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# $^3\Delta$-1,2,3,4-Disilagermastannetene: the first cyclic germastannene*

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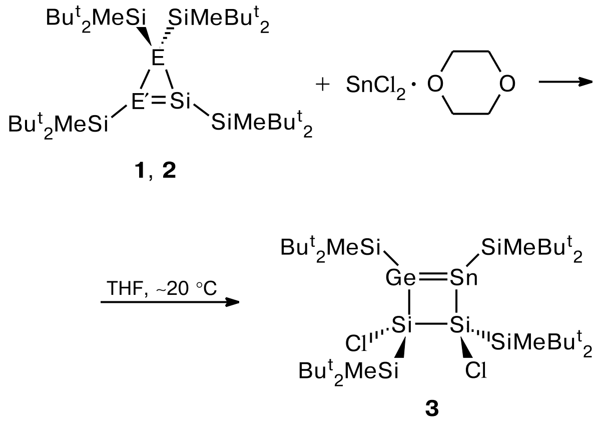
$^3\Delta$-1,2,3,4-Disilagermastannetene, the first cyclic germastannene, was quantitatively synthesized by the reaction of 1- and 2-disilagermirenes with the dichlorostannylene—dioxane complex in THF. The title germastannene is quite stable in the solution, which was explained by the appreciable $\pi$(Ge=Sn)-$\sigma^*$(Si—Cl) orbitals mixing.

**Key words:** disilagermirene, germastannene, disilagermastannetene, dichlorostannylene.

The doubly bonded derivatives of heavier Group 14 elements of the type >E=E< became widely accessible after West's pioneering work on the synthesis of tetramesityldisilene, $Mes_2Si=SiMes_2$, in 1981.[1] Since then, many new stable representatives of this class of highly reactive compounds, so-called dimetallenes, have been synthesized.[2] In contrast to the homonuclear dimetallenes >E=E<, their heteronuclear congeners >E=E′< were unknown as stable compounds until quite recently. The first stable representatives of such compounds, the cyclic germasilenes 2-disilagermirene **1** [3] and 1,2-disila-3-germacyclopenta-2,4-diene[4] incorporating an endocyclic Si=Ge double bond in the three- and five-membered rings respectively, were reported by Lee and Sekiguchi in 2000. The first stable silastannene[5] and germastannenes[6,7] were also reported very recently by Sekiguchi and Weidenbruch groups. The chemistry of the unsaturated three-membered ring compounds, 2- and 1-disilagermirenes **1** and **2**, was found to be extremely interesting, providing easy and fast access to a variety of new cyclic and polycyclic compounds of heavier Group 14 elements.[8] In this communication we report the results of interaction of **1** and **2** with the dichlorostannylene dioxane complex.

The reaction of both **1** and **2** with an equivalent amount of $SnCl_2 \cdot diox$ (diox is 1,4-dioxane) in THF in a sealed tube proceeds very quickly and cleanly to form exclusively one product, *trans*-1,2-dichloro-1,2,3,4-tetrakis[di-*tert*-butyl(methyl)silyl]-$^3\Delta$-1,2,3,4-disilagermastannetene (**3**), which was quantitatively isolated as orange crystals by recrystallization from hexane (Scheme 1). The structure of germastannene **3** was unambiguously determined on the basis of NMR spectra, elemental analysis and X-ray crystallography data. Having no elements of symmetry, germastannene **3** exhibited all non-equivalent methyl and *tert*-butyl groups in the $^1H$ and $^{13}C$ NMR spectra, as well as six distinct resonances for all non-equivalent silicon atoms in the $^{29}Si$ NMR spectrum. The $^{119}Sn$ NMR signal of the endocyclic Sn atom appeared at +439.3 ppm, characteristic of sp$^2$-hybridized Sn atoms.[9] In the UV spectrum of **3**, the longest wavelength absorption band corresponding to a $\pi$—$\pi^*$ electronic transition was observed at 471 nm.

**Scheme 1**



**1:** E = Si, E′ = Ge
**2:** E = Ge, E′ = Si

The structure of **3** was undoubtedly established by X-ray analysis to show a folded four-membered ring (folding angle 23°) with a *trans*-arrangement of the two chlorine atoms. However, the insuperable disorder problems associated with the positional refinement of the doubly bonded Ge and Sn atoms prevented the exact determina-

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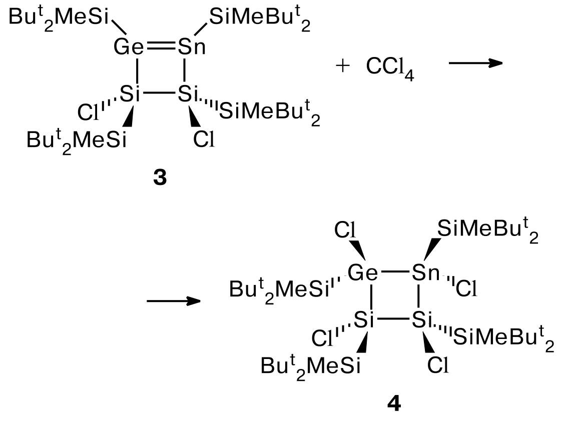
tion of the Ge=Sn double bond length, therefore we do not discuss the details of the crystal structure of **3**.

In contrast to tetrakis(2,4,6-triisopropylphenyl)germastannene synthesized previously,[6] which gradually dissociates in solution at room temperature into germylene and stannylene species, cyclic germastannene **3** does not undergo such dissociation, being indefinitely stable in both non-polar and polar solvents. Such amazing stability of **3** is particularly striking in the light of the apparent weakness of the Ge=Sn double bond and inherent strain of the unsaturated four-membered ring. We can ascribe such abnormal stability of **3** to both electronic and steric stabilization effects of the electropositive σ-donating bulky silyl substituents.[8] Another important factor is the geometry of **3**, favoring appreciable π(Ge=Sn)—σ*(Si—Cl) orbital mixing, which lowers the π-energy level of the Ge=Sn double bond, thus stabilizing the HOMO of the molecule. It is well known that highly electronegative substituents, for example Cl, significantly increase the degree of such π—σ*-conjugation.[10] Although we have already met such a phenomenon in the case of halogen-substituted cyclotrigermenes,[11] in the case of cyclic germastannene **3**, the molecule enjoyed an even more pronounced effect of π—σ*-conjugation due to the more extended delocalized system: one donating π-orbital (Ge=Sn) and two accepting σ*-orbitals (Si—Cl). Such electronic stabilization of the doubly bonded system is similar to the case of *trans*-1,2-dichloro-1,2,3,4-tetrakis[di-*tert*-butyl(methyl)silyl]-$^3\Delta$-1,2,3,4-disiladigermetene previously reported by us.[12]

Being thermally quite stable, germastannene **3** expectedly exhibited a high reactivity of the Ge=Sn double bond towards addition and cycloaddition reactions. Thus, it smoothly and quantitatively reacts with $CCl_4$ to form the 1,2-chlorine addition product across the Ge=Sn double bond, *trans*,*trans*,*trans*-1,2,3,4-tetrachloro-1,2,3,4-tetrakis[di-*tert*-butyl(methyl)silyl]-1,2,3,4-disilagermastannetane **4**, isolated as bright yellow crystals (Scheme 2).

**Scheme 2**



The structure of **4** was established by NMR spectra, elemental analysis and finally confirmed by X-ray crystallography, which revealed a perfectly planar four-membered ring with an all-*trans* arrangement of Cl-substituents. Tetrachloro derivative **4** does not exhibit a downfield shifted resonance in the $^{119}$Sn NMR spectrum, a resonance at +83 ppm was observed instead. The detailed description of the compound **4** will be given in the forthcoming paper.

## Experimental

The $^1$H, $^{13}$C, $^{29}$Si, and $^{119}$Sn NMR spectra were recorded on a Bruker ARX-400FT spectrometer ($^1$H, 400.23; $^{13}$C, 100.64; $^{29}$Si, 79.52; and $^{119}$Sn, 149.26 MHz) for solutions in $C_6D_6$ relatively to $Me_4Si$ ($^1$H, $^{13}$C, and $^{29}$Si) or $Me_4Sn$ ($^{119}$Sn). UV spectra were obtained on a Shimadzu UV-3150 spectrophotometer (hexane solutions).

The starting 1- and 2-disilagermirenes were synthesized as described previously.[3]

1-Disilagermirene **2** (or 2-disilagermirene **1**) (50 mg, 0.07 mmol) and $SnCl_2 \cdot$diox (20 mg, 0.07 mmol) were reacted in dry oxygen-free THF (0.5 mL) in a sealed tube. The reaction immediately took place, and the color of the reaction mixture changed from dark red to dark orange. After evaporation of the solvent, the residue was recrystallized from hexane to give **3** quantitatively as dark orange cubes; m.p. 85—87 °C. Found (%): C, 45.69; H, 8.76. $C_{36}H_{84}Cl_2GeSi_6Sn$. Calculated (%): C, 45.62; H, 8.93. $^1$H NMR (300 MHz), δ: 0.32, 0.37, 0.53, 0.54 (all s, 3 H each, Me); 1.13, 1.15, 1.17, 1.23, 1.30, 1.32, 1.407, 1.413 (all s, 9 H each, Bu$^t$). $^{13}$C NMR (75.47 MHz), δ: –5.4, –5.3, –3.5, –2.8 (all Me); 21.9, 22.3, 22.4, 22.5, 22.6, 23.0, 23.1, 23.2 (all $Me_3\underline{C}$); 29.7 (($\underline{C}H_3)_3C$); 29.8 (2 C, ($\underline{C}H_3)_3C$); 30.0 (($\underline{C}H_3)_3C$); 30.4, 30.6 (2 C each, ($\underline{C}H_3)_3C$)). $^{29}$Si NMR (59.63 MHz), δ: 15.5; 17.3; 22.2, 27.4 (both Si cycl.); 38.8; 54.2. $^{119}$Sn NMR (149.28 MHz), δ: 439.3. UV, $\lambda_{max}$/nm (ε): 471 (8300), 335 (13400), 249 sh (114000).

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