Synthesis and Reactivity of Low-Coordinate Compounds, 7[◇]

Reaction of a Stable Silylene with Divalent Group 14 Compounds☆

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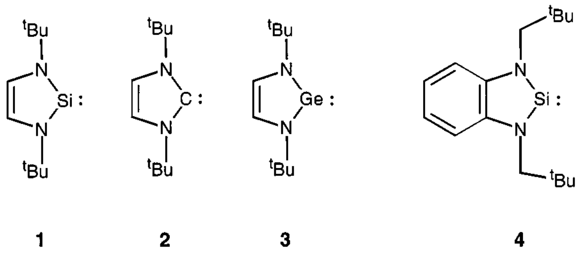
The reaction of the stable silylene **1** (L′Si:) with CO, $SnCl_2$, $PbCl_2$, the stable carbene L′C: (**2**) and the stable germylene L′Ge: (**3**) was investigated as a possible approach for the synthesis of *hetero*-polysilanes (*poly*-carbosilanes, *poly*-germasilanes, *poly*-stannasilanes). The silylene **1** was found to be inert towards all substrates except $SnCl_2$ and $PbCl_2$. Reaction with $SnCl_2$ led to the formation of the yellow, tris(silyl)stannane [(L′SiCl)$_3$SnCl] (**5**) and elemental tin. The photolabile (**5**) was characterized by multinuclear NMR (^{1}H, ^{13}C, ^{29}Si, ^{119}Sn) and single crystal X-ray diffraction: $C_{30}H_{60}Cl_4N_6Si_3Sn$, $M = 849.60$, orthorhombic, space group $Pca2_1$. The bond angles of 115.89 ° (ave. Si–Sn–Si) and 101.87 ° (ave. Cl–Sn–Si) show a slightly flattened tetrahedral geometry around the tin atom. – Thermolysis of **5** at 100 °C led to the deposition of thin films of tin; photolysis resulted in the formation of tin powder. All thermolysis products could be isolated and were characterized as $SnCl_2$, elemental tin, L′Si: (**1**), L′SiCl$_2$ (**6**) and the new disilane L′Si(Cl)-(Cl)SiL′ (**7**). Photolysis led to a reduced product spectrum (formation of Sn + $SnCl_2$ + **7**). Reaction of **1** with $PbCl_2$ gave elemental lead and L′SiCl$_2$ as the only products.

The heavy analogs of carbenes R_2E: (E = Si, Ge, Sn, Pb) are attractive building blocks for the synthesis of inorganic polymers $[R_2E]_n$. *Homo*-polymers of silicon, germanium, and tin are typically obtained by the reduction of the dihalides R_2SiCl_2,[1] R_2GeCl_2,[2] or R_2SnCl_2.[3] These reactions may proceed through the intermediacy of free silylenes, germylenes or stannylenes as reactive intermediates. The unique electronic structure of *poly*-silanes[1], *poly*-germanes[2], and *poly*-stannanes[3] has prompted detailed investigations of their physical properties. The partial replacement of silicon in *poly*-silanes by germanium or tin is of special interest as a 1-dimensional model for Si−Ge and Si−Sn alloys. The dehalogenation of mixtures of dichlorides R_2ECl_2 has been used to obtain copolymers of type $[R_2Si]_n[R'_2Si]_k$[4] and $[R_2Si]_n[R_2Ge]_k$,[4] but the very different susceptibility of the SiCl, GeCl, and SnCl bonds towards reduction limits the scope of the dehalogenation approach.

The recent synthesis of a number of stable carbenes[5][6] and silylenes[7][8] presents a new possible strategy to obtain group 14 polymers by copolymerization of these reactive molecules. We now report preliminary results on the reaction of the stable silylene L′Si (**1**)[7] with the stable divalent group 14 compounds: CO, $SnCl_2$, $PbCl_2$, L′C: (**2**)[9] and L′Ge: (**3**)[10] (Scheme 1).

Scheme 1



The reaction of the stable silylene **4** with the germylenes, stannylenes, and plumbylenes $M[N(SiMe)_3]_2$ (M = Ge, Sn and Pb) was investigated by Gehrhus, Hitchcock, and Lappert and was shown to proceed by insertion of the silylene **4** into the MN bond rather than formation of Si,Ge-, Si,Sn- or Si,Pb copolymers.[8a][8b] Similar MN insertion products were obtained by Weidenbruch et al. from the reaction of a stable diaminogermylene with a stable diaminosilylene.[8c]

No reaction was observed between the silylene **1** (L′Si:) and CO, L′C: or L′Ge: or any other combination of these compounds even after prolonged heating to 150 °C in sealed NMR tubes. Rapid reaction occurred between **1** and tin(II) chloride, however, to give the tris(silyl)stannane **5**.[11]

Compound **5** was characterized by multinuclear NMR (^{1}H, ^{13}C, ^{29}Si, and ^{119}Sn)[11], CI-MS[11] and single crystal X-ray diffraction[12][19] as a tris(silyl)stannane with Sn^{IV} and Si^{IV} centers. The oxidation of both divalent silicon and

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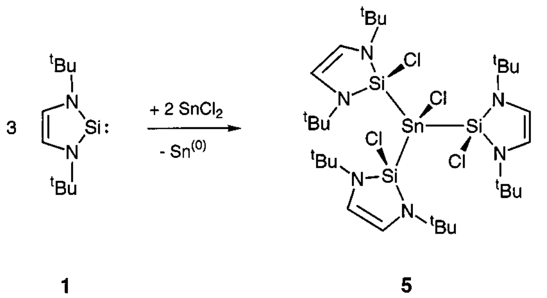
[◇] Part 6: Ref.[6].

1434−1948/98/0808−1067 $ 17.50+.50/0



tin in the course of the reaction is balanced by the formation of a stoichiometric amount of metallic tin. Compound **5** can be stored at −10 °C in the dark for months, but slowly decompose to give deposits of metallic tin at r. t. especially if exposed to light.

The decomposition of **5** under thermolytic[13] or photolytic[14] conditions follows different pathways. Both reactions lead to a fragmentation of the Si_3Sn framework and the formation of the disilane **7**.[15] Elemental tin is deposited as film (thermolysis) or powder (photolysis). Under thermolytic conditions, the silylene **1**,[7a] and the silane **6**[7a] are formed as additional products. The thermolytic decomposition pathway of **5** matches the CI-MS fragmentation pattern[11] (high abundance of the fragments $[L'Si:]^{+\bullet}$ and $[L'SiCl_2]^{+\bullet}$).

The crystal structure of **5**[12][19] (Figure 1) shows the tin atom in a distorted tetrahedral environment. The Si−Sn−Si bond angles (114.60−116.70°) and Si−Sn−Cl bond angles (100.07−102.96°) deviate from the ideal tetrahedral geometry. Few structural data are available on silyl-stannanes, but the Si-Sn bond distances in **5** (263.0−264.2 pm) closely match those reported for the recently characterized silylstannanes $[(Me_3Si)_3Si]_2SnCl_2$ (259.7−260.4 pm)[16] and $[(Me_3Si)_3Sn]_2$ (260.9−261.1 pm).[17]

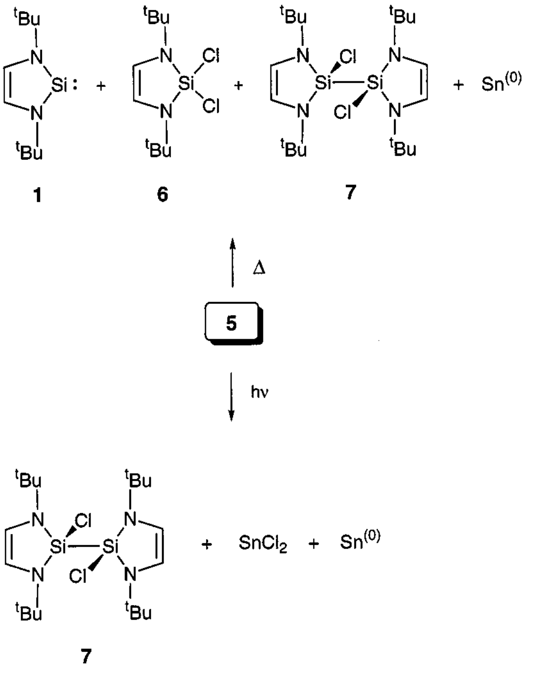
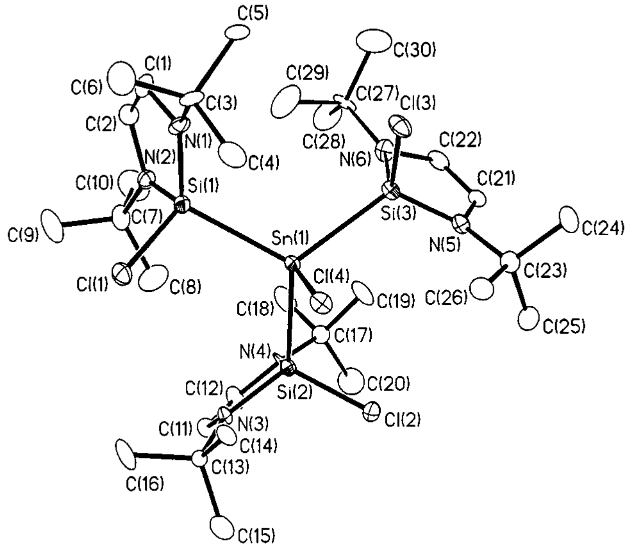


Figure 1. Molecular structure of **5** (ORTEP plot, 50% probability level, hydrogen atoms have been omitted for clarity)[a]



[a] Selected bond lengths [pm] and angles [°]: Sn(1)−Cl(4) 238.8(3), Sn(1)−Si(1) 263.0(4), Sn(1)−Si(2) 264.2(4), Sn(1)−Si(3) 264.0(3), Cl(1)−Si(1) 211.2(5), Cl(2)−Si(2) 209.3(5), Cl(3)−Si(3) 211.6(4); Cl(4)−Sn(1)−Si(1) 102.96(11), Cl(4)−Sn(1)−Si(2) 102.57(13), Cl(4)−Sn(1)−Si(3) 100.07(12), Si(1)−Sn(1)−Si(2) 116.38(11), Si(1)−Sn(1)−Si(3) 116.7(2), Si(2)−Sn(1)−Si(3) 114.60(12); Torsional angles: Cl(4)−Sn(1)−Si(1)−Cl(1) −50.15(0.18), Cl(4)−Sn(1)−Si(3)−Cl(3) −50.50(0.23), Cl(4)−Sn(1)−Si(2)−Cl(2) −47.95(0.17)

The normal Si−Sn bond distances, and especially the fact that the Si−Sn bonds of **5** are freely rotating in solution (equivalence of 6 *t*Bu groups and 6 ring protons in the ^1H NMR at r.t.), show that **5** is free of strong steric congestion. By contrast, the disilane L′Si(Cl)−(Cl)SiL′ (**7**, vide infra) shows hindered rotation of the *t*Bu-groups at r.t, as evidenced by the broad signals found for the methyl groups in the ^1H- and ^{13}C-spectrum. The $(SiCl)_3Sn-Cl$ framework has the idealized symmetry C_3, with Cl−Sn−Si−Cl torsional angles ranging from −47.95 to −50.15.

The reaction of **1** with $PbCl_2$ leads to the clean formation of elemental lead (powder) and $L'SiCl_2$ (**6**) as the only products.

Stable silylenes of type **1** can at present only be obtained by reduction of the corresponding dihalosilanes R_2SiCl_2 with potassium at elevated temperatures[7a]. The thermolytic generation of **1** from a stannylsilane such as **5** presents a potential alternative synthetic approach. The stannylsilanes $L'Si(SnR_3)(Cl)$ and $L'Si(SnR_3)_2$ are now under investigation as new precursors for stable silylenes.

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Experimental Section

General: All reactions were carried out under argon (99.994% purity) with usual Schlenk equipment or inside an inert-gas glovebox (O_2 and H_2O < 1 ppm). Solvents were purified by distillation over benzophenone/potassium (THF, hexanes, benzene) or by 30 minute sonication with CaH_2. − IR: Nicolet. − NMR: Varian Gemini 200, Unity 400 and 500. − The starting materials L′Si (**1**)[7a] L′C: (**2**)[9] and L′Ge: (**3**)[10] were obtained according to published procedures. The compounds **1−3** were purified by sublimation under exclusion of air and moisture. Anhydrous $SnCl_2$ was used as received (Aldrich). Reactions of **1** with CO, L′C: and L′Ge: were studied in ca. 5 wt.-% solutions in C_6D_6. Flame sealed samples were heated to 150°C for 4 weeks in 5-mm NMR tubes. For the synthesis and characterization of **6** see reference[7a].

Synthesis of **5**: $SnCl_2$ (10.0 mmol, 1.896 g) is added to a solution of the silylene **1** (20.0 mmol, 3.927 g) in 15 ml of THF at −10°C. The reaction mixture turns red and the starting material is completely consumed after 60 min. The crude reaction mixture contains **5** (> 85%) and small amounts (ca. 5%) of **6** and **7**. Analytically pure $(L'SiCl)_3SnCl$ (**5**) is isolated from the crude reaction mixture by chromatography on Celite (hexane as eluent), followed by recrystallization from toluene as orange crystals (46%) that decompose at 172°C without melting.

☆) Dedicated to Professor *Heinrich Nöth* on the occasion of his 70th birthday.

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[11] $(L'SiCl)_3SnCl$ (**5**): ^1H NMR (200 MHz, C_6D_6): δ 1.45 (s, 54 H, CH_3), 5.83 [s, 6 H, $=CH$, tin satellites corresponding to $^4J(^1H,^{117/119}Sn) = 7.8$ Hz]. − ^{13}C NMR (100 MHz, C_6D_6): δ 31.43 [q, $^1J(C,H) = 121.5$ Hz, CH_3], 53.13 [s, $C(CH_3)_3$], 115.33 [dd, $^1J(C,H) = 181.6$ Hz, $^2J(C,H) = 8.8$ Hz, $=CH$]. − ^{29}Si NMR (79.0 MHz, C_6D_6): δ −20.08 [$^1J(^{29}Si,^{117}Sn) = 881$ Hz, $^1J(^{29}Si,^{119}Sn) = 923$ Hz]. − ^{119}Sn NMR (186.0 MHz, C_6D_6): −222.6 ppm [$^1J(^{29}Si,^{119}Sn) = 922$ Hz]. − CI-MS (+, *iso*-butane) *m*/*z* (rel. int.): 849 $[M + 1]^+$ (1), 582 $[M^{+\bullet} - L'Si:]$ (2), 462 (11), 266 $[L'SiCl_2]^{+\bullet}$ (90), 196 $[L'Si]^{+\bullet}$ (100). − IR (nujol): ν = cm^{-1}: 3107 w, 1639 m, 1598 m, 1393 m, 1368 s, 1343 m, 1270 s, 1212 s, 1196 s, 1122 s, 1106 s, 1089 s, 1048 s, 999 s, 810 m, 744 s, 663 s, 647 s.

[12] *X-ray Crystallographic* Study[19]: $C_{30}H_{60}Cl_4N_6Si_3Sn$, **5**, $M = 849.60$, orthorhombic, space group $Pca2_1$, $a = 11.365(3)$ A, $b = 18.999(4)$ A, $c = 19.808(5)$ A, $V = 4277(2)$ A^3, $Z = 4$, $D(calc.) = 1.319$ g/cm³, $\mu = 0.959$ mm^{-1}. Data were collected on an Siemens P4 diffractometer using graphite monochromator, λ (Mo-K_α) = 0.71073 A. The intensities of standard reflections measured every 97 reflections showed no decay. The data were corrected for Lorentz and polarization effects and semiempirical absorption correction was applied using ψ-scans. Minimum and maximum absorption corrections were 0.5712 and 0.5276. The structure were solved and refined using the SHELXTL\PC[18] package. Refinement was by full-matrix least-squares on F^2 using all data (negative intensities included). The weighting scheme was $w = 1/[\sigma^2(F_o^2) + (0.00295P)^2 + 4.7P]$ where $P = (F_o^2 + F_c^2)/3$. Hydrogen atoms were included in fixed positions and treated as riding atoms. Maximum residual electron densities were +0.875 and −0.557 e/A^3.

[13] Sealed NMR samples of **5** in C_6D_6 were monitored by ^1H, ^{13}C, and ^{29}Si NMR. After 3 h at 100°C, the decomposition was complete and L′Si: (**1**), $L'SiCl_2$ (**6**) and L′Si(Cl)−(Cl)SiL′ (**7**) were formed in the molar ratio 2:6:3 (^1H NMR). The NMR tubes were stored "upside down" during the thermolysis to prevent the formation of a tin film in the bottom part of the NMR tube.

[14] Irradiation of **5** (5% in hexanes) in a quartz tube for 6 days resulted in 60% conversion of **5** to L′Si(Cl)−(Cl)SiL′ (**7**), $SnCl_2$ and tin powder as sole products.

[15] The disilane **7** has been obtained earlier in our group from reactions of **1** with different chlorinating agents. L′Si(Cl)−(Cl)SiL′ (**7**): ^1H NMR (200 MHz, C_6D_6): δ 1.25−1.50 (br, 36 H, CH_3), 5.8 (s, 4 H, $=CH$). − ^{13}C NMR (100 MHz, C_6D_6): δ 30.25−31.50 (br, CH_3), 52.88 [s, $C(CH_3)_3$], 114.08 ($=CH$). − ^{29}Si NMR (79.0 MHz, C_6D_6): δ −33.18. EI-MS (40 eV) *m*/*z* (rel. int.): 466 (4), 465 (5), 464 (14), 463 (7), 462 (20), 295 (6), 294 (3), 293 (9), 270 (7), 269 (6), 268 (39), 267 (10), 266 (55) $L'SiCl_2 = [M - L'Si:]^{+\bullet}$, 253 (2), 251 (3), 239 (11), 238 (7), 237 (15), 236 (5), 233 (8), 232 (4), 231 (22) $[L'Si-Cl]^+$, 222 (3), 214 (7), 213 (6), 212 (36), 211 (12), 210 (51), 209 (7), 198 (6), 197 (20), 196 (100) $[L'Si]^{+\bullet}$, 195 (5), 158 (9), 156 (7), 156 (41), 155 (12), 154 (62), 153 (7), 140 (21), 133 (3), 125 (16), 121 (32), 120 (12), 119 (87), 99 (5), 94 (4), 92 (10), 85 (14), 84 (53), 83 (3), 57

(8). The identity of the compound has also been confirmed by single crystal X-ray diffraction (M. Denk, unpublished results).

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[19] Crystallographic data (excluding structure factors) for the structure of **5** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101272. Copies of the data can be obtained free of charge on applications to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: Int. Code +44(0)1223/ 336-033. E-mail: deposit@chemcrys.cam.ac.uk).

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