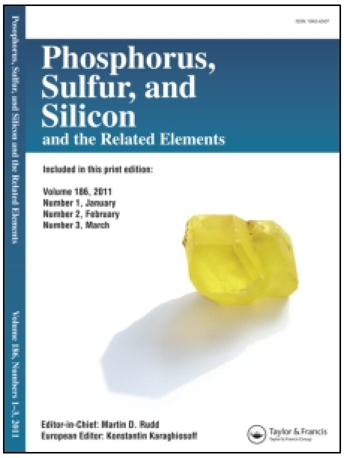

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Trichlorosilylation of Trialkylgermanium and -Tin Moieties to Unexpected Heteroneopentanes

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Reactions of chlorogermanes and chlorostannanes with trichlorosilane / triethylamine and reactions of germyl- and stannylphosphanes with hexachlorodisilane lead to new compounds with Ge-Si and Sn-Si bonds, among them unexpected novel heteroneopentanes $(R_3M)_2Si(SiCl_3)$ ($M = Ge$, Sn; $R = alkyl$). Reaction sequences leading to these highly branched trialkylgermyl- or stannyloligosilanes were followed by heteronuclear n.m.r. spectroscopy.

Keywords: silylation; trichlorosilylgermanes; trichlorosilylstannanes; branched silanes; base catalysis

Introduction. Trihalogenosilyl compounds are of importance as trifunctional precursors for the synthesis of highly functionalised silicon compounds, like branched silicones and silasesquioxanes. The cleavage of trimethylgermyl and -stannyl phosphanes with hexachlorodisilane was reported by us to lead to trichlorosilylphosphanes and to previously unknown trichlorosilylgermanes and -stannanes Me_3MSiCl_3 ($M = Ge$: **1**, $M = Sn$: **2a**) [1]. Subsequently, attempts were made to synthesise these

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compounds by reactions of chlorotrimethylgermane and -stannane with trichlorosilane / triethylamine [2]. This reagent had recently been shown to be quite efficient for the synthesis of a number of trichlorosilylphosphanes from the corresponding chlorophosphanes [2, 3]. Contradictory data concerning pure liquid $Me_3GeSiCl_3$ (**1**) made by this new method and a solid product of rather similar C, H content which was taken to be **1** [4] led us to reinvestigate the reactions that had been expected to furnish trichlorosilylgermanes and -stannanes.

Reactions of chloro(methyl)germanes with $HSiCl_3$ / NEt_3.

Chlorotrimethylgermane reacts with the trichlorosilane/triethylamine reagent at room temperature in pentane solution under precipitation of triethylammonium chloride leading to compound **1** as main product, that was identified by new singlet signals in ^1H-, ^{13}C- and ^{29}Si-NMR-spectra of the reaction mixture. **1** was, however, accompanied by another new compound **3**, that was detected by second set of singlet signals in ^1H-, ^{13}C- and ^{29}Si-NMR-spectra of the reaction mixture. When stirring of the mixture was continued for several days, the intensity of the NMR-signals of compound **3** increased at the expense of **1**. Species **3** became the main product within several days; however, its formation was never close to quantitative. The ^{29}Si-NMR spectrum 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 **1**) and a weaker one far upfield at - 84 ppm. Work-up of reactions mixtures from Me_3GeCl with $HSiCl_3/NEt_3$ after a rather short reaction time (20 hours) by filtration, evaporation of the solvent, and distillation furnished pure **1** in about 50 % yield as colorless liquid. **1** gave satisfactory elemental analyses and allowed the detection of its molecular ion by mass spectroscopy. Its physical data are different from those previously reported [1]. The pure compound is moisture-sensitive, but thermally quite stable. Addition of small amounts of triethylamine to liquid **1** leads to its incomplete decomposition yielding a mixture of **1**, **3**, Me_3GeCl, and $SiCl_4$.

Work-up of reactions mixtures from Me_3GeCl with $HSiCl_3/NEt_3$ after several days by filtration and evaporation of the solvent gave a yellowish waxy solid (about 40 % crude yield). After dissolving the residue in C_6D_6, colorless crystals of C_6D_6-solvated **3** separated from the solution. Long drying of the cystals at 0.05 mbar led to **3** as amorphous solid. Its molcular ion in the mass spectrum, its elemental analysis, and its ^{29}Si-NMR spectrum (as well as its comparison with the related tin compound) suggest that **3** is $(Me_3Ge)_2Si(SiCl_3)_2$. 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 (decepting !) rather similar to that of **1**. Single crystals of **3** from C_6D_6 solutions contain one equivalent of C_6D_6 [5].

$$Me_3GeCl + HSiCl_3 + NEt_3 \text{ -----> } \underset{\mathbf{1}}{Me_3GeSiCl_3} + HNEt_3Cl$$

$$4\ \underset{\mathbf{1}}{Me_3GeSiCl_3} \overset{NEt_3}{\text{ -----> }} \underset{\mathbf{3}}{(Me_3Ge)_2Si(SiCl_3)_2} + SiCl_4 + 2\ Me_3GeCl$$

$$Me_2GeCl_2 + 2\ HSiCl_3 + 2\ NEt_3 \text{ -----> } \underset{\mathbf{4}}{Me_2Ge(SiCl_3)_2} + 2\ HNEt_3Cl$$

Dichlorodimethylgermane reacts with the trichlorosilane/triethylamine reagent at room temperature in pentane solution under precipitation of triethylammonium chloride. Work-up after several days stirring provided bis(trichlorosilyl)dimethylgermane (**4**) in fair yield. Surprisingly, a decomposition reaction of **4** related to the one from **1** to **3** was not observed even when the work-up procedure was untertaken after several weeks. Distillation furnished pure 4 in very good yield as colorless liquid. 4 gave satisfactory elemental analyses and allowed the detection of its molecular ion by mass spectroscopy. 4 is thermally stable, but sensitive to moisture.

Reactions of trialkylchlorostannanes with $HSiCl_3/NEt_3$ [5].

The reactions of trialkylchlorostannanes R_3SnCl (R = Me, Et, *n.*-Bu) with the trichlorosilane/triethylamine reagent were monitored by ^{13}C, ^{119}Sn and ^{29}Si NMR.

The reaction of chlorotrimethylstannane with $HSiCl_3/NEt_3$:

Within 3 days at room temperature in pentane, about 25% of Me_3SnCl (its ^{19}Sn-NMR resonance in the reaction mixture, δ $^{119}Sn = + 117$ ppm, indicates coordination with triethylamine) were converted into a new tin compound that give a δ ^{119}Sn signal at - 53 ppm). This compound is not **2a**, as previously proposed [1, 2], but the new compound $(Me_3Sn)_2Si(SiCl_3)_2$ (**5a**), as shown by a set singlet signals in ^1H-, ^{13}C- and ^{119}Sn-NMR-spectra of the reaction mixture and two signals in its ^{29}Si-NMR spectrum. To complete the reaction as far as possible,. stirring was continued for 2 weeks. After separation of the solution from the triethylammonium chloride residue, the crude compound was obtained in about 40 % yield. From benzene solution, colorless crystals of benzene-solvated **5a** were isolated [5]. Removal of benzene at 0.05 mbar gave **5a** as amorphous colorless solid that gave satisfactory analytical data. In an EI-mass spectrum, the molecular ion of **5a** showed the expected isotopic pattern.

The reaction of chlorotriethylstannane with $HSiCl_3/NEt_3$:

Upon addition of triethylamine to Et_3SnCl / $HSiCl_3$ spontaneous crystallisation of Et_3NHCl occurs. However, after 7 d stirring, a ^{119}Sn NMR-spectrum shows, that about 50 % of Et_3SnCl are still unconsumed. Within 31 days, about 80 % consumption of the chlorostannane was confirmed by NMR. Besides the signals of starting material **6b** and main product $(Et_3Sn)_2Si(SiCl_3)_2$ (**5b**), a another small signal at δ $^{119}Sn = -59$ ppm assignable to $Et_3SnSiCl_3$ (**2b**) was also observed. Isolation of pure **5b** was not achieved.

The reaction of chlorotri-*n*-butylstannane with $HSiCl_3/NEt_3$:

After 4d, work-up by removal of Et_3NHCl and pentane gave a liquid, that was still containing 50 % of n-Bu_3SnCl besides (n-$Bu_3Sn)_2Si(SiCl_3)_2$ (**5c**), traces of $Bu_3SnSiCl_3$ (**2c**), and another new branched compound, which appears to be n-$Bu_3SnSi(SiCl_3)_3$ (**6c**) . Destillation at 106 °C/0.1 mbar allowed to remove the chlorostannane, but attempts to isolate **2c** or **5c** from the residue failed.

In additional experiment, we checked, if compounds **5** could be used as alternative to the *Benkeser*-like trichlorosilylation of benzyl chloride with $HSiCl_3/NEt_3$: After decomposing samples containing **5a** - **c** by heating them with excess benzyl chloride, ^{13}C-, ^{29}Si-, and ^{119}Sn-NMR-spectra indicated the formation of benzyltrichlorosilane which was accompanied by the trialkyltin chlorides.

UV-photochemical cleavage of compound **5a** in benzene solution led to partial decomposition. Analysis of the mixture after removal of the solvent by ^{13}C- and ^{119}Sn-NMR and by EI-MS allowed to detect among the products compound **2a** (25 %, by rough estimation from the ^{119}Sn signal intensity), which appears to be comparatively stable in absence of nucleophiles.

Reactions of germyl- and stannylphosphanes with Si_2Cl_6.

The observation, that triethylamine catalyses the decomposition of compounds Me_3MSiCl_3 (M = Ge:**1**, M = Sn: **2a**) to neopentane-like branched silanes **3** and **5**, led us to reinvestigate the reactions of trialkylgermyl- and -stannylphosphanes with hexachlorodisilane by following them with help from ^{31}P-, ^{29}Si- and ^{119}Sn-NMR. As starting materials we chose moderately bulky phosphanes *t*-Bu(*i*-Pr)PMR$_3$ (M = Ge, Sn).

At an early stage of the reaction of Si_2Cl_6 with *t*-Bu(*i*-Pr)PGeMe$_3$ (**7**), *t*-Bu(*i*-Pr)PSiCl$_3$ (**8**), *t*-Bu(*i*-Pr)PSi$_2$Cl$_5$ (**9**), $Me_3SiGeCl_3$ (**1**) and $(Me_3Ge)_2Si(SiCl_3)_2$ (**3**) besides unconsumed **7** were detected. Subsequently, **9** was consumed in favour of **8**, **1** and **3**.

Stannylphosphanes *t*-Bu(*i*-Pr)PSnR$_3$ (R = Me: **10a**, R = Et: **10b**, R = n-Bu : **10c**) were consumed completely by reactions with Si_2Cl_6 within few minutes. They gave large amounts of **9** in the first stage of the reaction, but subsequently, the amount of **8** increased at the expense of **9** whereas silylstannanes $R_3SnSiCl_3$ (**2a - c**) and $(R_3Sn)_2Si(SiCl_3)_2$ (**5a - c**) and could be detected. **5c** was accompanied by a further product, which will be **6c** (see above) [5]. Subsequently, compounds **2a - c** decompose providing increasing amounts of compounds **5a**, **5b**, and **5c**/**6c**. Bulkier substituents (*n*-Bu > Et > Me) help to increase the the lifetime of compounds **2**.

Conclusion. Stannylphosphanes are much more reactive towards Si_2Cl_6 than germylphosphanes. The first reaction step is a transmetalation reaction at phosphorus (trialkylstannyl / pentachlorodisilanyl exchange) leading to the transient pentachlorodisilanylphosphane **9**.

$$\underset{\textbf{2c}}{R_2PSnBu_3} + Si_2Cl_6 \quad \text{----->} \quad \underset{\textbf{9}}{R_2PSi_2Cl_5} + 2\,Bu_3SnCl$$

$$\textbf{9} + Bu_3SnCl \quad \text{----->} \quad \underset{\textbf{8}}{R_2PSiCl_3} + \underset{\textbf{2c}}{Bu_3SnSiCl_3}$$

$$\text{----->} \quad \underset{\textbf{5c}}{(Bu_3Sn)_2Si(SiCl_3)_2} + \underset{\textbf{6c}}{Bu_3SnSi(SiCl_3)_3}$$

In the next step, **9** transfers $SiCl_2$ or $SiCl_3^-$ functions to the organotin moiety (reductive silylation of the alkylchlorostannanes) leading to silylstannanes $R_3SnSiCl_3$ (**2a - c**), which are sensitive to the phosphane nucleophiles present in solution. This step could be modeled by treating pure $Me_3GeSiCl_3$ (**1**) with a trialkylphosphane: i-Pr_3P catalyses the formation of the branched compound **3**, Me_3GeCl, and $SiCl_4$ from **1**.

For the course of disilane disproportionations, (hidden) trichlorosilyl anions and / or base-stabilised silylenes may be the reactive intermediates [6 - 8]. A retrosynthetic analysis of compounds $(R_3M)_2Si(SiCl_3)_2$ from R_3MSiCl_3 allows both pathways (via $\{Nu\text{->}SiCl_2\}$ or $\{SiCl_3^-\}$) to explain the formation of Si-Si bonds and of one of the M-Si bonds. The attachment of a second R_3M group to the central silicon atom, however, would be consistent with the transfer of anionic R_3M^- moieties (or radicals). This consideration suggests, that both, Si and Sn (or Ge) atoms of metastable compounds R_3MSiCl_3 (M = Ge, Sn) are susceptible to nucleophilic attack of amines and phosphanes as long as nucleophilic attack at Ge or Sn is not prevented by bulky substituents.

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