Synthesis and properties of a stable 6-stannapentafulvene†

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The first donor-free 6-stannapentafulvene 1a stable at ambient temperature was synthesized and isolated, exhibiting the shortest tin–carbon bond length among those previously reported.

In the past few decades, much attention has been focused on the chemistry of heavier congeners of alkenes, *i.e.*, "metallenes and dimetallenes" (>M=C< and >M=M<: M = Si, Ge, Sn, Pb),[1] and a number of reports have appeared on their syntheses, structures, and properties. In the field of metallenes, the chemistry of stannenes (>Sn=C<) has been undeveloped due to their high reactivity toward self-oligomerization in contrast to the relatively well-established chemistry of silenes (>Si=C<) and germenes (>Ge=C<). In view of the small overlap between the p orbitals of tin and carbon atoms, one can make a natural question whether a concrete Sn=C double bond can exist as a stable stannene in spite of the weak π-bond. Although several reports on the theoretical calculations of a parent stannene, $H_2Sn=CH_2$, predicted its double bond character,[2] no clear conclusion can be drawn from only theoretical studies and the experimental verification has long been sought for an Sn=C double bond. The structural analyses of the Sn=C double-bond compounds ever reported are limited to only two types, both of which are thermodynamically stabilized by heteroatoms such as B and/or N. While Berndt *et al.* reported a series of diboryl-substituted stannenes **2** having an extremely short Sn=C bond [**2a** (2.025 Å), **2c** (2.036 Å) and **2d** (2.032 Å)],[3] the formal Sn=C compounds such as **3**,[4] **4**,[5] and **5**,[6] the Sn–C bond lengths of which (**3**: 2.314 Å, **4a**: 2.290 Å, **4b**: 2.379 Å, **5**: 2.303 Å) are markedly longer than the typical Sn–C single bond lengths (av. 2.14 Å),[7] have also been synthesized and characterized (Fig. 1). Although 6-stannapentafulvene **1b** bearing only carbon substituents on the Sn=C moiety was synthesized by Escudié *et al.*,[8] **1b** was not structurally characterized due to its ready dimerization at room temperature. In order to study the chemical behavior of tin–carbon double bond in detail, we examined the synthesis of stannene **1a** kinetically stabilized by the combination of an extremely bulky, effective steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt), and Mes group. Here, we report the synthesis and structure of the donor-free 6-stannapentafulvene **1a**, the first tetraarylstannene stable at ambient temperature.

Fluorenyl(fluoro)stannane **7**, a suitable precursor of **1a**, was prepared according to Scheme 1. Although chlorostannane **6** was also considered to be a good precursor, the reactions of **6** with *n*- or *tert*-butyllithium as a base resulted in some side reactions, such as direct substitution on the tin atom or reduction of the Sn–Cl bond.

6-Stannapentafulvene **1a** was successfully synthesized by the dehydrofluorination of **7** using *tert*-butyllithium as a base in Et_2O at −40 °C (Scheme 2).‡ Initially the reaction mixture became yellow solution indicating the formation of the lithiated compound **8**, and then it turned deep violet at room temperature. Removal of LiF and the solvents afforded violet crystals of **1a**, the ^1H and ^{13}C NMR spectra of which showed no coordinated Et_2O. Compound **1a** was found to be thermally stable under an inert atmosphere in solution (benzene-d_6, at 80 °C in a sealed tube) and highly moisture- and air-sensitive. Indeed, **1a** undergoes a ready addition reaction with water across its Sn=C moiety to give the corresponding hydroxystannane **9** (76%, Scheme 2).

The molecular geometry of **1a** was determined by X-ray crystallographic analysis (Fig. 2).§ The structural parameters for **1a** are summarized in Table 1 together with the calculated values for a

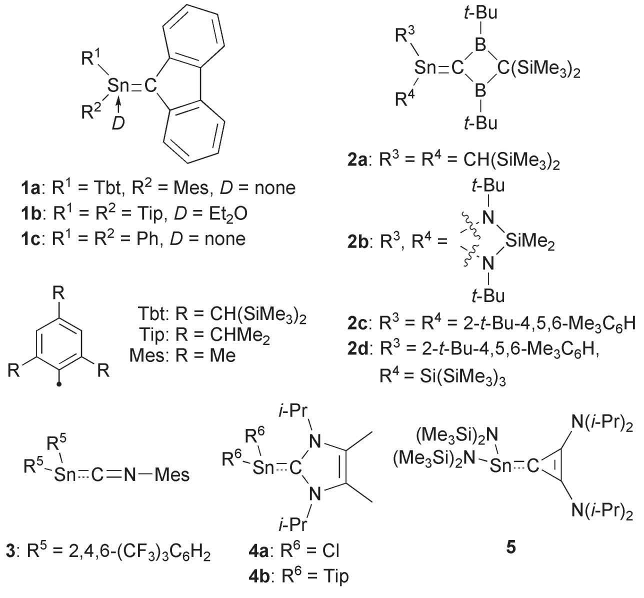
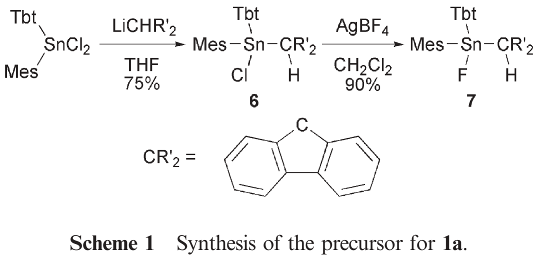


Fig. 1



Scheme 1 Synthesis of the precursor for **1a**.

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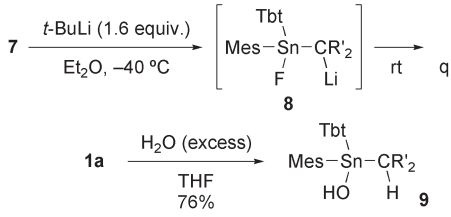
† Electronic supplementary information (ESI) available: Experimental procedures and physical properties for new compounds and the optimized structure of **1c**. See DOI: 10.1039/b512097g



Scheme 2

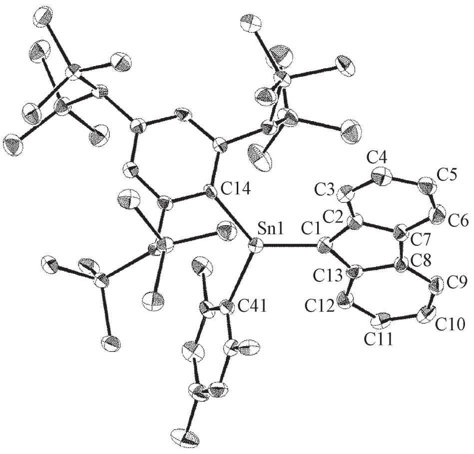


Fig. 2 ORTEP drawing of 6-stannapentafulvene **1a** (50% probability). Hydrogen atoms are omitted for clarity.

Table 1 Observed and calculated bond lengths (Å) and angles (°) for 6-stannapentafulvenes

	1a: obs.	**1c**: calc.[a]
Sn–C1	2.016(5)	1.998
C1–C2/C1–C13	1.452(6)/1.456(6)	1.465
C2–C7/C8–C13	1.410(6)/1.425(6)	1.426
C7–C8	1.446(6)	1.457
C14–Sn1–C41	118.27(17)	110.15
C1–Sn1–C14/C1–Sn1–C41	127.92(19)/113.67(19)	124.92
C2–C1–C13	106.3(4)	106.19
C2–C1–Sn1/C13–C1–Sn1	128.3(4)/125.3(3)	126.93

[a] Calculated at the B3LYP/6-31G(d) (LANL2DZ on Sn) level.

model compound **1c**. The bond length of the Sn1–C1 bond [2.016(5) Å] is the shortest among those of tin–carbon bonds ever reported. In addition, it is *ca.* 6% shorter than the typical Sn–C single bond length (*ca.* 2.14 Å)[7] and is close to the observed values for **2** and that calculated for **1c** (1.998 Å). The structural analysis revealed the completely trigonal planar geometry around the Sn1 (359.9°) and C1 (359.9°) atoms. The large twisted angle between the C14–Sn1–C41 plane and the fluorenylidene moiety (28.5°) is probably due to the steric reason, since such twisted structures have already been observed in bifluorenylidene[9] (43°) and Mes_2Ge=C(fluorenylidene)[10] (5.9°). Although the calculated parameters for **1c** are almost similar to those observed for **1a**, the twisted angle around the Sn=C unit of **1c** (13.1°) is smaller than that of **1a** probably due to the lower bulkiness of the substituents on the tin atom.

In-plane vibration modes for the 6-stannapentafulvene skeleton of **1a** were observed by the Raman spectra. A part of the Raman spectrum of **1a** is shown in Fig. 3. The signals at 287 and 674 cm^{-1} were assigned to the skeletal vibrations on the 6-stannapentafulvene plane based on the theoretical calculations. The experimentally observed spectrum showed close resemblance with the simulated spectrum for **1c** as shown in Fig. 3, indicating that the calculated structure for **1c** reproduces the characters of **1a** adequately.

The ^{119}Sn NMR spectrum of **1a** in C_6D_6 showed a signal at 270 ppm, which is characteristic of doubly bonded tin derivatives. This value is slightly upfield-shifted in comparison to that of **1b** (288 ppm). The assignments of the ^{1}H, ^{13}C and ^{119}Sn NMR signals are listed in Table 2 along with the calculated values for **1c**. The observed values are in good agreement with the calculated ones except for the case of ^{119}Sn NMR at B3LYP level (central row). At MPW1PW91 level (right row), which was evidenced to be effective for the GIAO calculations for Tip_3Sn^+,[11] the calculated values for **1c** are consisted with the observed ones for **1a**. The ^{13}C NMR signal of the Sn=*C* (144.9 ppm) reasonably appeared in the sp^2 region. It is noteworthy that all the signals of the fluorenylidene unit were observed nonequivalent probably due to the restricted rotation of the Sn–C bond, indicating that doubly bonded structure **1a** rather than **1a′** (Scheme 3) might be dominant in solution. In addition, **1a** reacts with 2,3-dimethyl-1,3-butadiene at

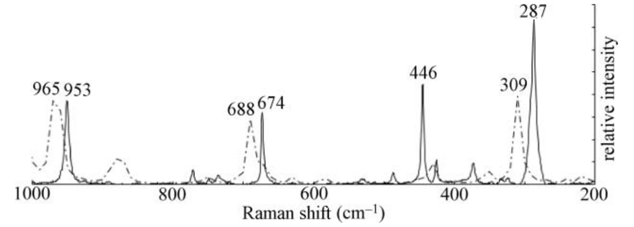
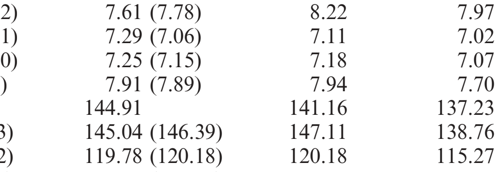


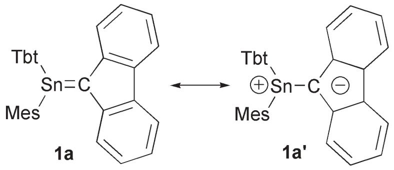
Fig. 3 Raman spectra of 6-stannapentafulvenes. Solid line: FT-Raman spectrum of **1a** measured with the excitation by He–Ne laser (833 nm). Dashed line: Spectrum of **1c** simulated by the theoretical calculation at the B3LYP/6-31G(d) [TZ(2d) on Sn] level.

Table 2 Observed and calculated ^{1}H, ^{13}C and ^{119}Sn NMR chemical shifts (ppm) for 6-stannapentafulvenes

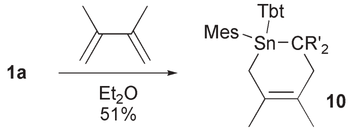


	1a: obs.[a]	**1c**: calc.[b]	**1c**: calc.[c]
Sn	270	185	259
H3 (H12)	7.61 (7.78)	8.22	7.97
H4 (H11)	7.29 (7.06)	7.11	7.02
H5 (H10)	7.25 (7.15)	7.18	7.07
H6 (H9)	7.91 (7.89)	7.94	7.70
C1	144.91	141.16	137.23
C2 (C13)	145.04 (146.39)	147.11	138.76
C3 (C12)	119.78 (120.18)	120.18	115.27
C4 (C11)	124.13 (120.59)	120.49	120.06
C5 (C10)	125.23 (126.64)	125.44	119.06
C6 (C9)	122.84 (122.99)	125.13	114.90
C7 (C8)	134.24 (134.40)	136.87	128.88

[a] Measured in benzene-d_6. [b] Calculated at the GIAO-B3LYP/6-311+G(2d,p) (TZV on Sn)//B3LYP/6-31G(d) (LANL2DZ on Sn) level. [c] Calculated at the GIAO-MPW1PW91/6-31G(d) (TZV on Sn)//B3LYP/6-31G(d) (LANL2DZ on Sn) level.



Scheme 3



Scheme 4

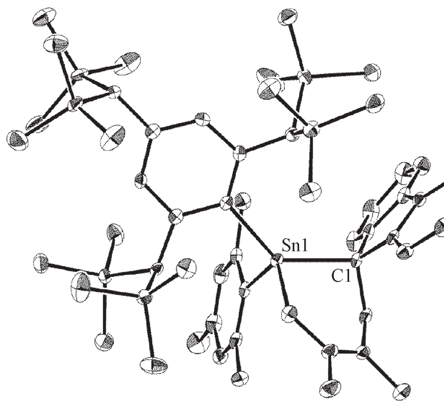


Fig. 4 ORTEP drawing of **10** (50% probability). Hydrogen atoms and benzene molecule are omitted for clarity.

room temperature to afford the [2 + 4] cycloadduct **10** in 51% yield (Scheme 4, Fig. 4§), suggesting that **1a** has an Sn=C double-bond character rather than an ionic character (**1a′**) from the viewpoints of the chemical reactivity.

In summary, we succeeded in the synthesis and X-ray crystallographic analysis of 6-stannapentafulvene **1a** stable at ambient temperature for the first time. Judging from the NMR spectra, molecular structure, and reactivities, **1a** has a sufficient Sn=C double-bond character. These results demonstrate a possibility of forming a π-bond between tin and carbon atoms, when it is kinetically well stabilized.

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Notes and references

‡ **1a**: Purple crystalline solid; mp 167–171 °C (decomp.); ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ −0.02 (s, 9H), 0.02 (s, 9H), 0.12 (s, 18H), 0.18 (s, 9H), 0.26 (s, 9H), 1.56 (s, 1H), 1.91 (s, 1H), 2.06 (s, 1H), 2.10 (s, 3H), 2.59 (br s, 3H), 2.66 (s, 3H), 6.73 (br s, 1H), 6.84 (br s, 1H + 2H), 7.06 (ddd, ^3J = 8 Hz, ^3J = 8 Hz, ^4J = 2 Hz, 1H), 7.15 (dd, ^3J = 8 Hz, ^3J = 8 Hz, 1H), 7.25 (ddd, ^3J = 7 Hz, ^3J = 6 Hz, ^4J = 2 Hz, 1H), 7.29 (ddd, ^3J = 7 Hz, ^3J = 7 Hz, ^4J = 2 Hz, 1H), 7.61 (dd, ^3J = 7 Hz, ^4J = 2 Hz, 1H), 7.78 (d, ^3J = 8 Hz, 1H), 7.89 (dd, ^3J = 8 Hz, ^4J = 2 Hz, 1H), 7.91 (dd, ^3J = 6 Hz, ^4J = 2 Hz, 1H); ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ 1.07 (q), 1.20 (q), 1.45 (q), 1.65 (q), 21.13 (q), 27.62 (q), 28.63 (q), 31.25 (d), 35.96 (d), 37.59 (d), 119.78 (d), 120.18 (d), 120.59 (d), 122.84 (d), 122.99 (d), 123.20 (d), 124.13 (d), 125.23 (d), 125.64 (d), 128.29 (d), 129.12 (d), 129.40 (d), 134.24 (s), 134.40 (s), 140.61 (s), 142.75 (s), 143.35 (s), 143.62 (s), 144.91 (s), 145.04 (s), 145.87 (s), 146.39 (s), 150.73 (s), 151.33 (s); ^{119}Sn NMR (111 MHz, C_6D_6, 25 °C): δ 270; UV/vis (hexane, rt) 552 nm (ε 1 × 10^4); High resolution FAB-MS *m/z*: calc. for $C_{49}H_{79}Si_6{}^{120}Sn$: 955.3827, found: 955.3851.

§ *Crystal data* for **1a**: $C_{49}H_{78}Si_6Sn$, M = 953.34; monoclinic, space group $C2/c$ (no. 15); a = 21.0447(6), b = 13.5070(5), c = 38.1717(13) Å, β = 96.1949(12)°, V = 10787.0(6) Å^3; Z = 8; D_c = 1.175 g cm^{-3}; μ = 0.636 mm^{-1}; $2\theta_{max}$ = 50°; T = 103 K; $R_1(I > 2\sigma(I))$ = 0.0488; wR_2 (all data) = 0.1065; GOF = 1.001 for 32670 reflections and 526 parameters.

Crystal data for **10**: $C_{55}H_{88}Si_6Sn{\cdot}0.5C_6H_6$ M = 1075.54; triclinic, space group $P\bar{1}$ (no. 2); a = 12.347(2), b = 13.0052(18), c = 20.418(4) Å; α = 71.537(7), β = 81.570(7), γ = 74.856(7)°, V = 2994.7(8) Å^3; Z = 2; D_c = 1.193 g cm^{-3}; μ = 0.581 mm^{-1}; $2\theta_{max}$ = 50°; T = 103 K; $R_1(I > 2\sigma(I))$ = 0.0350; wR_2 (all data) = 0.0750; GOF = 1.068 for 19733 reflections and 667 parameters.

CCDC 282727 and 282728. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b512097g

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