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A Nearly Planar Stannene with a Reactive Tin–Carbon Double Bond

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Bis(2,4,6-triisopropylphenyl)-2,7-di-*tert*-butylfluorenylidene stannane, $Tip_2Sn{=}CR_2$, an isolable stannene that displays a deep-purple colour, was synthesized by dehydrofluorination of the corresponding fluorostannane by *tert*-butyllithium. It exhibits the shortest Sn=C distance [2.003(5) Å] and the slightest twisting around this unsaturation (10°) among the known stannenes. Its reaction with benzaldehyde according to a [2+2] cycloaddition and that with α-ethylenic aldehydes and ketones such as crotonaldehyde and methyl vinyl ketone by a [2+4] cycloaddition proceeded in near-quantitative yield. With acetone, an ene reaction occurred. The four-membered ring 1,2-oxastannacyclobutane obtained with benzaldehyde underwent a ring expansion with a second molecule of benzaldehyde to afford the six-membered ring dioxastannacyclohexane.

Introduction

Over the past 25 years, dramatic and exciting progress has been made in the field of the heavier congeners of heteroalkenes >M=C< (M = Si, Ge, Sn). It is particularly true for silenes[1] and (to a lesser extent) for germenes[2] regarding the number of reports about their synthesis, their physicochemical characteristics and theoretical studies. Also, their chemical behaviour is now well known. By contrast, relatively few stable Sn=C compounds have been prepared[3–9] (Scheme 1). The main synthetic methods consist in stannylene–carbene coupling[3–6] or in dehydrohalogenation of halostannanes[7–9] with lithium compounds as bases. Noteworthy is the accurate description of the reaction outcomes of nucleophilic carbenes (imidazol-2-ylidenes, cyclopropylidenes) with stannylenes as the ylidic resonance structure A.[10–12] Their ^{119}Sn chemical shifts at low frequency [$\delta(^{119}Sn) = -59.4$,[10] –44.7 ppm[12]], their geometries and their large Sn–C separation,[10–12] which is markedly longer than the standard single bond length, differ greatly from those expected for true alkene analogues. A similar bonding situation was reported for the unique formal stannaketenimine,[13] which is better described as a Lewis acid–base adduct of a stannylene (Lewis acid) with isocyanide. The significant contribution of the opposite limit form B accounts for the NMR spectroscopic data and the X-ray structures of the products obtained from an electrophilic cryptodiborylcarbene and stannylenes (Scheme 1).[3–6]

The chemistry of the Sn=C bond has been sparsely explored. Only punctual studies of the reactions of long-lived stannenes with protic reagents,[3,7,8] benzophenone,[14] 2,3-dimethylbutadiene,[8] methyl iodide,[7b] reduction by $LiAlH_4$[7b] along with their head-to-tail dimerization have been reported.[7] Investigation of the chemical behaviour of the transient stannene $Me_2Sn{=}C(SiMe_3)_2$[15] has been limited to its reaction with alkenes, dienes, azides and phenyllithium.

The dehydrohalogenation method allowed us to prepare the first stannapentafulvene **1** some years ago.[7] This stannene possesses the Sn=C bond as the principal reaction site and seemed to fit well for the study of the chemical behaviour of this unsaturation. However, it converts readily into its head-to-tail dimer, the corresponding 1,3-distannacyclobutane, above 0 °C,[7] which makes the extensive study of its reactivity less convenient than with a stannene stable at room temperature. Therefore, it was characterized only by some trapping reactions and by tin NMR spectroscopy. Recently, Tokitoh succeeded in preparing the first stable stannapentafulvene **2** by increasing the steric hindrance on the tin atom while keeping the fluorenylidene group.[8] We then became interested in probing the reverse steric shielding of the Sn=C bond to stabilize it, that is, by enlarging the steric hindrance on the fluorenylidene unit by substituting the 2,7-positions by two *tert*-butyl groups. Indeed, the stannapentafulvene skeleton presents the advantage of easier crystallization and enhanced stabilization by conjugation of the Sn=C with the fluorenylidene system.

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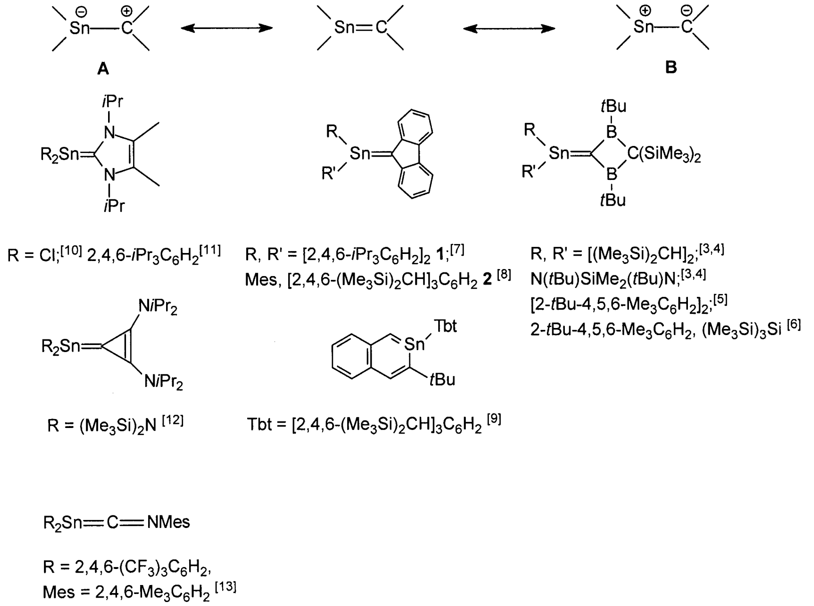
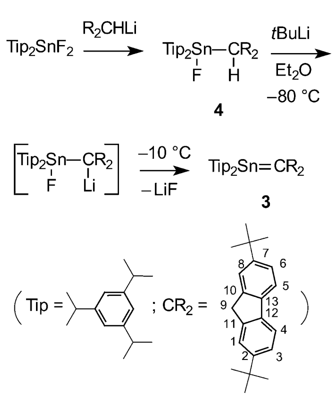


Scheme 1.

Here we report the synthesis of the stable stannene namely bis(2,4,6-triisopropylphenyl)-2,7-di-*tert*-butylfluorenylidene stannane **3** and the first aspects of its reactivity toward some carbonyl compounds.

Results and Discussion

The best synthetic route to stannene **3** appeared to be, as in the case of **1**[7] and **2**,[8] the dehydrofluorination of (di-*tert*-butylfluorenyl)fluorostannane **4**. The latter was prepared from 2,7-di-*tert*-butylfluorene,[16] *n*-butyllithium and bis(2,4,6-triisopropylphenyl)difluorostannane[7a] (Scheme 2). Deprotonation of fluorenylfluorostannane **4** by *tert*-butyllithium at –78 °C gave immediately a red coloration due to the related lithium compound. A deep-purple colour appeared around –10 °C indicating the formation of stannene **3**.



Scheme 2. Synthesis of stannapentafulvene **3**.

Stannene **3** was isolated from a Et_2O/pentane mixture as extremely air- and moisture-sensitive, but thermally stable, purple crystals. Et_2O solutions of **3** were recovered unchanged when heated at 120 °C for 15 h in a sealed tube. Its decomposition occurred only after 20 h at 150 °C to give still-unidentified derivatives.

Stannene **3** was characterized by a ^{119}Sn NMR signal at the expected field for a double-bond tin compound (δ = 277 ppm). This chemical shift is very close to those previously reported for similar stannenes with a fluorenylidene group [δ(^{119}Sn) = 288 and 270 ppm for **1**[7] and **2**,[8] respectively] and for a stable stannanaphthalene [δ(^{119}Sn) = 264 ppm].[9] Thus, it seems that the introduction of two *tert*-butyl groups increases dramatically the thermal stabilization of the stannene, but has practically no influence on the tin chemical shift. The great difference in chemical shifts observed with stannenes derived from the electrophilic cryptodiborylcarbene (647–835 ppm[3,4]) is rationalized by the more positive tin nuclei due to noticeable contribution of the resonance structure B (Scheme 1). The introduction of aryl groups on tin in such adducts shifts the ^{119}Sn signal to lower frequency (δ = 374 ppm[5]).

The sp^2 Sn=C carbon atom resonates at δ = 146.9 ppm, which is a ^{13}C chemical shift comparable to those reported for analogous stannapentafulvenes (δ = 133.85 ppm in **1**[7a] and 144.9 ppm in **2**[8]). In the UV/Vis spectrum, the absorption maximum was observed at 560 nm, close to that reported by Tokitoh for stannene **2** (552 nm).[8]

The molecular structure of **3** (Figure 1) displays the shortest Sn=C bond [2.003(5) Å] ever reported. This Sn–C separation is even shorter than that of the previous stable stannapentafulvene **2** ($d_{Sn=C}$ = 2.016 Å),[8] which was reported to be the shortest Sn=C bond length among those known (2.025–2.032 Å).[3–5] This value of 2.003(5) Å is in agreement with the computed value (1.95–2.06 Å[8,17] depending on the basis set used). The shortening, in relation to the Sn–C single bond (2.14–2.15 Å)[18] is about 7%. Furthermore, a completely trigonal planar geometry around the Sn1 and C1 atoms is observed (sum of bond angles of 360° in both cases) with a very small torsion angle (10°) between the planar fluorenylidene and the C22–Sn1–C37 plane. It is the smallest twisting ever reported for such heavier metallaalkenes, comparable to that of 5.9° observed for the germene $Mes_2Ge=CR'_2$ (CR'_2 = 9-fluorenylidene group),[19] whereas a larger angle was observed for stannapentafulvene **2** (28.5°).[8] Depending on the groups on the tin atom, cryptodiborylcarbene–stannylene adducts display a twist angle (11.9°) comparable to that of **3** − with a *trans* bending structure and a bent angle of 13.2 (Sn) and 9.7° (C) [6] − or even greater twist angle ranging from 36 to 61°.[3–5]

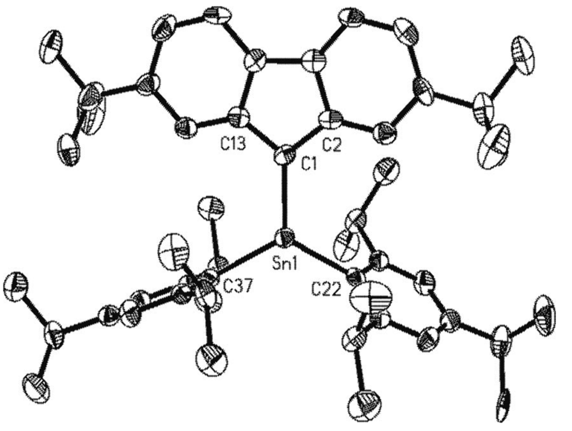
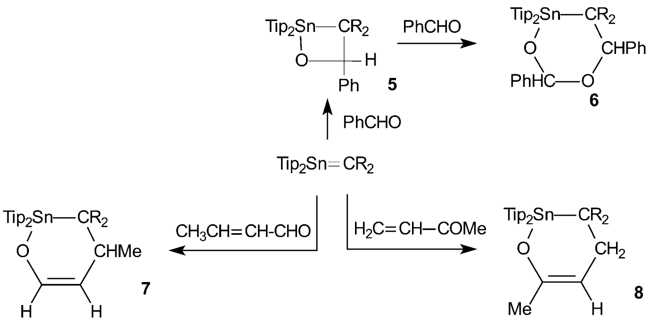


Figure 1. X-ray molecular structure of stannene **3** (50% probability level). H atoms and disorder are omitted for clarity. Selected bond lengths [Å] and angles [°]: Sn1–C1 2.003(5), Sn1–C22 2.138(4), Sn1–C37 2.156(4), C1–C2 1.457(6), C1–C13 1.464(6), C22–Sn1–C37 124.69(17), C22–Sn1–C1 119.04(18), C37–Sn1–C1 116.27(18).

Thus, stannene **3** exhibits the geometric parameters (planarity, amount of bond shortening) that are the closest to those of the ideal double bond in alkenes and predicted by theoretical calculations.

Reactivity of Stannene 3

Despite the steric hindrance, stannene **3** is very reactive, particularly toward carbonyl compounds. It underwent [2+2] cycloaddition with the C=O group of benzaldehyde leading to 1,2-oxastannacyclobutane **5** (Scheme 3). A ring-expansion reaction was observed by addition of a second equivalent of benzaldehyde to the highly strained four-membered heterocycle **5**: the six-membered ring compound, 1,2,4-dioxastannacyclohexane **6**, was obtained due to the insertion of the C=O moiety of benzaldehyde into the Sn–O bond of **5**. [2+4] Cycloadditions with α-ethylenic aldehydes and ketones such as crotonaldehyde and methyl vinyl ketone occurred with stannene **3** to form 1,2-oxastannacyclohexenes **7** and **8**. An ene reaction with methyl vinyl ketone has not been observed. All these cycloadditions are nearly quantitative and occurred around –20 °C, as shown by the loss of the characteristic purple colour of starting stannene **3**. The reactions are regioselective, with the oxygen atom bonded to the tin atom, as expected from the well-known oxophilic character of tin and the polarities of the tin–carbon double bond ($Sn^{\delta+}=C^{\delta-}$) and of the carbonyl derivatives. The regioselectivity is also proved by the fragment at m/z = 543 corresponding to [Tip_2SnO + 1] in the mass spectra of compounds **5**, **7** and **8**. The cleavage leading to $Tip_2Sn=CR_2$ is also observed. The ^{13}C NMR spectrum of oxastannacyclobutane **5** displays, as expected, a signal at δ = 81.5 ppm for the carbon atom bonded to the oxygen atom with $^2J_{^{117/119}Sn,C}$ coupling constants of 80.0/86.1 Hz.



Scheme 3. Reactivity of stannapentafulvene **3**.

As a result of the very high steric hindrance, a slow rotation, as proved by the presence of broad signals, is generally observed for the Tip groups, which renders the *o*-*i*Pr groups inequivalent. As derivatives **5**, **6** and **7** have also at least one asymmetric carbon atom, the two Tip groups and the Me groups of every *i*Pr are diastereotopic. Thus, for example in the case of **7**, 13 doublets (12 for the Me of *i*Pr groups and 1 for the Me on the ring) are observed in the ^1H NMR spectrum.

In four-membered ring derivative **5** and in six-membered heterocycles **6** and **7**, the Sn–C(R_2) bond lengths (2.217 to 2.223 Å) are slightly longer than the standard Sn–C distance (2.14–2.15 Å)[18] and the endocyclic Sn–C(Tip) bonds (2.15 to 2.18 Å) probably for steric reasons. Sn–O bond lengths (2.003 to 2.038 Å) lie in the normal range. In oxastannacyclobutane **5** and in oxastannacyclohexene **7**, the sum of angles on the tin atom with the three bonded carbon atoms is surprisingly close to 360° (356.72 and 357.53°, respectively) like in starting stannene **3**. In the six-membered ring of **7**, the four C1, Sn, O and C4 atoms lie practically in a plane (C1SnO1C4 = 0.05°) (Figures 2, 3 and 4).

Unlike methyl vinyl ketone, acetone underwent an exclusive ene reaction with stannene **3** to afford vinyloxystannane **9** (Scheme 4). This air- and moisture-sensitive compound rapidly hydrolyzes to give hydoxystannane **10**, which is also quantitatively obtained by direct hydrolysis of stannene **3**. Vinyloxystannane **9** is easily characterized by ^{119}Sn (δ = –96.3 ppm), ^{13}C ($OC=CH_2$ δ = 160.2 and 86.5 ppm) and ^1H NMR ($=CH_2$: δ = 3.83 and 3.88 ppm) spectra. Un-

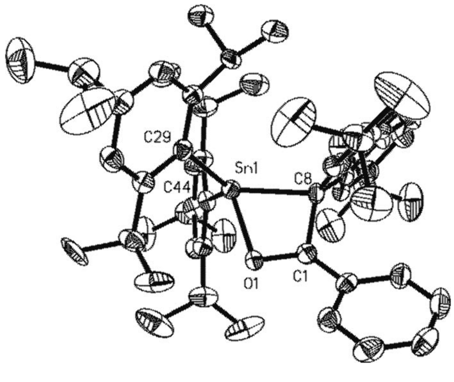


Figure 2. Molecular structure of oxastannacyclobutane **5** (50% probability level); H atoms, noncoordinated solvent molecules (1/2 THF) and disorder are omitted for clarity. Selected bond lengths [Å] and angles [°]: Sn1–C8 2.223(5), Sn1–O1 2.038(3), O1–C1 1.419(6), C1–C8 1.559(7), Sn1–C29 2.168(5), Sn1–C44 2.182(5), C29–Sn1–C44 123.98(18), C29–Sn1–C8 119.80(18), C44–Sn1–C8 112.94(18), O1–Sn1–C8 68.43(16), Sn1–C8–C1 83.8(3), C8–C1–O1 107.4(4), C1–O1–Sn1 94.5(3).

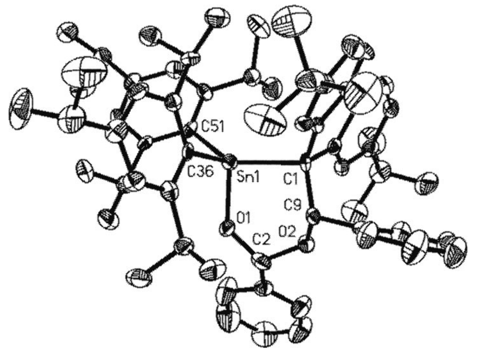


Figure 3. Molecular structure of dioxastannacyclohexane **6** (50% probability level); H atoms, noncoordinated solvent molecules (pentane) and disorder are omitted for clarity. Selected bond lengths [Å] and angles [°]: Sn1–C1 2.217(5), Sn1–O1 2.003(4), O1–C2 1.383(7), C2–O2 1.424(6), O2–C9 1.436(6), C1–C9 1.551(7), Sn1–C36 2.176(6), Sn1–C51 2.150(5), C36–Sn1–C51 103.8(2), C36–Sn1–C1 109.06(19), C51–Sn1–C1 134.5(2), O1–Sn1–C1 95.84(18).

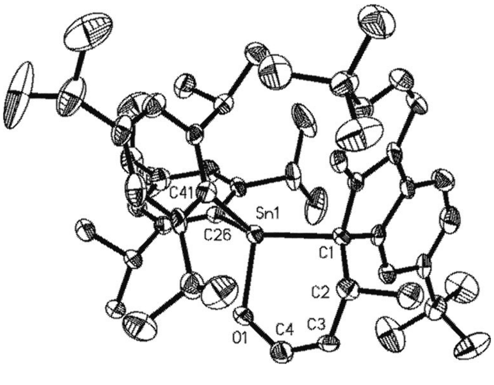
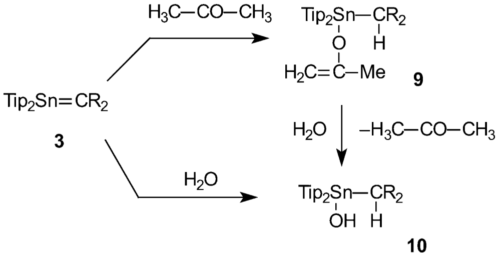


Figure 4. Molecular structure of oxastannacyclohexene **7** (50% probability level); H atoms and disorder are omitted for clarity. Selected bond lengths [Å] and angles [°]: Sn1–C1 2.220(4), Sn1–O1 2.027(3), O1–C4 1.329(6), C4–C3 1.339(7), C3–C2 1.514(7), C2–C1 1.560(6), Sn1–C41 2.166(4), Sn1–C26 2.164(5), C41–Sn1–C26 103.57(18), C41–Sn1–C1 119.07(19), C26–Sn1–C1 134.89(18), O1–Sn1–C1 96.53(15).

like its germene analogue $Mes_2Ge{=}CR_2$,[20] it does not undergo a Lutsenko-like rearrangement, which would give $Tip_2Sn(CH_2COMe)CHR_2$.



Scheme 4. Reactivity of stannapentafulvene **3**.

Conclusions

The introduction of two *tert*-butyl groups in the 2,7-positions on the fluorenylidene group dramatically increases the stability of the related nearly planar stannene, which, however, still remains very reactive. The study of its chemical behaviour is under active investigation.

Experimental Section

General Information: All experiments were carried out in flame-dried glassware under an argon atmosphere by using high-vacuum-line techniques. Solvents were dried and freshly distilled from sodium benzophenone ketyl and carefully deoxygenated on a vacuum line by several "freeze–pump–thaw" cycles. Unless otherwise mentioned, $CDCl_3$ was the NMR solvent. NMR spectra were recorded with the following spectrometers: ^1H, Bruker Avance 300 (300.13 MHz); $^{13}C\{^1H\}$, Bruker Avance 300 (75.47 MHz) (reference TMS); ^{19}F, Bruker AC200 (188.30 MHz) (reference $CFCl_3$); $^{119}Sn\{^1H\}$, Bruker Avance 300 (111.92 MHz) (reference Me_4Sn). Melting points were determined with a Wild Leitz-Biomed apparatus. Mass spectra were obtained with a Hewlett–Packard 5989A spectrometer by electron impact (EI) at 70 eV and with a Nermag R10–10 spectrometer by chemical ionization (CI).

Starting compounds were synthesized according to the literature: Tip_2SnF_2,[7a] and 2,7-di-*tert*-butylfluorene.[16] The carbon atoms of the fluorenyl group are labelled as mentioned in Scheme 2.

Bis(2,4,6-triisopropylphenyl)-2,7-di-*tert*-butylfluorenylfluorostannane (4): To a solution of 2,7-di-*tert*-butylfluorene (1.70 g, 6.11 mmol) in THF (10 mL) cooled to –78 °C was added a solution of *n*BuLi (1.6 M in hexane, 3.8 mL 6.11 mmol); the solution turned immediately red. After stirring for 15 min, this solution was added dropwise to a solution of Tip_2SnF_2 (3.44 g, 6.11 mmol) in THF (15 mL) cooled to –78 °C. The brown reaction mixture was slowly warmed to room temperature and then turned light yellow. After removal of the solvents under reduced pressure, pentane (20 mL) was added, and the lithium salts were removed by filtration. White crystals of fluorostannane **4** (3.76 g, 75%) were obtained from pentane at –20 °C. M.p. 153 °C. ^1H NMR (300.13 MHz, $CDCl_3$): δ = 0.75 (d, $^3J_{H,H}$ = 6.6 Hz, 12 H, *o*-CH*Me*Me′), 0.84 (d, $^3J_{H,H}$ = 6.6 Hz, 12 H, *o*-CHMe*Me*′), 1.07 (s, 18 H, *t*Bu), 1.11 (d, $^3J_{H,H}$ = 6.6 Hz, 12 H, *p*-CH*Me*$_2$), 2.41 (sept., $^3J_{H,H}$ = 6.6 Hz, 4 H, *o*-C*H*MeMe′), 2.77 (sept., $^3J_{H,H}$ = 6.6 Hz, 2 H, *p*-C*H*Me$_2$), 4.69 (s, 1 H, C*H*R$_2$), 6.87 (s, 4 H, arom H of Tip), 7.25 (dd, $^3J_{H,H}$ = 8.0 Hz,

$^4J_{H,H}$ = 1.1 Hz, 2 H, H on C3 and C6), 7.35 (d, $^4J_{H,H}$ = 1.1 Hz, 2 H, H on C1 and C8), 7.68 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H, H on C4 and C5) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 23.9 (*p*-CH*Me*$_2$), 24.7 and 24.8 (*o*-CH*MeMe′*), 31.5 (C*Me*$_3$), 34.1 ($J_{Sn,C}$ = 5.7 Hz, *p*-*C*HMe$_2$), 34.7 (*C*Me$_3$), 37.9 (d, $^4J_{C,F}$ = 3.3 Hz, $^3J_{Sn,C}$ = 35.2 Hz, *o*-*C*HMeMe′), 50.47 ($^1J_{Sn,C}$ = 152.5 Hz, *C*HR$_2$), 122.2 ($^3J_{Sn,C}$ = 57.4 Hz, *m*-CH of Tip), 119.6, 121.1 and 123.7 (other arom CH), 154.7 ($^2J_{^{117}Sn,C}$ = 51.3 Hz, $^2J_{^{119}Sn,C}$ = 53.6 Hz, *o*-C of Tip), 137.9 ($J_{Sn,C}$ = 24.9 Hz), 140.3, 144.0, 149.1 ($J_{Sn,C}$ = 13.1 Hz) and 151.1 ($J_{Sn,C}$ = 11.9 Hz, other arom C) ppm. ^{19}F NMR (188.30 MHz, $CDCl_3$): δ = –184.6 (s, $^1J_{^{117}Sn,F}$ = 2320.9 Hz, $^1J_{^{119}Sn,F}$ = 2428.0 Hz) ppm. ^{119}Sn NMR (111.92 MHz, $CDCl_3$): δ = –22.4 (d, $^1J_{^{119}Sn,F}$ = 2428.0 Hz) ppm. MS (EI, 70 eV): *m/z* (%) = 803 (2) [M – F], 561 (7) [M – Tip – *t*Bu + 1], 545 (100) [Tip_2SnF], 525 (12) [Tip_2Sn – 1], 321 (12) [TipSn – 2], 277 (60) [CHR_2], 262 (40) [CHR_2 – Me]. $C_{51}H_{71}FSn$ (821.81): calcd. C 74.54, H 8.71; found C 74.38, H 8.50.

Stannene 3: To a solution of fluorostannane **4** (1.00 g, 1.22 mmol) in Et_2O (20 mL) cooled to –78 °C was slowly added by syringe a solution of *t*BuLi (1.6 M in pentane, 0.76 mL, 1 equiv.). The reaction mixture turned immediately deep red. After 10 min, the reaction mixture was warmed to room temperature; it turned deep purple around –10 °C. A ^{119}Sn NMR analysis showed the nearly quantitative formation of stannene **3**. The solvents were removed under vacuum and replaced by pentane (20 mL). The lithium salts were filtered out, and the purple residue was crystallized from pentane at –20 °C to afford deep purple crystals of **3** (0.76 g, 78%). M.p. 140 °C. ^{1}H NMR (300.13 MHz, C_6D_6): δ = 1.22 (s, 18 H, *t*Bu), 1.25 (d, $^3J_{H,H}$ = 6 Hz, 24 H, *o*-CH*Me*$_2$), 1.27 (d, $^3J_{H,H}$ = 6 Hz, 12 H, *p*-CH*Me*$_2$), 2.71 (sept., 2 H, *p*-C*H*Me$_2$), 2.82 (sept., 4 H, *o*-C*H*Me$_2$), 7.15 (s, 4 H, arom H of Tip), 7.25 (dd, $^3J_{H,H}$ = 8.0 Hz, $^4J_{H,H}$ = 1.5 Hz, 2 H, H on C3 and C6), 7.58 (d, $^4J_{H,H}$ = 1.5 Hz, 2 H, H on C1 and C8), 7.88 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H, H on C4 and C5) ppm. ^{13}C NMR (75.47 MHz, C_6D_6): δ = 23.8, 24.4 and 25.5 (*o*- and *p*-CH*Me*$_2$ and *p*-*C*HMe$_2$), 31.4 (C*Me*$_3$), 43.0 (*o*-*C*HMe$_2$), 117.8, 118.6 and 119.4 (arom CH of CR_2), 122.5 (*m*-CH of Tip), 154.6 (*o*-C of Tip), 131.3, 143.6, 145.7, 146.5 and 152.0 (other arom C), 146.9 (Sn=C) ppm. ^{119}Sn NMR (111.92 MHz, C_6D_6): δ = 277.4 ppm. UV/Vis (pentane, r.t.): λ (ε, M^{-1}cm^{-1}) = 560 (8000) nm. MS (EI, 70 eV): *m/z* (%) = 802 (1) [M], 745 (0.5) [M – *t*Bu], 599 (2) [M – Tip], 543 (33) [M – Tip – *t*Bu + 1], 525 (21) [Tip_2Sn – 1], 482 (1) [Tip_2Sn – *i*Pr – 1], 321 (16) [TipSn – 2], 277 (100) [CHR_2]. $C_{51}H_{70}Sn$ (801.80): calcd. C 76.40, H 8.80; found C 76.65, H 8.91.

General Procedure for the Reactions of $Tip_2Sn=CR_2$: Crude solutions of stannene **3** (containing LiF) prepared from fluorostannane **4** (1.00 g) were used without purification. After 0.5 h at room temperature, the solution containing the stannene was cooled again to –50 °C and the carbonyl compound (1 equiv.) was slowly added by syringe. The reaction mixture turned immediately brown. After warming to room temperature, ^{119}Sn NMR spectroscopic analysis showed in all cases the disappearance of the starting stannene and the formation of only one compound. After evaporation of the solvents under vacuum and addition of pentane (20 mL), the lithium salts were removed by filtration; the crude brown residue was crystallized at –20 °C from Et_2O or pentane (see the solvent used in each case).

Oxastannacyclobutane 5 [from Stannene 3 and Benzaldehyde (1 equiv.)]: Brown crystals from pentane. Yield: 0.83 g, 75%. M.p. 145 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 1.20–1.40 (very br. s due to coalescence, 24 H, CH*MeMe′*), 1.26, 1.27, 1.36 and 1.37 (4 d, $^3J_{H,H}$ = 6 Hz, 4 × 3 H, CH*MeMe′*), 0.95 (s, 9 H, *t*Bu), 1.15 (s, 9 H, *t*Bu), 2.71–2.98 (m, 2 H, *o*-C*H*MeMe′), 2.89 and 2.99 (2 sept., $^3J_{H,H}$ = 6 Hz, 2 × 1 H, *p*-C*H*MeMe′), 3.27–3.55 (m, 2 H, *o*-C*H*MeMe′), 6.68 (s, 1 H, OCH), 6.79–6.95 (m, 7 H), 7.05 (dd, $^3J_{H,H}$ = 6 Hz, 1 H), 7.15–7.25 (m, 3 H), 7.28–7.33 (m, 2 H), 7.58 (dd, $^3J_{H,H}$ = 6.0 Hz, $^4J_{H,H}$ = 1.0 Hz, 1 H) and 7.70 (dd, $^3J_{H,H}$ = 6.0 Hz, $^4J_{H,H}$ = 0.5 Hz, 1 H, arom H) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 23.9, 24.0, 24.1, 25.8, 26.4 and 34.5 (*o*- and *p*-CH*MeMe′* and *C*HMeMe′), 31.4 and 31.6 (C*Me*$_3$), 34.6 and 34.8 (*C*Me$_3$), 78.9 (*C*R$_2$), 81.5 ($^2J_{^{117}Sn,C}$ = 80.0 Hz, $^2J_{^{119}Sn,C}$ = 86.1 Hz, OCH), 118.6, 118.9, 119.6 ($J_{Sn,C}$ = 24.2 Hz), 122.2, 122.3, 122.5, 122.8 and 122.9 (*m*-C of Tip and arom CH of CR_2), 124.5 and 126.9 (*o*- and *m*-CH of Ph), 125.4 (*p*-CH of Ph), 135.5, 136.0, 137.9, 139.3, 144.9, 145.4, 145.8, 147.5 ($J_{Sn,C}$ = 16.6 Hz), 148.6 ($J_{Sn,C}$ = 21.1 Hz), 150.8 ($J_{Sn,C}$ = 13.6 Hz) and 151.1 ($J_{Sn,C}$ = 13.6 Hz) (arom C) ppm. ^{119}Sn NMR (111.92 MHz, $CDCl_3$): δ = 16.0 ppm. MS (FAB): *m/z* (%) = 908 (8) [M], 803 (50) [M – PhCHO + 1], 543 (70) [Tip_2SnO + 1], 525 (82) [Tip_2Sn – 1], 321 (100) [TipSn – 2], 277 (40) [CHR_2]. $C_{58}H_{76}OSn$ (907.93): calcd. C 76.73, H 8.44; found C 76.97, H 8.52.

Dioxastannacyclohexane 6 [from Stannene 3 and Benzaldehyde (2 equiv.)]: Brown crystals from pentane. Yield: 0.40 g, 80%. M.p. 135 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.71–1.80 (m, 36 H, CH*MeMe′*), 1.72–3.51 (m, 6 H, C*H*MeMe′), 6.52–8.14 (m, 20 H, arom H) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 22.6, 22.8, 23.0, 23.4, 23.8, 23.9, 24.0, 24.1, 24.4, 24.7, 24.9, 25.7, 31.1, 31.4, 34.1, 34.2, 34.3 and 36.6 (CH*MeMe′*), 31.2 and 31.5 (C*Me*$_3$), 34.5 and 34.9 (*C*Me$_3$), 65.6 (*C*R$_2$), 83.8 (O*C*HPh), 101.4 (OCO), 119.0, 119.2, 121.7, 122.9, 123.3, 123.7, 124.2, 124.6, 125.6, 125.6, 125.9, 126.1, 126.1, 126.7, 126.9 and 127.1 (arom CH), 136.4, 137.2, 137.8, 138.4, 141.0, 142.7, 143.2, 144.3, 146.6, 147.6, 148.7, 150.4, 150.5, 152.8, 154.7 and 155.1 (arom C) ppm. ^{119}Sn NMR (111.92 MHz, $CDCl_3$): δ = –84.8 ppm. MS (FAB): *m/z* (%) = 907 (100) [M – PhCHO – 1], 863 (53) [M – PhCHO – *i*Pr – 2], 802 (50) [M – 2 PhCHO], 647 (48) [M – CR_2 – PhCH – 1], 525 (82) [Tip_2Sn – 1]. $C_{65}H_{82}O_2Sn$ (1014.05): calcd. C 76.99, H 8.15; found C 77.21, H 8.30.

Oxastannacyclohexene 7 (from Stannene 3 and Crotonaldehyde): Light-brown needles from Et_2O. Yield: 1.25 g, 95%. M.p. 237 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = –0.10, 0.17, 0.24, 0.35, 0.44, 0.65, 1.10, 1.13, 1.20, 1.22, 1.29, 1.43 and 1.54 (13 d, $^3J_{H,H}$ = from 5.2 to 6.8 Hz, 39 H, CH*MeMe′* and =CH*Me*), 0.95 (s, 9 H, *t*Bu), 1.36 (s, 9 H, *t*Bu), 2.71, 2.84 and 3.11 (3 sept., $^3J_{H,H}$ = 5.8 Hz, 3 × 1 H, C*H*MeMe′), 3.20–3.31 (m, 1 H, C*H*MeMe′), 3.82–4.03 (m, 2 H, C*H*MeMe′), 4.41–4.44 (m, 1 H, =C*H*-CHMe), 6.71 (s, $^4J_{Sn,H}$ = 12 Hz, 2 H, H of Tip), 6.88 (s, 2 H, H of Tip), 6.94 (s, 1 H, arom H of CR_2), 7.12–7.30 (m, 2 H, H of CR_2), 7.42, 7.72 and 7.79 (3 dd, $^3J_{H,H}$ = 8.2 Hz, $^4J_{H,H}$ = 1.5 Hz, 3 × 1 H, arom H of CR_2), 8.22 (s, 1 H, C*H*O) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 22.7, 22.8, 23.2, 23.3, 23.8, 23.9, 24.0, 24.1, 24.9, 25.0, 25.6, 26.2, 34.1, 34.3, 34.5, 34.9, 35.5, 36.9, 39.8 and 41.9 (*o*- and *p*-*C*H*MeMe′* and *C*H*Me*CR$_2$), 31.2 and 31.7 (C*Me*$_3$), 34.9 (*C*Me$_3$), 60.2 (*C*R$_2$), 106.1 (OCH =*C*H), 118.7, 118.9, 121.3, 121.5, 122.0, 122.5, 122.7, 123.1, 123.3 and 123.6 (arom CH), 137.2, 138.6, 141.1, 144.2, 147.4, 148.1, 148.6, 149.3, 150.2, 150.3, 152.4, 153.9, 154.9 and 155.0 (arom C), 148.7 (O*C*H=CH) ppm. ^{119}Sn NMR (111.92 MHz, $CDCl_3$): δ = –52.7 ppm. MS (EI, 70 eV): *m/z* (%) = 802 (2) [M – crotonaldehyde], 669 (3) [M – Tip], 611 (5) [M – Tip – *t*Bu – 1], 597 (4) [M – Tip – *t*Bu – Me], 543 (35) [Tip_2SnO + 1], 525 (34) [Tip_2Sn – 1], 322 (100) [TipSn – 1], 57 (67) [*t*Bu]. $C_{55}H_{76}OSn$ (871.89): calcd. C 75.77, H 8.79; found C 76.05, H 8.92.

Oxastannacyclohexene 8 (from Stannene 3 and Methyl Vinyl Ketone): Brown-yellow needles from Et_2O. Yield: 0.90 g, 70%. M.p. 213 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = –0.05 (br. s, 3 H), 0.32 (br. s, 6 H), 0.54 (br. s, 3 H), 0.67 (br. s, 3 H) and 0.79–1.55

(m, 41 H, CH*MeMe*′, CH$_2$ and *t*Bu), 2.01 (s, 3 H, OC*Me*), 2.69–2.95 (m, 3 H), 3.10–3.29, 3.45–3.67 and 3.80–3.92 (3 m, 3×1 H, C*H*MeMe′), 4.63 (t, $^3J_{H,H}$ = 6.0 Hz, 1 H, C*H*CH$_2$), 6.74 (br. s, 2 H), 6.85–7.05 (m, 2 H), 7.15–7.50 (m, 3 H), 7.69–7.90 (m, 2 H) and 8.10 (br. s, 1 H, arom H of Tip and CR$_2$) ppm. ^{13}C NMR (75.47 MHz, CDCl$_3$): δ = 22.8, 23.9, 24.7, 25.7, 31.2, 31.5, 34.3 (*o*- and *p*-CH*Me*$_2$, *C*H$_2$R$_2$ and OC*Me*), 23.9 (C*Me*$_3$), 33.2 (*C*Me$_3$), 54.1 (CH$_2$*C*R$_2$), 92.8 ($^3J_{Sn,C}$ = 46.8 Hz, *C*H=CMe), 118.9, 121.1, 121.9, 122.2, 122.5, 123.3 and 123.6 (br. and small s, arom CH), 148.5, 149.0, 150.3 ($^2J_{Sn,C}$ = 11.3 Hz), 154.0, 155.4 and 156.4 (arom C and O*C*Me) ppm. ^{119}Sn NMR (111.92 MHz, CDCl$_3$): δ = –57.5 ppm. MS (EI, 70 eV%): *m*/*z* (%) = 872 (5) [M], 802 (10) [M – methyl vinyl ketone], 595 (4) [M – CR$_2$], 543 (15) [Tip$_2$SnO + 1], 525 (45) [Tip$_2$Sn – 1], 322 (100) [TipSn – 1], 57 (67) [*t*Bu]. C$_{55}$H$_{76}$OSn (871.89): calcd. C 75.77, H 8.79; found C 75.85, H 8.83.

Vinyloxystannane 9 (from Stannene 3 and Acetone): White crystals from Et$_2$O. Yield: 0.65 g, 61%. M.p. 172 °C. ^{1}H NMR (300.13 MHz, CDCl$_3$): δ = 0.70, 0.86 and 1.24 (3 d, $^3J_{H,H}$ = 6 Hz, 36 H, CH*MeMe*′), 1.19 (s, 18 H, *t*Bu), 1.92 (s, 3 H, OC*Me*), 2.55 (very br. s, half width: 30 Hz, 2 H, *p*-C*H*MeMe′), 2.82 (sept., $^3J_{H,H}$ = 6 Hz, 4 H, *o*-C*H*MeMe′), 3.83 (d, $^2J_{H,H}$ = 2.2 Hz, 1 H, H *trans*/Me of C*HH*′=COMe), 3.88 (d, $^2J_{H,H}$ = 2.2 Hz, 1 H, H *cis*/Me of C*HH*′=COMe), 4.86 (s, $^2J_{^{117}Sn,H}$ = 126.0, $^2J_{^{119}Sn,H}$ = 135.0 Hz, 1 H, C*H*R$_2$), 6.87 (s, 4 H, arom H of Tip), 7.28 (br. s, 2 H, H of CR$_2$), 7.55 (br. s, 2 H, H of CR$_2$), 7.75–7.79 (m, 2 H, H of CR$_2$) ppm. ^{13}C NMR (75.47 MHz, CDCl$_3$): δ = 22.8, 23.1, 23.6, 28.7, 30.5, 36.7 and 37.4 (*o*- and *p*-CH*MeMe*′ and OC*Me*), 30.7 (C*Me*$_3$), 33.7 (*C*Me$_3$), 45.3 (*C*HR$_2$), 86.5 (*C*H$_2$=CO), 118.0, 120.8 and 121.3 (arom CH), 121.8 (*m*-CH of Tip), 136.4, 140.7, 147.4, 148.9, 152.7 and 153.0 (arom C), 160.3 (=C–O) ppm. ^{119}Sn NMR (111.92 MHz, CDCl$_3$): δ = 96.3 ppm. MS (EI, 70 eV): *m*/*z* (%) = 803 (10) [M – OC(Me)=CH$_2$], 583 (55) [M – CHR$_2$ – OC(Me)=CH$_2$], 543 (12) [Tip$_2$SnO + 1], 525 (45) [Tip$_2$Sn – 1], 482 (3) [Tip$_2$Sn – *i*Pr – 1], 321 (70) [TipSn – 2], 277 (100) [CHR$_2$]. C$_{54}$H$_{76}$OSn (859.88): calcd. C 75.43, H 8.91; found C 75.40, H 9.03.

Hydroxystannane 10 (from Stannene 3 and Water): White crystals from Et$_2$O. Yield: 0.75 g, 75%. M.p. 160 °C. ^{1}H NMR (300.13 MHz, CDCl$_3$): δ = 0.85, 0.93 and 1.19 (3 d, $^3J_{H,H}$ = 6 Hz, 3×12 H, CH*MeMe*′), 1.15 (s, 18 H, *t*Bu), 2.68–2.90 (m, 6 H, C*H*MeMe′), 4.86 (s, $^2J_{^{119}Sn,H}$ = 105.0 Hz, 1 H, C*H*R$_2$), 6.94 (s, $^4J_{^{119}Sn,H}$ = 24.0 Hz, 4 H, arom H of Tip), 7.33 (dd, $^3J_{H,H}$ = 6 Hz, $^4J_{H,H}$ = 1.3 Hz, 2 H, H on C3 and C6), 7.39 (br. s, 2 H, H on C1 and C8), 7.75 (d, $^3J_{H,H}$ = 6 Hz, 2 H, H on C4 and C5) ppm. ^{13}C NMR (75.47 MHz, CDCl$_3$): δ = 24.0, 24.4, 24.8 (*o*- and *p*-CH*MeMe*′), 30.7 (C*Me*$_3$), 34.3 (*p*-*C*HMeMe′), 34.8 (*C*Me$_3$), 37.6 ($^3J_{^{119}Sn,C}$ = 35.6 Hz, *o*-*C*HMeMe′), 49.5 (*C*HR$_2$), 119.3, 121.3 and 123.3 (arom CH of CR$_2$), 122.1 (*m*-CH of Tip), 137.7, 141.7, 144.6, 148.7 and 150.6 (arom C of CR$_2$, *ipso*- and *p*-C of Tip), 154.8 ($^2J_{^{119}Sn,C}$ = 49.8 Hz, *o*-C of Tip) ppm. ^{119}Sn NMR (111.92 MHz, CDCl$_3$): δ = –61.1 ppm. MS (EI, 70 eV): *m*/*z* (%) = 803 (3) [M – OH], 599 (5) [M – Tip – 1], 543 (55) [Tip$_2$SnOH], 525 (25) [Tip$_2$Sn – 1], 321 (27) [TipSn – 2], 277 (100) [CHR$_2$]. C$_{51}$H$_{72}$OSn (819.82): calcd. C 74.72, H 8.85; found C 74.97, H 9.08.

X-ray Structural Determination: All data for all structures represented in this paper were collected at low temperatures by using an oil-coated shock-cooled crystal with a Bruker-AXS CCD 1000 diffractometer with Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods[21] and all non hydrogen atoms were refined anisotropically by using the least-squares method on F^2.[22] ADP- and distances restraints were used to refine several disorders: a rotation disorder of a *t*Bu group and an *i*Pr for **3**, two

Table 1. Crystal data for compounds **3**, **5**, **6** and **7**.

	3	**5**	**6**	**7**
Empirical formula	C$_{51}$H$_{70}$Sn	C$_{60}$H$_{80}$O$_{1.5}$Sn	C$_{70}$H$_{94}$O$_2$Sn	C$_{55}$H$_{76}$OSn
Formula weight	801.76	943.93	1086.14	871.85
Temperature [K]	173(2)	173(2)	173(2)	173(2)
Crystal system	monoclinic	monoclinic	triclinic	orthorhombic
Space group	*P*2$_1$/*c*	*C*2/*c*	*P*$\bar{1}$	*Pbca*
a [Å]	14.817(1)	23.109(2)	12.508(1)	11.073(1)
b [Å]	26.652(2)	12.996(1)	13.686(1)	25.256(1)
c [Å]	12.457(1)	35.439(2)	21.076(2)	35.368(2)
α [°]	–	–	71.094(2)	–
β [°]	110.920(2)	91.618(1)	75.049(2)	–
γ [°]	–	–	68.321(2)	–
Volume [Å^3]	4595.1(6)	10638.8(12)	3132.4(6)	9891.3(9)
Z	4	8	2	8
Absorption coefficient [mm^{-1}]	0.587	0.519	0.449	0.552
Reflections collected	20354	23239	13999	42206
Independent reflections	6530	7564	8863	7025
R(int)	0.0909	0.0838	0.0682	0.1236
Absorption correction	semiempirical	semiempirical	semiempirical	semiempirical
Min./max. transmission	0.759050	0.748219	0.297743	0.767978
Data	6530	7564	8863	7025
Restraints	105	81	64	60
Parameters	554	642	720	558
Goodness-of-fit on F^2	1.013	1.071	0.988	1.055
Final *R* indices [$I > 2\sigma(I)$]				
R_1	0.0485	0.0567	0.0625	0.051
wR_2	0.0777	0.0931	0.1059	0.0764
R indices (all data) R_1	0.0947	0.0955	0.1153	0.1017
wR_2	0.0884	0.1032	0.1221	0.0884
Largest diff. peak/hole [e Å^{-3}]	0.523/–0.362	0.621/–0.664	0.996/–0.909	0.474/–0.662

*i*Pr groups for **5**, a *t*Bu group and noncoordinating pentane for **6** and again a rotation disorder of a *t*Bu group for **7** (Table 1). CCDC-667053 (for **3**), -667054 (for **5**), -667055 (for **6**) and -667056 (for **7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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