Main-Group Compounds

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Reversible Stannylenoid Formation from the Corresponding Stannylene and Cesium Fluoride

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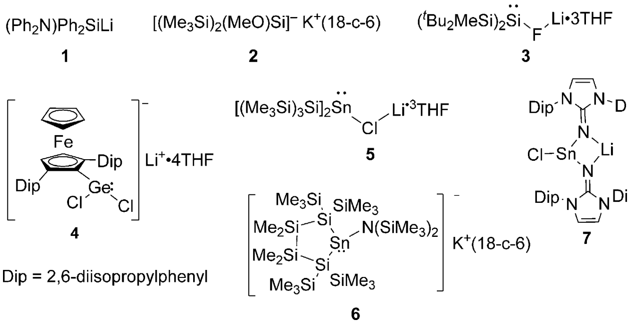
Abstract: *A fluorostannylenoid ($Cs^+[R_2SnF]^-$ (**9**), $R_2 = (TMS)_2CCH_2CH_2C(TMS)_2$) was prepared by reacting a stable dialkylstannylene (R_2Sn (**8**), $R_2 = (TMS)_2CCH_2CH_2C(TMS)_2$) with cesium fluoride at room temperature in THF. While **9** is stable in THF and DME, removal of the solvent leads to the regeneration of stannylene **8**. No reaction occurred when **8** was treated with CsF in a hydrocarbon solvent. Addition of dibenzo-21-crown-7 ether to the THF solution of stannylenoid **9** followed by usual workup affords the corresponding crystalline stannylenoid crown ether complex, the X-ray structural analysis of which revealed a fluorine-bridged contact ion-pair structure. The reaction of **9** with excess phenylacetylene gives the corresponding di(phenylethynyl)stannane.*

Like carbenoids,[1] heavier congeners of tetrylenoids R_2EXM (E = Si, Ge, and Sn; X = electronegative group; M = alkali metal) are interesting chemical species not only as key intermediates in the reduction of R_2EX_2 to the corresponding tetrylenes R_2E, but as distinctive synthetic reagents. A number of experimental[2–4] and theoretical studies[5] have revealed unique features of tetrylenoids or α-functional tetryl anions. For example, in their systematic studies of α-functionalized silyllithiums, Tamao, Kawachi, et al.[2e,f] have shown that silyllithiums serve as either nucleophiles or electrophiles depending on the leaving ability of the α functional groups, temperatures, and other reaction conditions. Typically, dimethylamino(diphenyl)silyllithium reacts with a chlorosilane to give the corresponding disilane at 0 °C in THF, while *tert*-butoxy(diphenyl)silyllithium undergoes bimolecular self-condensation with the loss of one tert-butoxylithium to afford the corresponding 2-(*tert*-butoxy)disilanyllithium in similar conditions. More recently, a related nucleophilic fluoride ion substitution of a fluorosilylenoid has been reported by Marschner et al.[2i] Molecular structures have been determined for amino- (**1**),[2h] alkoxy- (**2**),[2j] and fluorine-substituted (**3**) silylenoids[2l] as shown in Scheme 1. Less attention has been focused on germylenoids[3] and stannylenoids,[4] while molecular structures of tetrylenoids **4**,[3c] **5**,[4b] **6**,[4c] and **7**[4d] have been studied by X-ray crystallography (Scheme 1).

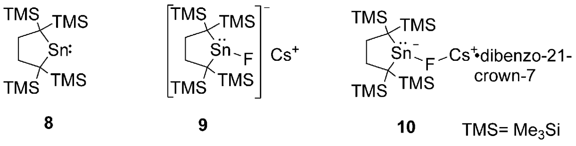


Scheme 1. Tetrylenoids characterized by X-ray crystallography. 18-c-6 = 18-crown-6 ether.

Heavy tetrylenoids R_2EXM (E = Si, Ge, and Sn) have been prepared by various methods, including reduction of R_2EXX' using alkali metals[2d,l] or lithium naphthalenide,[2k] the desilylation of $R_2E(X)SiMe_3$ with *t*-BuOK,[2j] tin–lithium exchange reaction of $R_2E(X)SnMe_3$ using an alkyllithium,[2e] and reactions of inorganic divalent tetrylenes EX_2 with RLi.[3a,c,4d] No formation of tetrylenoids through the direct reaction between the corresponding tetrylene and a metal halide has been reported to date, while the reversibility between R_2EXM and $R_2E\colon + MX$ has been assumed, sometimes without any evidence.

We have found that isolable dialkylstannylene **8**[6] reacts with cesium fluoride to give the corresponding stannylenoid **9** in an ethereal solvent like THF and DME, regenerating **8** by replacing the solvent with a hydrocarbon solvent. A similar reaction in the presence of dibenzo-21-crown-7 ether gives crystalline stannylenoid-crown ether complex **10**, the molecular structure of which has been studied by X-ray crystallography (Scheme 2).

When dialkylstannylene **8** is treated with an excess of anhydrous CsF in [D8]THF at room temperature, the color of the solution turns instantaneously from dark red to pale yellow. After stirring for 20 min, quantitative formation of stannylenoid **9** can be shown by NMR spectroscopy. In the ^1H NMR spectrum of **9** in [D8]THF, two singlet signals for Me_3Si groups are observed at $\delta = 0.06$ and 0.08 ppm, thus indicating spectroscopic C_s symmetry. In accord with the low symmetry, ring protons *trans* and *cis* to the fluorine atom of **9**



Scheme 2. Stable dialkylstannylene and stannylenoids.

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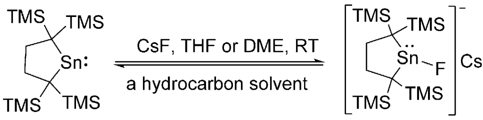
show signals at $\delta = 2.40$ and 2.25 ppm, with an AA′XX′coupling pattern. In the ^{119}Sn NMR spectrum, a doublet is observed at δ 505 ppm with a $J(^{119}\text{Sn-}^{19}\text{F})$ value of 1989 Hz. The resonance is shifted significantly upfield in comparison with that of **8** ($\delta = 2323$ ppm) [6a] but is downfield-shifted compared those of chloro- and fluorobenzylstannanes with the same cyclic ligands[7] and reported three-coordinated tin (II) complexes ($\delta = 138$ to -338 ppm).[8] The ^{19}F NMR resonance of **9** is observed at $\delta = -166$ ppm, with four satellite signals due to the coupling to ^{117}Sn and ^{119}Sn nuclei; $J(^{117}\text{Sn-}^{19}\text{F}) = 1901$ Hz, $J(^{119}\text{Sn-}^{19}\text{F}) = 1989$ Hz. The large J(Sn-F) values indicate the existence of Sn–F covalent bonding, though the values are significantly smaller than those for neutral fluorostannanes.[9]

Fluorostannylenoid **9** is stable in THF or DME at room temperature and remains intact for half a year under anaerobic and anhydrous conditions at room temperature. No decomposition is observed when a THF solution of **9** is heated at 60 °C for one day. Stannylene **8** does not react with CsF in hydrocarbon solvents such as *n*-pentane, *n*-hexane, benzene, and toluene. Interestingly, removal of the solvent from stannylenoid **9** in [D$_8$]THF under reduced pressure affords red crystals, thus indicating regeneration of stannylene **8**. After [D$_6$]benzene was added to the residue and then filtered, the ^{119}Sn NMR spectrum of the filtrate showed only a singlet signal at $\delta = 2323$ ppm corresponding to **8**.[6a] The reversible formation of a stannylenoid by changing the solvent polarity [Eq. (1)] is quite unique in the tetrylenoid chemistry; silylenoid **3** (Scheme 1) has been reported to give a disilene, a dimer of the corresponding silylene, photochemically or upon heating at 120 °C,[21] and efforts to remove the solvated LiCl from disilylstannylenoid **5** have been unsuccessful.[4b]



8 **9** (1)

Adding an equimolar amount of dibenzo-21-crown-7 ether to a THF solution of **9**, replacing THF with toluene, and then keeping the solution at −20 °C for two weeks affords colorless prismatic single crystals of the stannylenoid crown ether complex **10** [Eq. (2)].[10]

$$\mathbf{9} \xrightarrow[\text{2) } -20^{\circ}\text{C, toluene}]{\text{1) dibenzo-21-c-7/THF}} \mathbf{10} \qquad (2)$$

The molecular structure of **10** determined by X-ray crystallography is illustrated in Figure 1, together with relevant structural parameters (see Figure S2 in the Supporting Information for a side view). The Sn–F distance [2.065(3) Å] in **10** is longer than in monomeric tetracoordinate fluorostannanes such as Mes$_3$SnF (1.961 Å)[11a] and TsiSnPh$_2$F (1.965(8) Å)[11b] but shorter than that in fluorine-bridged polymeric Me$_2$SnF$_2$ (2.12(1) Å),[12] thus indicating covalent nature for the Sn–F bond in **10**, albeit significantly weakened. The Cs–F distance of 2.880(3) Å is even shorter than the sum of the covalent radii[13] or ion radii[14] of Cs and F. The lengths of the Sn–C bonds of **10** (av. 2.285 Å) are slightly longer than those of related cyclic stannanes[15] and stannylene **8** (av. 2.221 Å).[6a] The Sn-F-Cs angle of 157.1° is much larger than the Sn-Cl-Li angle in **5** (113.0°)[4b] and the Si-F-Li angle in **3** (135.2°),[21] thus suggesting large steric repulsion between the bulky substituents of **10** and the crown ether coordinated to the Cs$^+$ ion. The three-coordinate tin atom adopts pyramidal geometry, with the sum of bond angles around Sn (ΣSn) of 279°, which is smaller than those around silicon of **3** [308(3)°][4b] and the tin center of **5** [301.9(4)].[21]

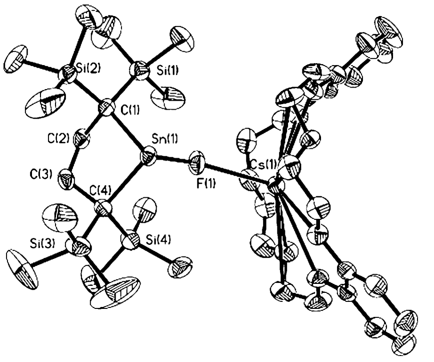
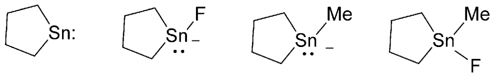


Figure 1. Molecular structure of **10**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths [Å], bond angles [°], and dihedral angles [°]: Sn1–F1 = 2.065(3), Cs1–F1 = 2.880(3), C1–Sn1 = 2.293(4), C4–Sn1 = 2.278(4), Cs1–O1 = 3.249(4), Cs1–O2 = 3.251(4), Cs1–O3 = 3.162(4), Cs1–O4 = 3.135(4), Cs1–O5 = 3.289(4), Cs1–O6 = 3.247(4), Cs1–O7 = 3.157(4); C1-Sn1-C4 = 85.41(16), C1-Sn1-F1 = 97.31(15), C4-Sn1-F1 = 96.27(14), Sn1-F1-Cs1 = 157.15(17).

Because the NMR spectra of stannylenoid **9** in [D$_8$]THF are very similar to those of **10**, as shown in the Supporting Information, the structure of **10** in the solution should be similar to that of **9**, which presumably exists as a free fluorostannyl anion separated from solvated Cs$^+$ countercation rather than the fluorine-bridged contact ion pair found in the solid state. In accordance with this view, no Cs–F coupling was observed in the ^{19}F NMR spectra of **9** and **10** in THF. To gain insight into the feature of the fluorostannyl anion, the DFT calculations were performed for model tin compounds **11**–**14** (Scheme 3) at the B$_3$LYP/6-31 + G(d,p) for C, H, F, and Si + LanL$_2$DZ for (Sn) level.[16] As shown in Table 1, the Sn–F bond distance of **12** is longer and its Wiberg bond index (WBI)[17] is smaller than those of **14**. The p character of the Sn atomic orbital forming the Sn–F bond in **12** is larger than that in **14**. The origin of relatively long Sn–F bond length as well as the small $J(^{119}\text{Sn-}^{19}\text{F})$ values observed for stannyleneoid **10** can be ascribed in part to the high degree of p character in the



11 **12** **13** **14**

Scheme 3. Model tin compounds chosen for DFT calculations.

Table 1: Structural and NBO parameters for **11**–**14** calculated at the B3LYP/6-31+G(d,p)level for C, H, F, and Si and the LanL2DZ level for Sn.

	11	**12**	**13**	**14**
Sn–F				
Distance [Å]	–	2.007	–	1.902
WBI[a]		0.336		0.417
Hybridization		$sp^{11.5}$(Sn) $sp^{2.36}$(F)		$sp^{4.21}$(Sn) $sp^{2.28}$(F)
ΣSn,[b] deg	–	268.7	270.9	
LP[c]				
Hybridization	$sp^{0.19}$	$sp^{0.33}$	$sp^{0.42}$	–
Energy level [eV]	−5.665	−0.470	−0.094	–

[a] Wiberg bond index. [b] Sum of the bond angles around Sn atom. [c] Lone-pair electrons.

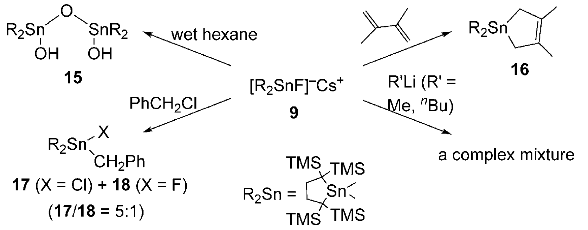
relevant Sn atomic orbital, in addition to weakening of the bond in **10** due to the Cs–F bonding. Geometry around the Sn atom in **12** is pyramidal with ΣSn of 269°, which is similar to those for **13** (271°) and **10** (279°). The s character of the lone-pair (LP) orbitals calculated using the NBO method decreases in the order **11** ⩾ **12** > **13**. In accordance with this order, the LP orbital level of stannylene **11** is the lowest and that of **12** is slightly lower than that of **13**. The present DFT calculations suggest that the fluorostannylenoids **9** and **10** in solution may work as a stannyl anion, the nucleophilicity of which is slightly weaker than that of the corresponding trialkylstannyl anion but much stronger than that of the stannylene.

The heterolytic Sn–F bond dissociation energy (BDE) calculated using Equation (3) at the same level is

$$\mathbf{11} \rightarrow \mathbf{10} + F^- \qquad (3)$$

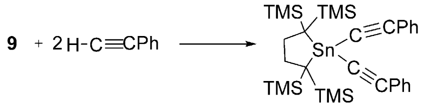
272 kJ mol^{-1},[18] which is much smaller than the homolytic BDE(Sn–F) of fluorostannanes[19] but large enough to prevent spontaneous Sn–F dissociation at room temperature. The reverse reaction of **9** to **8** + CsF is proposed to occur by the attack of the (desolvated) Cs$^+$ ion to the fluorine atom of **9**.

The existence of a dissociation equilibrium of **9** with **8** + CsF in solution, even though the latter components are not detected by NMR spectroscopy, is suggested by the following observations (Scheme 4): 1) Stannylenoid **9** in THF is rapidly hydrolyzed with wet hexane to give **15**, a condensed dimer of the corresponding dihydroxystannane.[20] 2) Addition of 2,3-dimethylbuta-1,3-diene to **9** in THF gives **16**, the [1+4] adduct between stannylene **8** and the diene.[21] 3) The reaction of **9** with benzyl chloride in THF affords a mixture of chloro- and fluorostannanes **17** and **18** in a ratio of 5:1; **17** is obtained through the insertion of stannylene **8** into the C–Cl bond of benzyl chloride,[20] while **18** is formed through nucleophilic chlorine substitution at the benzylic carbon by **9**. The ratio suggests that the C–Cl bond insertion of **8** is much faster than the nucleophilic substitution. 4) Stannylenoid **9** in THF reacts with MeLi or ^{n}BuLi in hexane at low temperatures but gives a complex mixture.



Scheme 4. The reactions of stannylenoid **9** with various reagents.

The distinctive reactivity of stannylenoid **9** is shown by the reaction of **9** with phenylacetylene. While stannylene **8** does not react with phenylacetylene,[22] treatment of stannylenoid **9** with 2 equivalents of phenylacetylene at room temperature gives the corresponding di(phenylethynyl)stannane **19** in a good yield [Eq. (4)].



(4)

19, 71%

The structure of **19** was determined by NMR spectroscopy and X-ray crystallography;[23] the molecular structure is shown in Figure S3. The mechanism of this multistep reaction remains open.[24]

In conclusion, the reaction of isolable stannylene **8** with CsF forms the corresponding fluorostannylenoid **9** quantitatively in an ethereal solution and removal of the solvent regenerates **8**. No formation of the fluorostannylenoid occurs in hydrocarbon solvents. Using a similar reaction in the presence of dibenzo-21-crown-7 ether, the corresponding stannylenoid-crown ether complex **10** is isolated as crystals. While the X-ray structure of **10** reveals a fluorine bridge between Sn and Cs, the stannylenoid in solution would be a free fluorostannyl anion separated from solvated Cs$^+$ countercation. Stannylenoid **9** reacts with phenylacetylene to give the corresponding di(phenylethynyl)stannane **19**. Further work, including the possible generation of the stannylenoids by the reactions of **8** with other metal halides, is in progress.[25]

Acknowledgements

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Keywords: DFT calculations · main-group compounds · fluorostannylenoids · tin · stannylenes

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[7] The ^{119}Sn NMR resonances of halostannane **17** and **18** (Scheme 1) are observed at 205 and 201 ppm, respectively (see the supporting Information).

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[9] Typically, the $J(^{119}\text{Sn-}^{19}\text{F})$ values for fluorostannanes Mes_3SnF,[12a] (o-Ans)$_3$SnF,[12a] TsiPh_2SnF,[12b] and Tip_2SnF_2[12c] are reported to be 2285.5, 2286.5 < 2463, and 2893 Hz, respectively. The $J(^{119}\text{Sn-}^{19}\text{F})$ for fluorostannane **18** is observed to be 2616 Hz (see the Supporting Information).

[10] Alternatively, **10** is prepared by the reaction of stannylene **8** with CsF in toluene in the presence of an equimolar amount of the crown ether (see the Supporting Information).

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[15] Typically, the Sn−C(ring) bond lengths for stannanes **15** (Scheme 1) and **19** [Eq. (4)] are found to be 2.175 and 2.178 Å, respectively.

[16] The DFT calculations were performed with the Gaussian 09 program package. See the Supporting Information for the calculation details and the full reference for Gaussian 09.

[17] K. B. Wiberg, *Tetrahedron* **1968**, *24*, 1083.

[18] The heterolytic BDE (ΔE) is determined as; ΔE = Total energy (TE, **10**) + TE (F$^-$) − TE (**11**). Zero-point vibrational energies (ZPE) are incorporated into the total energies without a scale factor.

[19] The homolytic Sn−F BDEs of Me_3SnF and H_3SnF are calculated to be 498–674 and 486–649 kJ mol^{-1}, respectively, depending on the theoretical levels: M. R. Adams, E. A. C. Bushnell, T. B. Grindley, R. J. Boyd, *Comput. Theor. Chem.* **2014**, *1050*, 7.

[20] Independent experiments on the hydrolysis of stannylene **8** with wet hexane and on the reaction of **8** with benzyl chloride give **15** (85% yield) and **17** (92% yield), respectively. See the Supporting Information for the details.

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[23] See the Supporting Information for the experimental details.

[24] The reaction mechanism is difficult to infer and is now under investigation. A mechanism initiated by the abstraction of acetylenic proton by CsF may be excluded because the acidity of phenylacetylene is not large enough. See: a) C. Spitz, J.-F. Lohier, V. Reboul, P. Metzner, *Org. Lett.* **2009**, *11*, 2776; b) A. J. Kresge, P. Pruszynski, P. J. Stang, B. L. Williamson, *J. Org. Chem.* **1991**, *56*, 4808. Alhough evolution of H_2 gas is expected during the reaction, it was not detected in appreciable amounts, probably due to the small-scale nature of the experiments.

[25] Fluorostannylenoid formation through the reactions of stannylene **8** with LiF, NaF, KF, and CsCl in THF was unsuccessful. Stannylene **8** reacts with LiCl but gives unidentified products.

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