.47, 38.02, 36.85, 34.85, 34.72, 34.38 ($iPr-CH$), 31.82 ($tBu-CH_3$), 25.69 (br.), 24.70, 24.19, 24.02, 23.86 ($iPr-CH_3$). **^{29}Si NMR** (99.36 MHz, C_6D_6 , room temp.): δ = 114.5 ($^2J(Sn,Si)$ = 106.9 Hz, $SiTip_2$), 40.9 ($^1J(Sn,Si)$ = 88.4 Hz, $SiTip$). **^{119}Sn NMR** (186.46 MHz, C_6D_6 , room temp.): δ = 109.5. **UV/Vis** (hexane): λ_{max} (ϵ) 431 nm (10000 L·mol $^{-1}$ ·cm $^{-1}$). **MS** (CI, isobutane) m/z = 935 (M^+), 909 ($M^+-O_2-C_4H_9$), 877 ($M^+-C_4H_9$), 853, 671, 665 (M^+-tBu_2SnCl), 469 (Tip_2SiCl^+), 435, 265, 230, 204, 189, 57 ($C_4H_9^+$), 43 ($C_3H_7^+$).

1,1-Dimethyl-2-chloro-2,3,3-tris(2',4',6'-triisopropylphenyl)-disilastannirane (4): A solution of disilene **1** (2.04 g, 2.390 mmol) in toluene (20 mL) was added dropwise to a solution of Me_2SnCl_2 (0.85 g, 3.869 mmol) over a period of 15 min at room temperature. The resulting orange suspension was stirred overnight at room temperature. All precipitates were filtered off and the filtrate was evaporated to give 2.25 g of a yellow solid. Crystallisation from hexane (10 mL) at 0 °C yields 0.43 g (21 %) of **4** as colourless blocks (mp. 168 °C, dec.).

1H NMR (500 MHz, $[D_8]toluene$, room temp.): δ = 7.10, 7.09, 7.07 (each s, each 1 H, $Tip-H$), 6.92 (s, 2 H, $Tip-H$), 6.86 (s, 1 H, $Tip-H$), 4.45–4.32 (m, 2 H, $iPr-CH$), 3.86 (hept., 1 H, $iPr-CH$), 3.60, 3.51, 3.18 (each br., each 1 H, $iPr-CH$), 2.71 (m, 2 H, $iPr-CH$), 2.63 (hept., 1 H, $iPr-CH$), 1.42 (d, 6 H, $iPr-CH_3$), 1.33 (br., 3 H, $iPr-CH_3$), 1.30, 1.27, 1.17, 1.16, 1.14, 1.13, 1.082, 1.077 (each d, altogether 36 H, $iPr-CH_3$), 0.81 ($Sn-CH_3$), 0.64, 0.44 (each br., altogether 9 H, $iPr-CH_3$), 0.16 ($Sn-CH_3$). **^{13}C NMR** (125 MHz, $[D_8]toluene$, room temp.): δ = 156.25, 156.18, 156.06, 156.01, 153.91 ($Tip-C_0$), 152.08, 150.80, 150.31 ($Tip-C_i$), 133.37, 130.42, 130.01 ($Tip-C_p$), 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 ($iPr-CH_3$), –8.72, –10.81 ($Sn-CH_3$). **^{29}Si NMR** (99.36 MHz, $[D_8]toluene$, room temp.): δ = –28.3, –57.3. **^{119}Sn NMR** (186.46 MHz, $[D_8]toluene$, room temp.): δ = –252.4. **Exact Mass** (ESI-MS) Calcd. m/z for $C_{47}H_{75}Si_2SnCl^+$ (M^+): 850.4118. Found: 850.4121. **MS** (CI, isobutane) m/z = 850 (M^+), 665 (M^+-Me_2SnCl), 469 (Tip_2SiCl^+), 449 (Tip_2SiMe^+), 435, 323, 265, 245, 231, 204, 189, 57, 43 ($C_3H_7^+$).

X-ray Crystallography: Single crystals of **2a**, **3**, and **4** were coated with perfluorinated polyether and quickly transferred to the cold nitro-

gen stream at the goniometer. The accumulation of data sets was carried out using a Bruker SMART CCD area-detector diffractometer with Mo- K_α 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^2 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, -728278, -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**.

| | 2a | 3 | 4 |
|---------------------------------|-------------------------|------------------------|------------------------|
| Formula | $C_{99}H_{163}Si_4Sn_2$ | $C_{53}H_{87}ClSi_2Sn$ | $C_{47}H_{75}ClSi_2Sn$ |
| T/K | 173(2) | 173(2) | 173(2) |
| System | triclinic | orthorhombic | triclinic |
| Space group | $P\bar{1}$ | $Pca2_1$ | $P\bar{1}$ |
| $a/\text{\AA}$ | 11.5193(6) | 22.389(5) | 14.1341(9) |
| $b/\text{\AA}$ | 17.6904(10) | 19.011(4) | 17.9108(11) |
| $c/\text{\AA}$ | 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)° |
| $V/\text{\AA}^3$ | 5069.7(5) | 11043(4) | 4769.3(5) |
| Z | 2 | 8 | 4 |
| $d/\text{g}\cdot\text{cm}^{-3}$ | 1.116 | 1.124 | 1.184 |
| μ/mm^{-1} | 0.580 | 0.585 | 0.671 |
| $F(000)$ | 1826 | 4000 | 1808 |
| θ_{max} | 26.08° | 26.02° | 26.37° |
| Refl. _{total} | 73180 | 92746 | 85064 |
| Refl. _{unique} | 20064 | 21703 | 19517 |
| S | 1.063 | 1.066 | 1.026 |
| R_1 ($I > 2\sigma$) | 0.0393 | 0.0344 | 0.0353 |
| wR_2 (all data) | 0.1080 | 0.0827 | 0.0898 |

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