

## Silylgermylstannylmethanes

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### Abstract

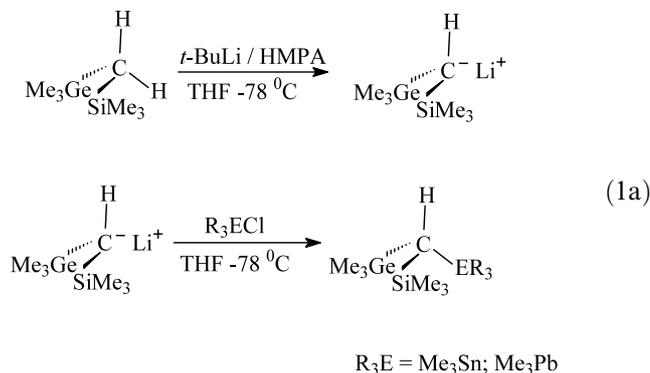
Three silylgermylstannylmethanes,  $\text{Me}_3\text{Si}(\text{Me}_3\text{Ge})(\text{R}_3\text{Sn})\text{CH}$ ,  $\text{R}_3 = \text{Me}_3$  (**1**),  $\text{Ph}_3$  (**2**) and  $\text{Me}_2\text{PhSi}(\text{Me}_3\text{Ge})(\text{Me}_3\text{Sn})\text{CH}$  (**3**) were synthesized from the reaction of the appropriate silyl(trimethylgermyl)methyl lithium,  $[\text{Me}_2\text{RSi}(\text{Me}_3\text{Ge})\text{CH}]^- \text{Li}^+$   $\text{R} = \text{Me}, \text{Ph}$  and the corresponding  $\text{R}_3\text{SnCl}$ . The single crystal X-ray structure of **2** is reported.

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**Keywords:** Group 14; Silyl; Germyl; Stannyl; Methane

### 1. Introduction

There has been interest in the synthesis and characterization of bulky molecules containing a variety of the Group 14 elements, in particular mixed Group 14-substituted methanes [1]. Several years ago we communicated the formation of a Group 14-substituted methane in which all the Group 14 elements were present, so-called *catorcanes*, e.g.  $\text{Me}_3\text{Si}(\text{Me}_3\text{Ge})(\text{Me}_3\text{Sn})(\text{Me}_3\text{Pb})\text{C}$  [2]. In this study we found that trimethylsilyl(trimethylgermyl)methane,  $\text{Me}_3\text{Si}(\text{Me}_3\text{Ge})\text{CH}_2$ , originally synthesized by Schmidbaur [3], was a useful starting material for further substitution. Treatment of this reagent with *t*-butyllithium in the presence of HMPA produced the corresponding methyllithium species  $[\text{Me}_3\text{Si}(\text{Me}_3\text{Ge})\text{CH}]^- \text{Li}^+$  which is readily quenched with a variety of species including  $\text{Me}_3\text{SnCl}$  and  $\text{Me}_3\text{PbCl}$ , Eq. (1).



Using this approach we describe the syntheses of  $\text{Me}_3\text{Si}(\text{Me}_3\text{Ge})(\text{R}_3\text{Sn})\text{CH}$ ,  $\text{R} = \text{Ph}$  (**1**),  $\text{Me}$  (**2**),  $\text{Me}_2\text{PhSi}(\text{Me}_3\text{Ge})(\text{Me}_3\text{Sn})\text{CH}$  (**3**) and the single crystal X-ray structure of **2**.

### 2. Experimental

#### 2.1. Synthesis

Schlenk techniques were used with dried solvents and argon–nitrogen atmospheres. *t*-Butyllithium was purchased from Aldrich; starting silicon, germanium and tin compounds from Gelest.

In a typical synthesis, a 250 ml Schlenk flask was charged with 60 ml THF solution containing 10.3 g (0.05 mol) of  $\text{Me}_3\text{Si}(\text{Me}_3\text{Ge})\text{CH}_2$  and 15 ml of HMPA. This solution was treated at  $-78^\circ\text{C}$  with 30 ml of a *t*-

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butyllithium solution (1.7-M in pentane) over a period of 20 min. The solution became a bright yellow and was permitted to stir for 1 h. At this time a solution of 19.3 g (0.05 mol) of  $\text{Ph}_3\text{SnCl}$  was added slowly (20 min) at the same temperature. The solution was stirred and permitted to warm slowly to room temperature and then was treated with 50 ml of hexanes to facilitate precipitation of  $\text{LiCl}$ . Four washings with a saturated solution of  $\text{NH}_4\text{Cl}$  were followed by separation of the organic layer. After drying with  $\text{MgSO}_4$  overnight, filtration and removal of the solvent produced a white solid material. This was recrystallized from a mixture of methylene chloride and hexane to yield 13.9 g (0.025 mol, 50%) of  $\text{Me}_3\text{Si}(\text{Me}_3\text{Ge})(\text{Ph}_3\text{Sn})\text{CH}$  (**2**), m.p. 96–98 °C. NMR data, ( $\text{CDCl}_3$ , ppm):  $^1\text{H}$ : 0.11 (s, 1H,  $\text{CH}$ ), 0.13 (s, 6H,  $\text{SiMe}_3$ ); 0.24 (s, 6H,  $\text{GeMe}_3$ ), 7.57–7.72 (m, 5H,  $\text{C}_6\text{H}_5$ );  $^{29}\text{Si}$ : 3.49 ( $^2J_{\text{Si-Sn}} = 26$  Hz);  $^{119}\text{Sn}$ : –86.7.

In a similar manner the permethylated silylgermylstannymethane,  $\text{Me}_3\text{Si}(\text{Me}_3\text{Ge})(\text{Me}_3\text{Sn})\text{CH}$  (**1**) was produced in 62% yield, purified by distillation at 72 °C/0.1 mmHg; Anal. (Galbraith Laboratories), Calc. (Found): C, 32.66 (33.01); H, 7.67 (8.00); NMR ( $\text{CDCl}_3$ , ppm):  $^1\text{H}$ : –0.60 ( $\text{CH}$ ), 0.03 ( $\text{SiMe}_3$ ); 0.12 ( $\text{GeMe}_3$ ), 0.18 ( $\text{SnMe}_3$ ,  $^{117}J_{\text{Sn-H}} = 74$  Hz,  $^{119}J_{\text{Sn-H}} = 77$  Hz,);  $^{13}\text{C}$ : –5.58 ( $\text{SnMe}_3$ ,  $J_{\text{C-Sn}} = 320$  Hz), –1.35 ( $\text{CH}$ ), 3.15 ( $\text{SiMe}_3$ ), 3.28 ( $\text{GeMe}_3$ );  $^{29}\text{Si}$ : 2.69 ( $^2J_{\text{Si-Sn}} = 26.5$  Hz);  $^{119}\text{Sn}$ : 12.1.

Using the known  $\text{PhMe}_2\text{Si}(\text{GeMe}_3)\text{CH}_2$  [**4**] as starting material in the same manner as above,  $\text{Me}_2\text{PhSi}(\text{Me}_3\text{Ge})(\text{Me}_3\text{Sn})\text{CH}$  (**3**) was obtained in 72% yield as a colorless oil purified by distillation at 108–110 °C at 0.05 mmHg. Anal. Calc. (Found) C, 41.9 (42.2), H, 7.04 (6.93); NMR ( $\text{CDCl}_3$ , ppm):  $^1\text{H}$ : –0.22 ( $\text{CH}$ ,  $^{119}J_{\text{Sn-H}} = 77.2$  Hz,  $^{117}J_{\text{Sn-H}} = 74.0$ ), 0.05 ( $\text{SnMe}_3$ ,  $^{119}J_{\text{Sn-H}} = 51.0$  Hz,  $^{117}J_{\text{Sn-H}} = 49.8$  Hz,); 0.16 ( $\text{GeMe}_3$ ), 0.33, 0.34 ( $\text{SiMe}_2$ );  $^{13}\text{C}$ : –5.89 ( $\text{SnMe}_3$ ,  $^{119}J_{\text{Sn-C}} = 328.0$  Hz,  $^{117}J_{\text{Sn-C}} = 313.0$  Hz), –2.82 ( $\text{CH}$ ), 1.20, 1.53 ( $\text{SiMe}_2$ ), 2.74 ( $\text{GeMe}_3$ ), 127.6, 128.5, 133.40, 142.0 (ipso) ( $\text{Ph}$ );  $^{29}\text{Si}$ : 1.72 ( $^2J_{\text{Si-Sn}} = 25.8$  Hz);  $^{119}\text{Sn}$ : 14.1.

## 2.2. X-ray data collection

A colorless fragment of approximate dimensions  $0.38 \times 0.36 \times 0.20$  mm. was mounted in a random orientation at the tip of glass fiber for X-ray examination and data collection. All data were collected at 296 K on a Siemens R3m/v single-crystal diffractometer with graphite-monochromated  $\text{Mo-K}_\alpha$  radiation;  $\lambda(\text{Mo-K}_\alpha) = 0.71073$ . Unit cell parameters and standard deviations were obtained by least-squares fit of 50 randomly selected reflections in the  $2\theta$  range of 15–30°. They indicated monoclinic symmetry which was confirmed by oscillation photographs around each crystallographic axis. Intensity data were collected in the  $\omega$ -scan mode with a scan range of 1.4° in  $\omega$  and a variable speed of 3–

20°  $\text{min}^{-1}$ . Background counts were taken with a stationary crystal and total background time to scan time ratio of 0.5. Three standard reflections were monitored every 97 reflections and showed an intensity decay of less than 2% which was considered acceptable. The collection was conducted over slightly more than one quadrant of reciprocal space, in the range  $-19 \leq h \leq 0$ ,  $0 \leq k \leq 9$ ,  $-18 \leq l \leq 19$  for a total of 3641 reflections which after merging equivalents produced a set of 3510 unique reflections with an reliability parameter  $R_{\text{int}} = 1.46\%$ . The data were corrected for Lorentz and polarization effects and a semi-empirical absorption correction was also applied.

## 2.3. Structure refinement

Analysis of the data set based on cell parameters, systematically absent reflections and counting statistics lead to selection of space group  $P2_1/c$  (no. 14). The structure was solved by direct methods and refined by full-matrix least-squares, based on  $F^2$ , in a PC using the SHELEX-97 public domain software package. All hydrogen atoms were placed at calculated positions with C–H bond distances of 0.96 Å and average isotropic thermal parameters of 0.08. For the last cycle of refinement of 268 parameters and 3510 reflections, the maximum and minimum residual electron densities were 0.306 and –0.443 electrons per Å<sup>3</sup> and the final  $R$ -values, as defined in SHELEX-97, were  $R = 0.0395$  and  $R_w = 0.0650$  for all data. The structure of **2** is presented in Fig. 1.

The germanium and silicon atoms are statistically distributed in two atomic positions in ca. 50/50% ratio. Pertinent crystallographic data are given in Table 1, and selected bond angles and lengths in Table 2.

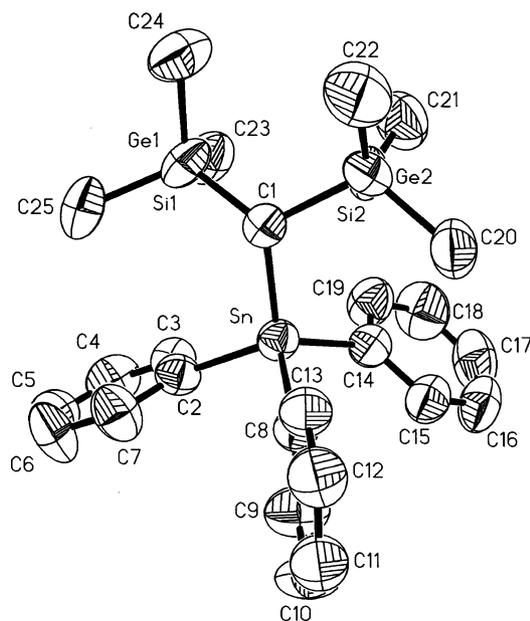


Fig. 1. Structure of **2**.

Table 1  
Crystal data and structure refinement for C<sub>25</sub>H<sub>34</sub>Ge<sub>0.95</sub>Si<sub>1.04</sub>Sn

Identification code	ah580f
Empirical formula	C <sub>25</sub> H <sub>34</sub> Ge <sub>0.95</sub> Si <sub>1.04</sub> Sn
Formula weight	551.89
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal system, space group	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>c</i>
Unit cell dimensions	
<i>a</i> (Å)	17.919(5)
<i>b</i> (Å)	8.760(2)
<i>c</i> (Å)	18.513(5)
α (°)	90
β (°)	112.95(2)
γ (°)	90
<i>V</i> (Å <sup>3</sup> )	2676.0(12)
<i>Z</i>	4
<i>D</i> <sub>calc</sub> (Mg m <sup>-3</sup> )	1.370
Absorption coefficient (mm <sup>-1</sup> )	2.061
<i>F</i> (0 0 0)	1117
Crystal size (mm)	0.38 × 0.36 × 0.20
θ Range for data collection (°)	2.22–22.55
Index ranges	−19 ≤ <i>h</i> ≤ 0, 0 ≤ <i>k</i> ≤ 9, −18 ≤ <i>l</i> ≤ 19
Reflections collected/unique	3641/3510 [ <i>R</i> <sub>int</sub> = 0.0146]
Completeness to 2θ = 22.55	92.4%
Absorption correction	Semi-empirical
Max and min transmission	0.229 and 0.166
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	3510/0/268
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.995
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0293, <i>wR</i> <sub>2</sub> = 0.0650
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0395, <i>wR</i> <sub>2</sub> = 0.0694
Largest difference peak and hole (e Å <sup>-3</sup> )	0.306 and −0.443

### 3. Discussion

The synthetic method outlined in Eq. (1) was a suitable method for the synthesis of a series of derivatives of silylgermylmethanes. The three silylgermylstannylmethanes described herein are stable materials that are useful precursors to further chemistry active in our laboratory. The spectroscopic data are in total accord with the proposed structures and present no surprises. For example the silicon methyl groups of **3** show up as diastereotopic as expected.

Crystals of suitable quality for X-ray diffraction for **2** were obtained from the slow evaporation of methylene chloride–hexane mixture and its structure is illustrated in Fig. 1, with selected bond length and bond angle data provided in Table 2. The central –C–Si, (–C–Ge) and –C–Sn bond lengths of 1.915 and 2.154 Å, respectively are within the expected range for such bonds. The Si(Ge)–C–Ge(Si) and Ge(Si)–C–Sn bond angles ~116 and 114° suggest a greater spatial requirement of the trimethylsilyl(germyl) groups over the triphenylstannyl group at the central C atom.

Table 2  
Bond lengths (Å) and angles (°) for C<sub>25</sub>H<sub>34</sub>Ge<sub>0.95</sub>Si<sub>1.04</sub>Sn

<i>Bond lengths</i>	
Sn–C(14)	2.144(4)
Sn–C(8)	2.144(4)
Sn–C(1)	2.154(4)
Sn–C(2)	2.151(4)
Ge(1)–C(23)	1.895(5)
Ge(1)–C(25)	1.897(5)
Ge(1)–C(24)	1.898(5)
Ge(1)–C(1)	1.915(4)
Ge(2)–C(21)	1.890(5)
Ge(2)–C(20)	1.905(5)
Ge(2)–C(22)	1.899(5)
Ge(2)–C(1)	1.921(4)
C(2)–C(3)	1.373(6)
C(2)–C(7)	1.376(6)
C(3)–C(4)	1.380(7)
C(4)–C(5)	1.355(7)
C(5)–C(6)	1.356(8)
C(6)–C(7)	1.377(7)
C(8)–C(9)	1.382(6)
C(8)–C(13)	1.385(6)
C(9)–C(10)	1.404(7)
C(10)–C(11)	1.363(7)
C(11)–C(12)	1.352(7)
C(12)–C(13)	1.374(6)
C(14)–C(19)	1.379(6)
C(14)–C(15)	1.390(6)
C(15)–C(16)	1.380(7)
C(16)–C(17)	1.360(8)
C(17)–C(18)	1.358(8)
C(18)–C(19)	1.383(7)
<i>Bond angles</i>	
C(14)–Sn–C(8)	109.32(16)
C(14)–Sn–C(1)	113.88(16)
C(8)–Sn–C(1)	107.90(16)
C(14)–Sn–C(2)	106.34(16)
C(8)–Sn–C(2)	105.96(16)
C(1)–Sn–C(2)	113.13(15)
C(23)–Ge(1)–C(25)	109.3(2)
C(23)–Ge(1)–C(24)	107.9(3)
C(25)–Ge(1)–C(24)	106.6(2)
C(23)–Ge(1)–C(1)	111.56(19)
C(25)–Ge(1)–C(1)	109.96(19)
C(24)–Ge(1)–C(1)	111.4(2)
C(21)–Ge(2)–C(20)	107.2(2)
C(21)–Ge(2)–C(22)	110.4(3)
C(20)–Ge(2)–C(22)	106.1(3)
C(21)–Ge(2)–C(1)	111.5(2)
C(20)–Ge(2)–C(1)	112.33(19)
C(22)–Ge(2)–C(1)	109.2(2)
Ge(1)–C(1)–Si(2)	116.5(2)
Si(2)–C(1)–Ge(2)	0.00(7)
Si(1)–C(1)–Sn	114.17(19)
Si(2)–C(1)–Sn	113.39(18)

Symmetry transformations used to generate equivalent atoms.

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- In this article only  $^1\text{H}$ -NMR was reported for  $\text{PhSiMe}_2\text{CH}_2\text{GeMe}_3$ . At present we add the  $^{13}\text{C}$ - and  $^{29}\text{Si}$ -NMR data ( $\text{CDCl}_3$ , ppm):  $^{13}\text{C}$ :  $-0.19$  ( $\text{CH}_2$ );  $0.75$  ( $\text{SiMe}_2$ );  $2.29$  ( $\text{GeMe}_3$ );  $127.7$ ,  $128.6$ ,  $133.3$ ,  $141.4$ (ipso) (Ph);  $^{29}\text{Si}$ :  $-2.96$ .