Compounds of Germanium and Tin, 16[◇]

A Tetraaryldistannene with a Long Tin–Tin Multiple Bond and Differing Environments at the Tin Atoms

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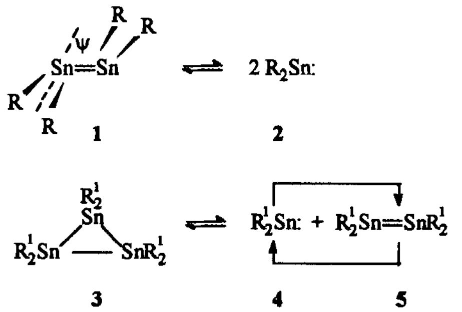
Although tetrakis(2-*tert*-butyl-4,5,6-trimethylphenyl)distannene (**9**), the first tetraaryl-distannene to be reported on, is stable in the solid state, only the monomeric stannylene **8** can be detected in solution. An X-ray crystal structure analysis of **9** reveals a long tin–tin bond length of 291.0(1) pm and a *trans*-bent Sn_2C_4 framework with different fold angles of 21.4° and 64.4°.

Lappert's tetraalkyldistannene **1** was the first molecule to be reported on with a homonuclear double bond between heavier elements of the fourth main group[2,3]. Even though numerous disilenes[4,5] as well as some digermenes[5] – compounds with Si=Si and Ge=Ge double bonds – have been discovered in the meantime, compound **1** has remained as the only structurally characterised distannene. Although **1** is stable in the solid state, it dissociates in solution to two stannylene molecules **2**. The distannene **5**, accessible from thermal or photochemical reaction of the cyclotristannane **3**[6], behaves differently and retains its structural integrity in solution, as evidenced by ^{119}Sn-NMR spectroscopy[6] and trapping reactions[7,8]. However, only the three-membered ring system **2** can be detected in the solid state at room temperature (Scheme 1)[6,9].

Scheme 1

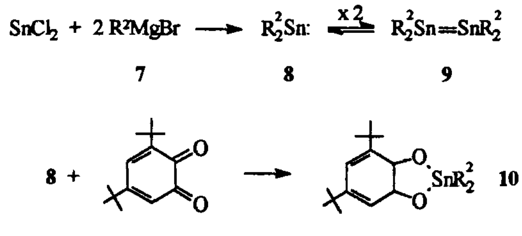


R = $CH(SiMe_3)_2$, R^1 = 2,4,6-$iPr_3C_6H_2$

The apparently promising idea to suppress the formation of the three-membered ring system by replacing the 2,4,6-triisopropylphenyl group in **5** by the even bulkier 2,4,6-tri-*tert*-butylphenyl group was not successful since the thus formed bis(2,4,6-tri-*tert*-butylphenyl)stannylene **6** exists only as the monomer also in the solid state[10]. A weak tin-tin interaction was observed[11] in one of the crystalline forms of the intramolecular donor atom-stabilised molecule $Sn[2,4,6-(CF_3)_3C_6H_2]_2$; however, the separation of 364 pm is much too large for a possible bonding situation[12].

Since the steric overcrowding in **6** was obviously too large for distannene formation, we reduced the steric requirements of the substituents and now report on the formation of the stannylene **8** and the distannene **9** which is stable in the solid state. The reaction of the Grignard compound **7** with tin(II) chloride affords a dark red solution of the stannylene **8**, the constitution of which is substantiated by spectral data and trapping reaction with, for example, 3,5-di-*tert*-butylbenzoquinone to yield the [4 + 1] cycloadduct **10**.

Scheme 2



R^2 = 2-tBu-4,5,6-Me_3C_6H

[◇] Part 15: Ref.[1].

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The ^{119}Sn-NMR spectral data of **8** are of particular interest: at 373 K a sharp signal at $\delta = 1401$ is observed in the same region as the signals for the structurally related stannylenes **4**[8] and **6**[10]. Stepwise lowering of the temperature leads to a broadening of the signal and concomitant shift to higher field until, at 298 K, only a very broad signal at $\delta = 1330$ can be seen; a further decrease in the temperature causes this signal to disappear completely. Accordingly, **8** behaves similarly to **2** since no ^{119}Sn-NMR signals can be observed for the latter at room temperature[13]. The assumption that, in analogy to the equilibrium **1** ⇔ **2**, a rapid equilibrium between **8** and **9** is established upon cooling of the solution was confirmed by the X-ray crystal structure analysis of the black – dark red in thin layers – extremely air-sensitive crystals obtained by crystallisation from an *n*-hexane solution (Figure 1a).

Figure 1a. Molecular structure of **9** (hydrogen atoms omitted). – Selected bond lengths [pm] and angles [°]: Sn(1)–Sn(2) 291.0(1), Sn(1)–C(1) 227.0(5), Sn(1)–C(7) 227.4(5), Sn(2)–C(27) 221.8(5), Sn(2)–C(40) 218.9(5), C(1)–Sn(1)–C(7) 114.4(2), C(27)–Sn(2)–C(40) 114.6(2), Sn(1)–Sn(2)–C(27) 126.3(1), Sn(1)–Sn(2)–C(40) 114.0(1), Sn(2)–Sn(1)–C(1) 109.6(1), Sn(2)–Sn(1)–C(7) 96.3(1)

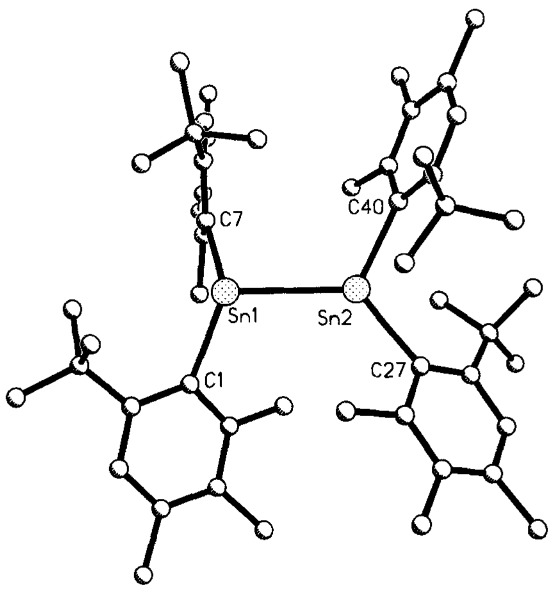
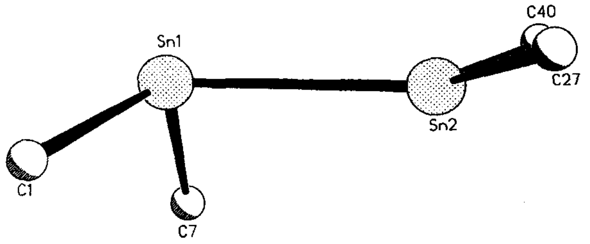


Figure 1b. Side view of the Sn_2C_4 framework of **9**



A conspicuous feature of the structure of **9** is the large tin–tin bond length of 291.0(1) pm which is markedly longer than the typical single-bond length of approx. 278 pm and also exceeds the separation between the tin atoms in **1** by 14 pm[2,3]. The unsymmetrical environments at the two tin atoms in **9** are also unusual. The angular sum at Sn(2) of 354.9° is indicative of a practically planar arrangement with the two *ipso*-carbon atoms and the other tin atom; in contrast, the angular sum of 320.9° at Sn(1) reveals a pronounced pyramidal orientation of its substituents. Altogether, we find a *trans*-bent structure with widely differing fold angles of 64.4° and 21.4° (Figure 1b). In addition, torsion of the Sn_2C_4 skeleton is present as evidenced by the dihedral angles C(1)–Sn(1)–Sn(2)–C(27) of 33.3° und C(7)–Sn(1)–Sn(2)–C(40) of 54.6°. The assumption that this unsymmetrical structure and the long Sn–Sn bond length could be due to additional hydrogen atoms at the two tin centres cannot be substantiated experimentally since no signals for Sn–H bonds are found either in the IR or the ^{1}H-NMR spectrum.

The structure of the ditin compound **9** observed here does not correspond to the calculated, centrosymmetric structure of the parent compound $H_2Sn{=}SnH_2$ for which fold angles between 46° and 51° were predicted[3,14–16]. The structural data indicate rather that, in contrast to **1**, although a donor–acceptor interaction between the doubly occupied 5s orbital of Sn(2) and the empty 5p orbital of Sn(1) does occur, the corresponding interaction Sn(1) → SN(2) is not fully developed. This should be accompanied by a charge separation in which Sn(2) would have a partial positive charge and Sn(1) a partial negative charge. Evidence in support of this situation is provided by the bond lengths between the tin atoms and the *ipso*-carbon atoms: those at Sn(1) are markedly longer than those at Sn(2).

The synthesis of the distannene **1** was thus not only a pioneering achievement in the development of the chemistry of homonuclear multiple bonds between the heavy main group elements but also a lucky coincidence for theoretical chemistry since this untwisted molecule with a *trans*-bent angle of $\psi = 41°$ is almost ideally compatible with the calculated results.

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Experimental

All manipulations were performed by using standard Schlenk techniques under dry argon. – ^{1}H and ^{13}C NMR: Bruker AM 300. – ^{119}Sn NMR (inverse gated, ^{1}H decoupled, Me_4Sn ext.): Bruker AMX 300. – MS: Varian MAT 212. – UV-Vis: Shimadzu UV-260. – Elemental analyses: Analytische Laboratorien, D-51647 Gummersbach, Germany.

Bis(2-tert-butyl-4,5,6-trimethylphenyl)stannylene (**8**) *and Tetrakis(2-tert-butyl-4,5,6-trimethylphenyl)distannene* (**9**): A solution of 1.85 g (9.79 mmol) of anhydrous tin(II) chloride in 30 ml of THF was added dropwise to a solution of approx. 19.6 mmol of **7**, prepared from 5.00 g (19.6 mmol) of 1-bromo-2-*tert*-butyl-4,5,6-trimethylbenzene and 0.48 g (19.6 mmol) of magnesium in 60 ml of THF, at 0 °C over a period of 30 min with stirring. The dark red reaction mixture was stirred for an additional 1 h and then the solvent was removed. The residue was extracted with 80 ml of *n*-hexane and the magnesium salts were filtered off. Concentration of the solution to 20 ml and cooling to −18 °C yielded black crystals which were recrystallized twice from a minimum amount of *n*-hexane to provide 1.37 g (30% yield) of black crystals of **9**, m.p. 125–130 °C. Spectroscopic data for **8**: ^{1}H NMR (C_6D_6, 25 °C): δ = 1.41 (s, 18H, *t*Bu), 1.95 (s, 6H), 2.17 (s, 6H), 2.31 (s, 6H), 7.31 (s, 2H). – ^{13}C NMR (C_6D_6, 25 °C): δ = 15.42, 21.38, 24.04, 33.91, 38.83, 125.63, 129.26, 123.36, 135.51, 140.97, 154.55. – ^{119}Sn NMR ([D_8]toluene, various temperatures): δ = 1401 (373 K), 1385 (broad, 353 K), 1369 (broad, 333 K), 1331 (very broad, 298 K). – MS (CI, isobutane), *m/z* (%): 469 (100) [M$^+$]. – UV-Vis λ_{max} (nm) 479. – $C_{52}H_{76}Sn_2$ (**9**, 938.6): calcd. C 66.54, H 8.16; found C 66.31, H 7.98.

5,7-Di-tert-butyl-2,2-bis(2-tert-butyl-4,5,6-trimethylphenyl)-1,3,2-benzodioxastannole (**10**): A solution of 0.56 g (2.55 mmol) of 3,5-di-*tert*-butyl-1,2-benzoquinone in 20 ml of toluene was added dropwise with stirring to a solution of 1.20 g (2.55 mmol) of **8** in 30 ml of toluene at room temperature over a period of 15 min until the dark-red solution became almost colourless. The reaction mixture was stirred for an additional 30 min and then the toluene was distilled off. The residue was dissolved in 40 ml of *n*-hexane and filtered. The precipitate was recrystallised twice from a minimum amount of *n*-hexane to provide 0.76 g (43%) of colourless rhombic crystals of **10**, m.p. 204 °C. – ^{1}H NMR (C_6D_6, 25 °C): δ = 1.41 (s, 9H), 1.43 (s, 18H), 1.74 (s, 9H), 1.75 (s, 6H), 2.01 (s, 6H), 2.63 (s, 6H), 7.09 (d, 1H, $^4J_{H,H}$ = 2.4 Hz), 7.20 (s, 2H), 7.41 (d, 1H). – ^{13}C NMR (C_6D_6, 25 °C): δ = 16.08, 21.12, 24.68, 30.51, 32.23, 33.16, 34.60, 35.37, 36.51, 111.71, 113.11, 134.49, 135.76, 138.33, 140.37, 141.85, 142.44, 147.62, 152.02, 152.65. – MS (CI, isobutane), *m/z* (%): 690 (56) [M$^+$]. – $C_{40}H_{58}O_2Sn$ (689.6): calcd. C 69.66, H 8.47; found C 69.48, H 8.34.

X-ray Structure Analysis of **9**: $C_{52}H_{76}Sn_2$ (938.6); crystal dimensions 0.65 × 0.85 × 0.95 mm, Siemens P4 diffractometer, ω-scan; temperature 296(2) K; monoclinic; space group $P2_1/c$; a = 1379.1(2), b = 1460.3(2), c = 2392.1(3) pm, β = 90.75(1)°. V = 4817(1) × 10^6 pm^3; $d_{calcd.}$ 1.294 g/cm^3; Z = 4; $2\Theta_{max}$ = 55°; μ(Mo-K_α) = 1.07 mm^{-1}; unique reflections 11040; observed [$F > 3\sigma(F)$] 8906; data-to-parameter ratio 18.3. The structure was solved by direct phase determination using the SHELXTL PLUS programme system and refined by full-matrix least-squares techniques. Hydrogen atoms were placed in calculated positions, and all other atoms were refined anisotropically; R = 0.055, R_w = 0.050; residual electron density 0.60 · 10^{30} e · m^{-3}[17].

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[17] Further details of the crystal structure determination are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-401765, the names of the authors, and the journal citation.

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