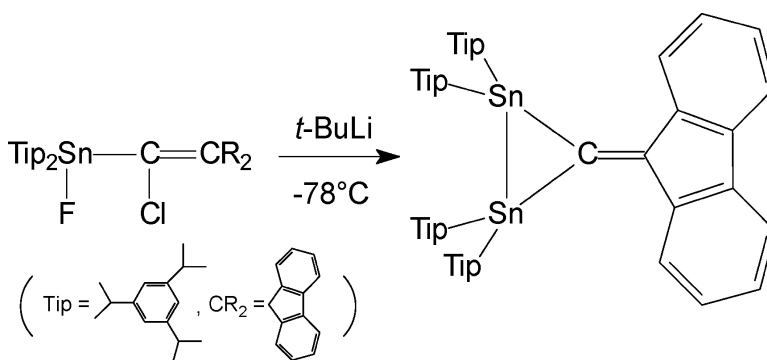


A Stable Distannirane

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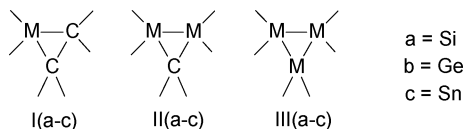
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Three-membered heterocycles comprising a main group element are important compounds that have attracted large interest. This is mainly due to their particular structure and to the strain of the cycle conferring great reactivity on them, which makes them interesting building blocks in organic and organometallic chemistry.

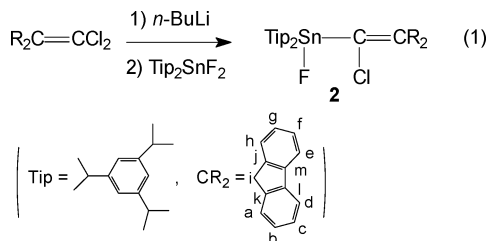
The synthesis of heavy analogues of cyclopropanes I–III (Chart 1) has been a great challenge for the last few years. Silicon and germanium heterocycles I(ab), II(ab), and III(ab) have been reported.¹ Going down the periodic table, the stabilization of three-membered heterocycles becomes more and more difficult. Thus, in the case of tin, all efforts to prepare I(c)^{2a} and II(c) have been unsuccessful thus far, and only the symmetrical III(c)^{2b–d} has been synthesized.

Chart 1

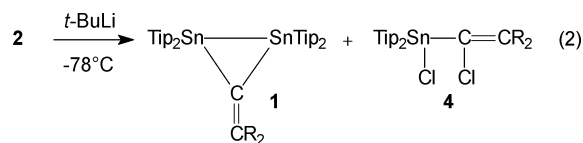


We present in this communication the synthesis in a two-step procedure of the first three-membered heterocycle of type II(c) containing two tin and one carbon atoms, 1,1,2,2-tetra(2,4,6-triisopropylphenyl)-3-fluorenylidene-1,2-distannirane **1**.

The first step of the synthesis of **1** involved the preparation of stannylalkene **2**³ by addition of Tip_2SnF_2 ⁴ ($\text{Tip} = 2,4,6\text{-triisopropylphenyl}$) to a THF solution of the carbenoid $\text{ClC}(\text{Li})=\text{CR}_2$ ($\text{CR}_2 = \text{fluorenylidene}$) obtained from $\text{Cl}_2\text{C}=\text{CR}_2$ ⁵ and *n*-butyllithium (eq 1). The structure of **2** was confirmed by an X-ray analysis (see Supporting Information), which displays standard bond lengths and angles and deserves no special comments.



Addition of 1 equiv of *tert*-butyllithium to **2** afforded distannirane **1**⁶ and the 9-[bis(2,4,6-triisopropylphenyl)chlorostannyl]chloromethylenefluorene **4**⁷ as a byproduct (eq 2); the formation of the latter is explained by a F/Cl exchange between **2** and LiCl formed



in the reaction (reaction of *t*-BuCl with *t*-BuLi). Both compounds **1** and **4** were isolated in pure form by fractional crystallization.

The molecular structure of **1** in the solid state is shown in Figure 1. The red crystals of **1** are thermally stable and can be handled in air, at least for a short time, and solutions of **1** in usual organic solvents show no change after two weeks. Such stability of this highly strained heterocycle displaying extremely acute angles on tin and carbon atoms in the three-membered ring ($50.7(3)^\circ$, $51.3(3)^\circ$, and $78.2(4)^\circ$, respectively) is very surprising; it is probably due to the large steric protection provided by the Tip groups.

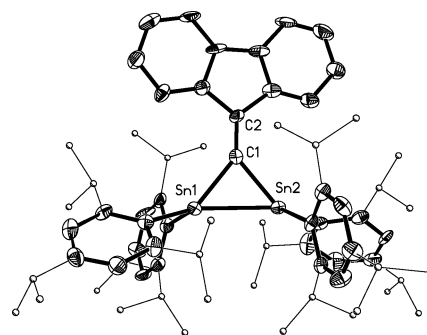


Figure 1. Structure of **1**. Ellipsoids are drawn at 50% probability level. *i*Pr groups are simplified for clarity. Selected bond lengths (Å) and angles (deg): Sn1–Sn2 2.777(2), Sn1–C1 2.209(12), Sn2–C1 2.196(12), C1–C2 1.360(16), Sn1–Sn2–C1 51.1(3), Sn2–C1–Sn1 78.2(4), C1–Sn1–Sn2 50.7(3).

The endo- and exocyclic Sn–C bond lengths (2.17–2.21 Å) lie in the normal range.⁸ The Sn–Sn bond length (2.777(2) Å) is significantly shorter than in other three- or four-membered ring compounds of tin⁹ substituted by the same Tip groups; for example, 2.827(1) Å in a telluradistannirane SnSnTe ,^{10a} 2.942 Å in $(\text{Tip}_2\text{Sn})_3$,^{10b} 2.840(1) Å in a 1,2-distannacyclobutene,^{10c} and 2.889(1) Å in a 1,2-dithiadistannetane SnSnSS .^{10d}

Especially interesting is the environment of the tin atoms: the sums of the bond angles at tin ignoring C1 are 354 and 352.3°; thus, the four ipso carbons of the Tip groups and the two tin atoms lie almost in the same plane. This nearly planar bonding geometry is in remarkable agreement with that found for a closely related disilirane SiSiC with an exocyclic C=C double bond^{11a} and a digermirane GeGeC .^{11b} Similar planar structures were found in other types of three-membered heterocycles containing two Ge, Sn, or Si atoms and a heteroelement such as SnSnX ($X = \text{N},^9 \text{Te}^{10a}$), GeGeX ($X = \text{N},^{11b} \text{S},^{11c} \text{Te}^{11d}$) and SiSiX compounds ($X = \text{O},^{11e} \text{S},^{11f} \text{Se}^{11g}$).

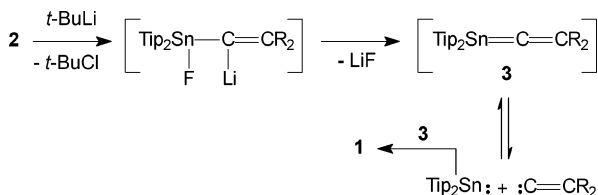
The above results were interpreted in terms of the Dewar–Chatt–Duncanson model of metal olefin bonding.¹² In our case, the short Sn–Sn bond and the almost planarity of Sn atoms also suggest that the bonding in **1** may be intermediate between that in a normal three-membered ring and that of a π -complex (Chart 2).

Chart 2



The reaction mechanism leading to the distannirane **1** is not clear at the moment. One of the possible routes to **1** involves the initial formation of the transient stannaallene **3** according to Scheme 1,

Scheme 1



since the germaallene $\text{Tbt}(\text{Mes})\text{Ge}=\text{C}=\text{CR}_2$ ¹³ (Tbt = 2,4,6-tris-[bis(trimethylsilyl)methyl]phenyl) has been obtained by a similar procedure from $\text{Tbt}(\text{Mes})\text{Ge}(\text{Cl})-\text{C}(\text{Cl})=\text{CR}_2$ and *tert*-butyllithium. More generally, $\text{E}(\text{X})-\text{C}(\text{Cl})=\text{E}'$ (E, E' = Si, Ge, P, As) systems are good precursors of heteroallenes.¹⁴ Stannaallene **3**, because of the probable lability of the tin-carbon double bond, could behave as a stannylene-carbene complex as observed in the related stannaketimine $\text{R}_2\text{Sn}=\text{C}=\text{NMe}$ (R = 2,4,6-tris(trifluoromethyl)phenyl) that behaves as stannylene R_2Sn and isocyanide $\text{C}=\text{NMe}$ in reactions with trapping agents;¹⁵ thus, a [2 + 1] cycloaddition between **3** and the stannylene Tip_2Sn : should lead to **1**.

Similar formations of three-membered ring derivatives from doubly bonded tin compounds have been previously reported: a distannagermirane SnSnGe was obtained by a similar [2 + 1] cycloaddition between a germastannene $>\text{Sn}=\text{Ge}<$ and a stannylene,¹⁶ an azadistanniridine SnSnN between a stannaamine $>\text{Sn}=\text{N}<$ and a stannylene,⁹ and a tristannirane between a stannylene and a distannene.^{8f} Thus, the postulated mechanism to obtain **1** could constitute the first evidence for the formation of a transient stannaallene still unknown, whereas its lighter analogues $>\text{M}=\text{C}=\text{C}<$ (M = Si,¹⁷ Ge^{13,18}) have been isolated.

The study of the chemical reactivity of distannirane **1** and the use of bulkier groups on the tin atom to stabilize the hypothetical stannaallenic intermediate are now under active investigation.

Supporting Information Available: X-ray structural information on **1** and **2** (CIF, ORTEP view of **2**) and experimental details of the preparation of **1**, **2**, and **4** and their physicochemical data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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