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Trichlorosilylation of chlorogermanes and chlorostannanes with $HSiCl_3/Net_3$ followed by base-catalysed formation of $(Me_3Ge)_2Si(SiCl_3)_2$ and related branched stannylsilanes☆

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Abstract

Chlorotrimethylgermane **1** and dichlorodimethylgermane **4** react with trichlorosilane and triethylamine to provide trichlorosilylgermanes $Me_{4-n}Ge(SiCl_3)_n$ ($n = 1$: **2**; $n = 2$: **5**) in fair yields, as distillable liquids. The formation of **2** is followed by base-catalysed decomposition reactions leading to novel solid $(Me_3Ge)_2Si(SiCl_3)_2$ **3**. Chlorotrialkylstannanes **6a**–**c** (**6a**: $R = CH_3$, **6b**: $R = C_2H_5$, **6c**: $R = n\text{-}C_4H_9$) react with trichlorosilane and triethylamine providing the branched silylstannanes $(R_3Sn)_2Si(SiCl_3)_2$ **7a**–**c** and traces of silylstannanes $R_3SnSiCl_3$ **8a**–**c**. Only **7a** was isolated in a pure state. Heating **7a** or crude **7b** and **7c** with benzyl chloride leads to the formation of benzyltrichlorosilane (**10**). The constitution of compounds **2**, **3**, **5** and **7a** was confirmed by MS, NMR and analytical data. The structures of C_6D_6-solvated **3** and C_6H_6-solvated **7a** were determined by X-ray diffraction, and shown to be isotypic.

Keywords: Organotin chlorides; Organogermanium chlorides; Trichlorosilane; Silylgermanes; Silylstannanes; Disproportionation

1. Introduction

Trihalogenosilyl compounds are of general importance as trifunctional precursors for the synthesis of highly functionalised silicon compounds, such as branched silicones and silsesquioxanes. Trichlorosilylstannanes and related germanes, being a kind of α-halogen(metal)silane, would be most desirable precursors for further transformations. According to Benkeser, trichlorosilane/triethylamine is a very useful reagent for the synthesis of organic trichlorosilanes from the related alkyl or acyl halides [1,2].

Recently, the application of the Benkeser reaction to organophosphorus halides led to an extremely useful new trichlorosilylphosphane synthesis [3,4], in addition to the known route using hexachlorodisilane [5–7].

$$RCl + HSiCl_3 + NEt_3 \rightarrow RSiCl_3 + HNEt_3Cl \text{ (Refs. [1,2])} \quad (1)$$

$$R_2PCl + HSiCl_3 + NEt_3 \rightarrow R_2PSiCl_3 + HNEt_3Cl \text{ (Refs. [3,4])} \quad (2)$$

We also found that trichlorosilane/triethylamine even reacts with chlorotrimethylstannane **6a** in a straightforward way producing a solid trichlorosilyl stannane that we believed to be $Me_3SnSiCl_3$ **8a** [4]. Similarly, $Me_3SiSiCl_3$ had been reported to be formed by the reaction of $HSiCl_3/NEt_3$ with trimethylsilyl triflate [8].

☆ Dedicated to Professor Reinhard Schmutzler on the occasion of his 65th birthday.

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When we extended this type of reaction to chlorotrimethylgermane **1**, we were surprised that, depending on the reaction time and the work-up procedure, two different products—a liquid or a solid—of similar carbon and hydrogen content could be isolated. This observation led us to reinvestigate the reaction of chlorotrimethylstannane **6a** with trichlorosilane/triethylamine and to extend it to other trialkylchlorostannanes **6b** and **6c** by following the course of the reactions by ^{119}Sn- and ^{29}Si-NMR. In the following we will report surprising results on the Benkeser reaction applied to methylchlorogermanes and we will show that, contrary to our previous report [4], trichlorosilylstannanes $R_3SnSiCl_3$ **8a–c** have only a short lifetime under the conditions of the Benkeser reaction. Novel branched silylstannanes $(R_3Sn)_2Si(SiCl_3)_2$ **7a–c** are the main products.

2. Results and discussion

2.1. Reactions of Me_3GeCl and Me_2GeCl_2 with $HSiCl_3/NEt_3$

Chlorotrimethylgermane **1** reacts with the trichlorosilane/triethylamine reagent at room temperature (r.t.) in pentane solution with precipitation of triethylammonium chloride leading to trichlorosilyltrimethylgermane **2** as the main product, which was identified by singlet signals in the ^{1}H-, ^{13}C- and ^{29}Si-NMR spectra of the reaction mixture.

$$\underset{\mathbf{1}}{Me_3GeCl} + HSiCl_3 + NEt_3 \rightarrow \underset{\mathbf{2}}{Me_3GeSiCl_3} + HNEt_3Cl \quad (3)$$

$$4\underset{\mathbf{2}}{Me_3GeSiCl_3} \xrightarrow{NEt_3} \underset{\mathbf{3}}{(Me_3Ge)_2Si(SiCl_3)_2} + SiCl_4 + 2\underset{\mathbf{1}}{Me_3GeCl} \quad (4)$$

However, when the mixture was stirred for several days, the intensity of the NMR-signals of compound **2** decreased in favour of another set of ^{1}H-, ^{13}C- and ^{29}Si-NMR singlet signals of the novel species **3**; some chlorotrimethylgermane **1** and small amounts of other unidentified compounds were also present. Species **3** became the main product after several days. The ^{29}Si-NMR spectra of a more concentrated solution revealed that the spectrum of the new compound **3** exhibits two ^{29}Si resonances, one at 17 ppm (close to that of compound **2**) and a weaker one far upfield at -84 ppm. Work-up of reaction mixtures from **1** with $HSiCl_3/NEt_3$ after moderate reaction time (20 h) by filtration and evaporation of the solvent and distillation furnished pure **2** in a ca. 50% yield as a colourless liquid. Compound **2** gave satisfactory elemental analyses and displayed its molecular ion by mass spectroscopy. Its physical data are different from those previously reported [7]. The pure compound is moisture-sensitive, but thermally quite stable. Work-up of reaction mixtures from **1** with $HSiCl_3/NEt_3$ after several days by filtration and evaporation of the solvent gave a yellowish waxy solid (ca. 40% crude yield). After dissolving the residue in C_6D_6, colourless crystals of C_6D_6-solvated **3** separated from the solution. Long drying of the crystals at 0.05 mbar led to **3** as an amorphous solid that gave satisfactory analytical data.

Its molecular ion in the mass spectrum, its elemental analysis, and its ^{29}Si-NMR spectrum (as well as the comparison with the related tin compound) suggested that **3** is $(Me_3Ge)_2Si(SiCl_3)_2$. Final proof was provided by an X-ray structure determination (see below).

Elemental analyses of several samples of **3** (increased C, H content) indicate that the removal of solvent molecules, especially aromatic hydrocarbons, from **3** is difficult. The C, H content of such samples can be (deceptively) rather similar to that of **2**. Single crystals of **3** from C_6D_6 solutions contain one equivalent of C_6D_6.

Dichlorodimethylgermane **4** reacts with the trichlorosilane/triethylamine reagent at r.t. in pentane solution with precipitation of triethylammonium chloride. Work-up after 10 days stirring provided dimethylbis(trichlorosilyl)germane **5**.

$$\underset{\mathbf{4}}{Me_2GeCl_2} + 2HSiCl_3 + 2NEt_3 \rightarrow \underset{\mathbf{5}}{Me_2Ge(SiCl_3)_2} + 2HNEt_3Cl \quad (5)$$

Surprisingly, a decomposition reaction of **5**, related to that of **2** to **3** (Eq. (4)), was not observed even when the work-up procedure was untertaken after several weeks. Distillation furnished pure **5** in very good yield as a colourless liquid. Compound **5** gave satisfactory elemental analyses and displayed its molecular ion by mass spectroscopy. Compound **5** is thermally stable, but sensitive to moisture.

The observation that the yield of **2** but not that of **5** was affected by long reaction times, implies that **2** decomposes steadily under the reaction conditions (presence of NEt_3, $HNEt_3Cl$) whereas **5** does not. Experimental evidence was provided by addition of a small amount of NEt_3 to pure distilled **2** and **5** in NMR tubes. After 2 days at r.t. ca. 50% of **2** was decomposed (formation of **3**, Me_3GeCl **1** and $SiCl_4$), whereas **5** was still completely unchanged.

More systematic studies concerning the different behaviour of **2** and **5** towards nucleophiles are under way.

Attempted extension of the Benkeser reaction to $MeGeCl_3$ and $GeCl_4$ was apparently accompanied by reduction; no single product could be isolated from the reaction mixtures.

2.2. Reactions of trialkylchlorostannanes with $HSiCl_3/NEt_3$

The reactions of trialkylchlorostannanes R_3SnCl (**6a**:

R = Me, **6b**: R = Et, **6c**: R = *n*-Bu) with the trichlorosilane/triethylamine reagent were monitored by ^{13}C-, ^{119}Sn- and ^{29}Si-NMR. Typically, triethylamine was added dropwise to mixtures of the chlorostannane with trichlorosilane.

2.2.1. Reaction of chlorotrimethylstannane **6a** with $HSiCl_3/NEt_3$

Within 3 days at r.t. in pentane, ca. 25% of chlorotrimethylstannane **6a** (its ^{119}Sn-NMR resonance in the reaction mixture, δ ^{119}Sn = + 117 ppm, indicating coordination with triethylamine) was converted into a new tin compound **7a** that exhibits a δ ^{119}Sn signal at − 53 ppm [4,7] and traces of $Me_3SnSiCl_3$ **8a** (δ ^{119}Sn = − 70 ppm). To complete the reaction as far as possible, stirring continued for 2 weeks. After separation of the solution from the triethylammonium chloride residue, the crude compound $(Me_3Sn)_2Si(SiCl_3)_2$ (**7a**) was obtained in a ca. 40% yield. Several days after dissolving **7a** in benzene, colourless crystals of benzene-solvated **7a** had separated. Removal of benzene at 0.05 mbar gave **7a** as an amorphous colourless solid that gave satisfactory analytical data. In an EI MS, the molecular ion of **7a** showed the expected, characteristic isotopic pattern.

$$\underset{\mathbf{6a-c}}{R_3SnCl} + HSiCl_3 + NEt_3 \rightarrow \underset{\mathbf{8a-c}}{R_3SnSiCl_3} + HNEt_3Cl \tag{6}$$

a: R = Me; **b**: R = Et, **c**: R = *n*-Bu

$$4\underset{\mathbf{8a-c}}{R_3SnSiCl_3} \xrightarrow{NEt_3} \underset{\mathbf{7a-c}}{(R_3Sn)_2Si(SiCl_3)_2} + SiCl_4 + 2R_3SnCl \tag{7}$$

2.2.2. Reaction of chlorotriethylstannane **6b** with $HSiCl_3/NEt_3$

Upon addition of triethylamine to $Et_3SnCl/HSiCl_3$, Et_3NHCl spontaneously crystallises. However, after 7 days of stirring, a ^{119}Sn-NMR spectrum shows that ca. 50% of **6b** is still unconsumed. Within 31 days, ca. 80% consumption of **6b** was confirmed by NMR. In addition to the signals of starting material **6b** and main product **7b**, another small signal at δ ^{119}Sn = − 59 ppm assignable to $Et_3SnSiCl_3$ **8b** was also observed. Isolation of pure **7b** was not achieved.

2.2.3. Reaction of chlorotri-n-butylstannane **6c** with $HSiCl_3/NEt_3$

At an early stage of the reaction, unconsumed **6c** is accompanied by **7c** (δ ^{119}Sn = − 53 ppm), and traces of **8c** (δ ^{119}Sn = − 71.8 ppm) and a third new compound **9c** (δ ^{119}Sn = − 46.8 ppm). After 4 days, work-up by removal of Et_3NHCl and pentane gave a liquid that still contained 50% of **6c** in addition to the branched silylstannane **7c**. Distillation at 106°C/0.1 mbar allowed the removal of **6c**, but attempts to isolate **7c** from the residue failed. Enrichment of **7c** up to ca. 85% was achieved by addition of an excess of $HSiCl_3$ and NEt_3 to a crude liquid mixture of **6c** and **7c** in pentane and stirring for another month. Enriched **7c** was accompanied by **6c** and small amounts of **8c**.

In a further experiment, **6c** was treated with four equivalents of the $HSiCl_3/NEt_3$ reagent. Under these conditions, **7c** was accompanied by ca. 15% of compound **9c**. A ^{29}Si-NMR spectrum of the mixture revealed, that, like **7c** (δ ^{29}Si = + 21 and − 107.7 ppm), **9c** contains trichlorosilyl groups and a central silicon atom (δ ^{29}Si = + 12 and − 88.3 ppm). We propose that **9c** is n-$Bu_3SnSi(SiCl_3)_3$.

In additional experiments, we investigated whether compounds **7a**–**c** could be used as alternative to the *Benkeser*-like trichlorosilylation of benzyl chloride with $HSiCl_3/NEt_3$. Decomposing samples containing **7a**–**c** by heating them with excess benzyl chloride provided benzyltrichlorosilane (**10**) accompanied by the trialkylchlorostannanes **6a**–**c**. Following the reactions with the help of ^{13}C-, ^{29}Si-, and ^{119}Sn-NMR spectra indicated that heating was required in each case and that (impure) **7b** and **7c** reacted faster than **7a**.

$$\underset{\mathbf{7a-c}}{(R_3Sn)_2Si(SiCl_3)_2} + C_6H_5CH_2Cl \rightarrow \underset{\mathbf{10}}{C_6H_5CH_2SiCl_3} + \underset{\mathbf{6a-c}}{R_3SnCl} \tag{8}$$

$$\underset{\mathbf{7a-c}}{(Me_3Sn)_2Si(SiCl_3)_2} \xrightarrow{h\nu} \underset{\mathbf{8a}}{Me_3SnSiCl_3} + \underset{\mathbf{8a}}{Me_3SnCl} + Me_2SnCl_2 \tag{9}$$

A first experiment concerning the photochemical cleavage of compound **7a** was also carried out: UV-irradiating a benzene solution (twice 45 min) of **7a** led to 50% decomposition. Analysis of the mixture after removal of the solvent by ^{13}C- and ^{119}Sn-NMR and by EI MS allowed the detection of compounds **6a** (ca. 50% relative to unconsumed **7a** (≡ 100%), from the ^{119}Sn signal intensity), **8a** (ca. 40%) and Me_2SnCl_2 (ca. 20%). The persistence of significant amounts of **8a** in the absence of base deserves further interest. Base-catalysed decomposition is obviously a common feature of compounds Me_3MSiCl_3 (M = Si [12], Ge, Sn).

2.3. NMR spectra and structure determination

Heteronuclear NMR data of **2**, **3**, **5** and **7a**–**c** and observed ^{119}Sn resonances of **8a**–**c** are collected in Table 1. Compounds **2**, **3**, **5** and **7a** give ^{1}H and ^{13}C-NMR singlets of the CH_3 groups, as well as ^{29}Si-NMR resonances of the $SiCl_3$ groups. The decisive distinction between compounds **2** and **3** and between **7** and **8**/**9** can be made on the basis of additional weaker ^{29}Si resonances in the upfield region (**3**: − 84, **7a**: − 106.4, **7b**: − 108.2, **7c**: − 107.4, **9c**: − 88.3 ppm). These resonances are comparable with those of the central silicon atoms of neopentane-like branched silanes such as $Si(SiCl_3)_4$ [9]. A ^{29}Si-CP-MAS measurement on an amorphous solid sample of **7a** indicates

Table 1
^{13}C-, ^{29}Si- and ^{119}Sn-NMR shifts of trichlorosilyl derivatives of C, Si, Ge and Sn and reference compounds

	$\delta\,^{13}$C	$\delta\,^{29}$Si	$\delta\,^{119}$Sn
Me_3CSiCl_3	$+24.37$ [$\underline{C}H_3$], $+26.14$ [$\underline{C}C_3$]	$+17.3$	
$Me_3SiSiCl_3$ [12]	*	$+17.5$ [$\underline{Si}Cl_3$], -7.2 [$\underline{Si}C_3$]	
$Me_3GeSiCl_3$ **2**	-2.8	$+17.8$	
$Me_3SnSiCl_3$ **8a**	-8.6	*	-70
$Et_3SnSiCl_3$ **8b**	*	*	-59
n-$Bu_3SnSiCl_3$ **8c**	*	*	-71.8
$Me_3SnSiMe_3$ [13]	$+1.13$ [$\underline{C}Si$], -11.52 [$\underline{C}Sn$]	-11.0	-126.7
$Me_2Ge(SiCl_3)_2$ **5**	-5.8	$+13.1$	
$Si(SiCl_3)_4$ [9]		$+3.5$ [$\underline{Si}Cl_3$], -80.0 [$\underline{Si}Si_4$]	
$(Me_3Ge)_2Si(SiCl_3)_2$ **3**	$+0.8$	$+17.2$ [$\underline{Si}Cl_3$], -84.2 [$Ge_2\underline{Si}Si_2$]	
$(Me_3Sn)_2Si(SiCl_3)_2$ **7a**	-8.0	$+19.6$ [$\underline{Si}Cl_3$], -106.4 [$Sn_2\underline{Si}Si_2$]	-55.2
^{29}Si-CP-MAS-NMR of **7a**		$+19$ [$\underline{Si}Cl_3$], -112 [$Sn_2\underline{Si}Si_2$]	
$(Et_3Sn)_2Si(SiCl_3)_2$ **7b**	$+3.8$ [$Sn\underline{C}$], $+12.1$ [$SnC\underline{C}$]	$+21.0$ [$\underline{Si}Cl_3$], -108.2 [$Sn_2\underline{Si}Si_2$]	-45.0
(*n*-$Bu_3Sn)_2Si(SiCl_3)_2$ **7c**	$+12.2$ [$Sn\underline{C}$], $+14.0$ [$SnC_3\underline{C}$], $+27.8$ [$SnC_2\underline{C}$], $+30.3$ [$SnC\underline{C}$]	$+21.3$ [$\underline{Si}Cl_3$], -107.4 [$Sn_2\underline{Si}Si_2$]	-52.7
n-$Bu_3SnSi(SiCl_3)_3$ **9c**		$+12.0$ [$\underline{Si}Cl_3$], -88.3 [$Sn\underline{Si}Si_3$]	-46.8

* Not available.

that the same kind of neopentane-related species $(Me_3Sn)_2Si(SiCl_3)_2$ **7a** exists in solution and in the solid state. ^{119}Sn-NMR spectra of compounds **7a**–**c** reveal that the resonances previously assigned to $Me_3SnSiCl_3$ **8a** [4,7] are in fact those of the branched compound **7a**. Due to insufficient resolution of the corresponding ^{29}Si-NMR spectra, a safe assignment of the 200 ± 1 Hz satellite pair in the ^{119}Sn-NMR spectrum of **7a** [J(SnSi) or J(SnSn), previously assigned to J(SnSi) of **8a**) cannot yet be made [4,7]. In the ^{29}Si-NMR spectrum of **7c**, $^1J(^{117,\,119}\mathrm{Sn}, ^{29}\mathrm{Si})$ was well resolved (92/89 Hz). The ^{119}Sn resonances of compounds **8** appear ca. 14–17 ppm upfield from those of the related branched compounds **7a**–**c**. Satisfactorily resolved ^{29}Si-NMR spectra of compounds **8a**–**c** were not yet obtained. Similar to **8a**, the previous assignments of the ^{13}C- and ^{29}Si-NMR-data of compound **2** (obtained from R_2PGeMe_3/Si_2Cl_6) were incorrect [7]. At present, the R_2PMMe_3/Si_2Cl_6 reaction (M = Ge, Sn) is under reinvestigation. The mode of decomposition of **2** and **8** and the formation of **3** and of related Si–Sn compounds **7a**–**c** deserves further study.

Definitive evidence for the formation of novel branched compounds **3** and **7a**–**c** is provided by the structure determination of solid **3** and **7a**, which are isotypic. The molecular structure and a cell plot of **3** solvated with one equivalent of C_6D_6 are depicted in Figs. 1 and 2, respectively.

The coordination geometry of the central Si atom of **3** and **7a** is slightly distorted tetrahedral. The angles Ge–Si–Ge of **3** and Sn–Si–Sn of **7a** are expanded to ca. 116° at the expense of $<$Si–Si–Si (104° for **3** and 105° for **7a**), i.e. the trimethylgermyl groups within **3** and the trimethystannyl groups within **7a** appear to be slightly more bulky than trichlorosilyl groups. Consistent with this, Cl–Si–Cl angles (106.20–107.08°) of **3** are smaller than C–Ge–C (110.0–111.5°) and Si–Cl bonds (2.037–2.042 Å) are longer than Ge–C bonds (1.945–1.952 Å). Si–Ge (2.394–2.396 Å) and Si–Si (2.307–2.310 Å) bond distances are as expected for comparable compounds with four-coordinated Si and Ge atoms ($Ph_3GeSi(SiMe_3)_3$: δ(SiGe) 2.415 Å, δ(SiSi) 2.366 Å, [10]; $C_5Me_5(CO)_2(Me_3P)WSiCl_2SiCl_3$: δ(SiSi) 2.350 Å, [11]). Analogous to the case of **3**, the Cl–Si–Cl angles (106.11–107.11°) of **7a** are smaller than C–Sn–C (109.8–113.3°) and the Si–Cl bonds (2.041–2.047 Å) are shorter than the Sn–C bonds (2.126–2.142 Å). Si–Sn (2.582–2.583 Å) and Si–Si (2.298–2.306 Å) bond distances are as expected. The benzene molecules occupy regions of the unit cell near $y = 0$, 0.5, 1,...; they are sandwiched between Me_3Sn and Me_3Ge groups, with distances from the Sn/Ge to the ring centroid of 4.3–4.5 Å.

3. Experimental

All experiments were carried out with exclusion of air and moisture. Solvents were dried according to standard procedures. Solution NMR spectra were determined with Bruker AC 200 instruments (200 MHz for ^{1}H, 50.3 MHz for ^{13}C, 39.8 MHz for ^{29}Si, 74.6 MHz for ^{119}Sn); the ^{29}Si MAS spectrum was run on a Bruker AMX 300 instrument (59.63 MHz for ^{29}Si, 25° pulse with 4 s recovery time, rotation: 3000 Hz, resolution: 30 Hz/point); shifts are given relative to TMS (^{1}H, ^{13}C,

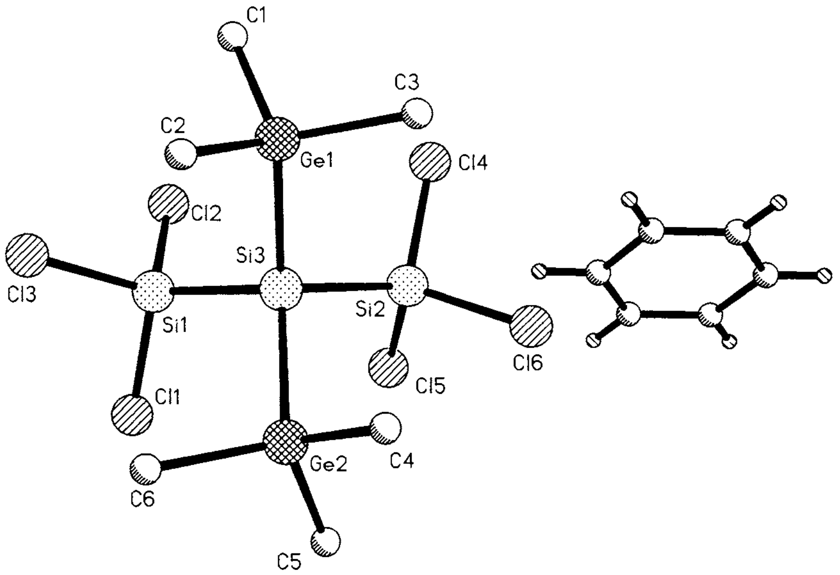

Fig. 1. Molecular structure of **3**. Selected geometric parameters (pm, °): Si(1)–Si(3) 230.98(13), Si(2)–Si(3) 230.74(14), Ge(1)–Si(3) 239.38(10), Ge(2)–Si(3) 239.62(10) pm; Si(2)–Si(3)–Si(1) 104.23, Ge(1)–Si(3)–Ge(2) 115.83(4), Si(2)–Si(3)–Ge(1) 109.18(5), Si(2)–Si(3)–Ge(2) 108.83°.

^{29}Si) and tetramethylstannane (^{119}Sn)); solvent benzene-d_6.—MS: Finigan Mat 8430.—Elemental analyses: Carlo Erba analytical gas chromatograph.

3.1. Synthesis of trimethyl(trichlorosilyl)germane **2**

Triethylamine (4.0 g, 40 mmol) was slowly added to a mixture of 5.5 g (36 mmol) of Me_3GeCl **1** and 5.4 g (40 mmol) of $HSiCl_3$ in 90 ml pentane. Stirring at r.t. continued for 20 h. Subsequently the solution was separated from the precipitate and evaporated at 0°C. Distillation of the brownish residue at 31°C (3.5 mbar) provided 4.4 g of (48%) **2** as a colourless liquid. After stirring the reaction mixture for 14 days at r.t., ^{29}Si-NMR signals of the mixture appeared at $\delta = 17.8$, 17.2, -22.3 (silicon grease) and -84.2 ppm. The ^{29}Si signals at $\delta = 17.2$ and -84.2 ppm were assigned to **3**.

Compound **2**: EI MS (70 eV) m/z (%) 252 (1) [M^+], 237 (16) [M^+–CH_3], 217 (4) [M^+–Cl], 139 (60) [M^+–CH_3, –$SiCl_2$], base peak 119 [M^+–$SiCl_3$]. ^{1}H-NMR: $\delta = 0.36$ ppm (s). ^{13}C-NMR: $\delta = -2.8$ ppm (s). ^{29}Si-NMR: $\delta = 17.8$ ppm (s). $C_3H_9Cl_3GeSi$ (252.14): Calc. C 14.29, H 3.60, Cl 42.18, Found C 14.24, H 3.59, Cl 41.99%.

3.2. Synthesis of bis(trichlorosilyl)bis(trimethylgermyl)-silane **3**

Triethylamine (2.5 g, 25 mmol) was added to a solution of 1.9 g (12 mmol) of Me_3GeCl **1** and 3.4 g (25 mmol) of $HSiCl_3$ in 30 ml pentane. This solution was stirred at r.t. for another 7 days. Subsequently the work-up (separation from the precipitate and evaporation at 0°C) gave 1.2 g (2.3 mmol) of a yellowish waxy solid (37% crude yield). This solid was dissolved in 5 ml of C_6D_6. From this C_6D_6 solution, a few colourless crystals of C_6D_6-solvated **3** were separated. One of these crystals was suitable for the X-ray diffraction study. Prolonged drying of the other crystals at 0.05 mbar led to **3** as an amorphous solid with analytical purity.

Compound **3**: EI MS (70 eV) m/z (%) 532 (6) [M^+], 517 (6) [M^+–CH_3], 497 (2) [M^+–Cl], 419 (4) [M^+–CH_3, –$SiCl_2$], 295 (8) [M^+–$(CH_3)_2Ge$, –$SiCl_3$], 265 (6) [M^+–$Ge(CH_3)_4$, –$SiCl_3$], 245 (3) [M^+–$(CH_3)_3Ge$, –$SiCl_4$], base peak 119 [$Ge(CH_3)_3$]. ^{1}H-NMR: $\delta = 0.42$ ppm (s). ^{13}C-NMR: $\delta = +0.8$ ppm (s). ^{29}Si-NMR: $\delta = +17.2$ ppm (s, $\underline{Si}Cl_3$), -84.2 ppm (s, $Ge_2\underline{Si}Si_2$). $C_6H_{18}Cl_6Ge_2Si_3$ (532.36): Calc. C 13.54, H 3.41, Cl 39.96, Found C 13.75, H 3.46, Cl 38.98%.

3.2.1. Structure determination of **3** · C_6D_6

Crystal data: $C_{12}H_{18}D_6Cl_6Ge_2Si_3$, $M = 616.51$, *Pbca*, $a = 12.796(3)$, $b = 17.135(3)$, $c = 23.211(3)$ Å, $V = 5089(2)$ Å^3, $Z = 8$, $D_{calc.} = 1.609$ mg m^{-3}, $\mu = 3.130$ mm^{-1}, $T = 143$ K. A colourless block (0.70 × 0.50 × 0.50 mm) was mounted in inert oil. A total of 6858 intensities were measured (2θ 6–55°) using Mo–K$_\alpha$ radiation on a STOE Stadi-4 diffractometer. After absorption correction (psi-scans) 5858 unique reflections ($R_{int} = 0.0220$) were used for all calculations (program SHELXL-93; G.M. Sheldrick, University of Göttingen). The structure was solved by direct methods and refined anisotropically on F^2. H atoms were included using rigid methyl groups. The final $wR(F^2)$ was 0.0912 with conventional $R(F)$ 0.0379 for 214 parameters.

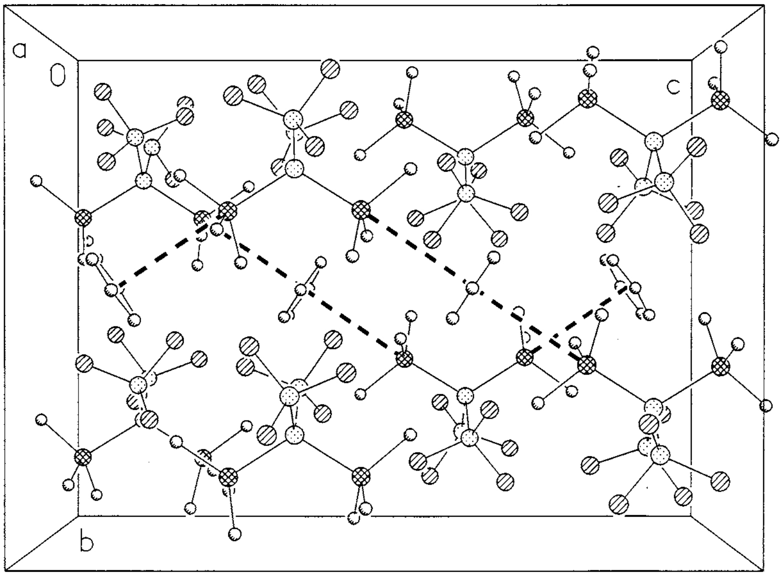

Fig. 2. Cell plot of C_6D_6-solvated **3**; C_6H_6-solvated **7a** is isotypic.

*3.3. Synthesis of dimethylbis(trichlorosilyl)germane **5***

To a solution of 13.5 g (0.1 mol) $HSiCl_3$ and 8.7 g (0.05 mol) Me_2GeCl_2 **4** in 120 ml pentane 10.1 g (0.1 mol) of triethylamine was added, and the mixture was stirred at r.t. for 10 days. After removal of the precipitate, the solvent was evaporated under reduced pressure at 0°C. Distillation of the brown residue at 35°C (0.05 mbar) provided 14.7 g (79%) of **5** as a colourless viscous liquid.

Compound **5**: EI MS (70 eV) m/z (%) 372 (2) [M^+], 357 (4) [M^+–CH_3], 337 (5) [M^+–Cl], 257 (18) [M^+–$SiCl_2$], 237 (71) [M^+–$SiCl_3$], base peak 135 [M^+–$SiCl_3$, –$SiCl_2$]. ^{1}H-NMR: $\delta = 0.49$ ppm (s). ^{13}C-NMR: $\delta = -5.8$ ppm (s). ^{29}Si-NMR: $\delta = +13.1$ ppm (s). $C_2H_6Cl_6GeSi_2$ (371.55): Calc. C 6.47, H 1.63, Cl 57.25, Found C 6.63, H 1.53, Cl 56.29%.

*3.4. Synthesis of bis(trichlorosilyl)bis(trimethylstannyl)silane **7a***

Triethylamine (20.2 g, 0.2 mol) was added dropwise to a mixture of 24.8 g (0.125 mol) of Me_3SnCl **6a** and 27.0 g (0.2 mol) of $HSiCl_3$ in 320 ml pentane. A small signal at δ ^{119}Sn = -70 ppm ($Me_3SnSiCl_3$ **8a**) was observed after 3 days stirring at r.t., in addition to the signals of the main product **7a** and the starting material **6a** coordinated with NEt_3 (δ ^{119}Sn = 117 ppm). Stirring at r.t. continued for 14 days to complete the reaction. The brownish mixture was separated from the precipitate by filtration (using 2–3 cm Celite® 545 (Merck)) several times until no further triethylammonium chloride was detectable; the solvent was evaporated off at 0°C (crude yield 43%). This brown crude product was dissolved in 120 ml of benzene. After several days, 3.6 g (6 mmol, 10% yield) of colourless crystals of **7a** had separated from this solution. One of these crystals was suitable for a X-ray diffraction study. Prolonged drying at 0.05 mbar led to **7a** as a colourless solid with analytical purity.

Compound **7a**: EI MS (70 eV) m/z (%) 624 (4) [M^+], base peak 609 [M^+–CH_3], 511 (10) [M^+–CH_3, –$SiCl_2$], 461 (16) [M^+–2CH_3, –$SiCl_3$], 431 (17) [M^+–4CH_3, –$SiCl_3$], 311 (31) [M^+–4CH_3, –Sn, –$SiCl_3$], 213 (17) [$Me_2SnSiCl$], 165 (44) [$Sn(CH_3)_3$], 135 (22) [$SiCl_3$]. ^{1}H-NMR: $\delta = 0.34$ ppm (s, ^2J(H, ^{117}Sn) = 51.1 Hz, ^2J(H, ^{119}Sn) = 53.2 Hz). ^{13}C-NMR: $\delta = -8.0$ ppm (s, ^1J(C, ^{117}Sn) = 297 Hz, ^1J(C, ^{119}Sn) = 311 Hz. ^{29}Si-NMR (resolution not sufficient to assign satellite signals): $\delta = 19.6$ ppm (s, $\underline{Si}Cl_3$), -106.4 ppm (s, $Sn_2\underline{Si}Si_2$). ^{29}Si-CP-MAS-NMR: $\delta = 19$ ppm (s, $\underline{Si}Cl_3$), -112 ppm (s, $Sn_2\underline{Si}Si_2$). ^{119}Sn-NMR: $\delta = -55.2$ ppm (s, two pairs of satellites resolved: $J = 199$ and 291 Hz). $C_6H_{18}Cl_6Si_3Sn_2$ (624.59): Calc. C 11.54, H 2.90, Cl 34.06, Found C 11.55, H 2.93, Cl 33.89%.

*3.4.1. Structure determination of **7a** · C_6H_6*

Crystal data: $C_{12}H_{24}Cl_6Si_3Sn_2$, $M = 702.66$, *Pbca*, $a = 13.022(2)$, $b = 17.412(2)$, $c = 23.463(3)$ Å, $V = 5320.2(12)$ Å^3, $Z = 8$, $D_{calc.} = 1.755$ mg m^{-3}, $\mu = 2.612$ mm^{-1}, $T = 173$ K. A colourless block (0.80 × 0.40 × 0.40 mm) was mounted in inert oil. A total of 4589 intensities were measured (2θ 6–50°) using Mo–K$_\alpha$ radiation on a Siemens P4 diffractometer. After absorption correction (psi-scans) 4586 unique reflections were used for all calculations (program SHELXL-93; G.M. Sheldrick, University of Göttingen). The structure was solved by direct methods and refined anisotropically on F^2. H atoms were included using rigid methyl groups. The final $wR(F^2)$ was 0.0715 with conventional $R(F)$ 0.0301 for 208 parameters.

3.5. Reaction of chlorotriethylstannane **6b** with $HSiCl_3/NEt_3$

To a solution of 12.7 g (53 mmol) Et_3SnCl **6b** and 13.5 g (100 mmol) of $HSiCl_3$ in 120 ml pentane 10.1 g (100 mmol) of triethylamine was slowly added. The immediate formation of triethylammonium chloride could be observed. A ^{119}Sn-NMR spectrum showed after 7 days of stirring at r.t. that ca. 50% of the starting material **6b** was still unconsumed. Subsequently the reaction mixture was stirred for another 24 days at r.t. The work-up by removing the Et_3NHCl and pentane at 0°C gave a dark brown, viscous liquid, which was very air- and moisture-sensitive. ^{13}C-, ^{29}Si- and ^{119}Sn-NMR spectra indicated ca. 80% consumption of **6b** and formation of bis(trichlorosilyl)bis(triethylstannyl)silane **7b**. The ^{119}Sn-NMR spectrum also showed a small signal for $Et_3SnSiCl_3$ **8b** at δ $^{119}Sn = -59$ ppm. Isolation of pure **7b** by distillation could not be achieved, because thermal decomposition of **7b** led to **6b**.

Compound **7b**: ^{13}C-NMR: $\delta = 3.8$ ppm (s, $^1J(C, Sn) = 296$ Hz, $Sn{-}\underline{C}H_2{-}CH_3$), 12.1 ppm (s, $Sn{-}CH_2{-}\underline{C}H_3$). ^{29}Si-NMR: $\delta = 21.0$ ppm (s, $^1J(Si, Si) = 62$ Hz, $\underline{Si}Cl_3$), -108.2 ppm (s, $^1J(Si, Si) = 63$ Hz, further broad satellites $J = $ ca. 86 Hz, $Sn_2\underline{Si}Si_2$). ^{119}Sn-NMR: $\delta = -45$ ppm (s, two pairs of satellites resolved: $J = $ ca. 75 Hz (broad), and $J = 308$ Hz).

3.6. Reaction of chlorotri-*n*-butylstannane **6c** with $HSiCl_3/NEt_3$

Triethylamine (6.1 g, 60 mmol) was added dropwise to a solution of 18.0 g (55 mmol) of *n*-Bu_3SnCl **6c** and 8.1 g (60 mmol) of $HSiCl_3$ in 130 ml pentane. Work-up after 4 days led to a yellowish, viscous liquid. ^{13}C- and ^{119}Sn-NMR spectra indicated the presence of **7c**, unconsumed **6c** (50%) and a small amount of *n*-$Bu_3SnSiCl_3$ **8c** (δ $^{119}Sn = -71.8$ ppm). Attempted distillation of **7c** led to thermal decomposition and compound **6c** (b.p. 106°C/0.1 mbar) was recovered. The liquid was therefore dissolved in 200 ml pentane and stirred for 14 days at r.t. Subsequently another 8.1 g (60 mmol) of $HSiCl_3$ and 6.1 g (60 mmol) of triethylamine were added to this yellow solution, which was stirred at r.t. for another 29 days to complete the reaction. Work-up in the same way led to a dark brown, oily liquid that was very sensitive to air and moisture. Enrichment of **7c** was possible up to 85%.

Compound **7c**: ^{13}C-NMR: $\delta = 12.2$ ppm (s, $^1J(C, {}^{117}Sn) = 284$ Hz, $^1J(C, {}^{119}Sn) = 296$ Hz, $Sn{-}\underline{C}H_2{-}(CH_2)_2{-}CH_3$), 14.0 ppm (s, $Sn{-}(CH_2)_3{-}\underline{C}H_3$), 27.8 ppm (s, $^3J(C, Sn)$ satellites overlapped by the signals of *n*-Bu_3SnCl, $Sn{-}(CH_2)_2{-}\underline{C}H_2{-}CH_3$), 30.3 ppm (s, $^2J(C, Sn) = 20.5$ Hz, $Sn{-}CH_2{-}\underline{C}H_2{-}CH_2{-}CH_3$). ^{29}Si-NMR: $\delta = 21.3$ ppm (s, $^1J(Si, Si) = 61$ Hz, $\underline{Si}Cl_3$), -107.4 ppm (s, $^1J(Si, Si) = 61$ Hz, $^1J(Si, {}^{117}Sn) = 89$ Hz, $^1J(Si, {}^{119}Sn) = 92$ Hz, $Sn_2\underline{Si}Si_2$). ^{119}Sn-NMR: $\delta = -52.7$ ppm (s, five pairs of satellites resolved: ca. 308 Hz (weak, broad), ca. 287 Hz (weak, broad), 93 Hz [$^1J(Si, {}^{119}Sn)$], 67.5 Hz (the strongest satellite signals), 21.5 Hz.

3.7. Reactions of **7a**, **7b** and **7c** with $PhCH_2Cl$

3.7.1. Reaction of $(Me_3Sn)_2Si(SiCl_3)_2$ **7a** with $PhCH_2Cl$

$(Me_3Sn)_2Si(SiCl_3)_2$ **7a** (400 mg, 0.64 mmol) was dissolved in 5 ml benzene. $PhCH_2Cl$ (200 mg, 1.5 mmol) was added to this mixture at r.t. The reaction mixture was refluxed for 26 h. ^{13}C- and ^{119}Sn-NMR examinations of the yellowish solution indicated the complete decomposition of **7a** and some formation of Me_3SnCl **6a** (δ $^{119}Sn = 161$ ppm) and **10** (δ $^{13}C = 32.6$ ppm (s, $Ph\underline{C}H_2SiCl_3$), 126.7 ppm (s, *p*-$\underline{C}$), 128.9 ppm (s, *m*-$\underline{C}$), 129.4 ppm (s, *o*-$\underline{C}$), 132.1 ppm (s, *ipso*-$\underline{C}$)).

3.7.2. Reaction of $(Et_3Sn)_2Si(SiCl_3)_2$ **7b** with $PhCH_2Cl$

$PhCH_2Cl$ (1.46 g, 11.5 mmol) was added to 3.9 g (5.5 mmol) of $(Et_3Sn)_2Si(SiCl_3)_2$ **7b**. The yellow mixture was refluxed for 2 h. A ^{119}Sn-NMR spectrum showed the complete decomposition of **7b** and the formation of Et_3SnCl **6b**. Distillation of the red–orange reaction mixture furnished 0.8 g (3.5 mmol, 32% yield) of **10** (45°C, 0.5 mbar) and 2.2 g (9.1 mmol, 83% yield) of Et_3SnCl **6b** (65°C, 0.5 mbar).

3.7.3. Reaction of $(n\text{-}Bu_3Sn)_2Si(SiCl_3)_2$ **7c** with $PhCH_2Cl$

$PhCH_2Cl$ (1.0 g, 7.8 mmol) was treated with 3.3 g (3.8 mmol) of $(n\text{-}Bu_3Sn)_2Si(SiCl_3)_2$ **7c**. The yellowish mixture was heated for 10 h at 100°C. ^{13}C-, ^{29}Si- and ^{119}Sn-NMR spectra of the dark yellow reaction mixture proved the complete decomposition of **7c** and formation of *n*-Bu_3SnCl **6c** (δ $^{119}Sn = 147$ ppm) and **10** (δ $^{29}Si = 7.8$ ppm).

3.8. Photochemical cleavage of **7a**

$(Me_3Sn)_2Si(SiCl_3)_2$ **7a** (320 mg, 0.5 mmol) was dissolved in 100 ml benzene. UV-irradiation (150 W) of the benzene solution for two periods of 45 min and subsequently removal of the benzene led to a brown residue that was dissolved in C_6D_6. About 50% decomposition of **7a** was indicated by a ^{119}Sn-NMR spectrum of this brown solution. The following signals were detected after UV-irradiation:

$(Me_3Sn)_2Si(SiCl_3)_2$ **7a**:	δ $^{119}Sn = -54$ ppm (intensity: 100), δ $^{13}C = -8.1$ ppm
$Me_3SnSiCl_3$ **8a**:	δ $^{119}Sn = -70$ ppm (intensity: 42), δ $^{13}C = -8.6$ ppm

Me_3SnCl **6a**: δ $^{119}Sn = +162$ ppm (intensity: 50), δ $^{13}C = -1.7$ ppm
Me_2SnCl_2: δ $^{119}Sn = +140$ ppm (intensity: 17), δ $^{13}C = +1.4$ ppm

4. Supplementary material

Further details of the structure determinations may be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk), on quoting the reference number CCDC-100274 for **3** and CCDC-102091 for **7a**.

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