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Synthesis and structure of tetrakis[(chloromethyl)dimethylsilylethynyl]silane and -germane

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Tetrakis[(chloromethyl)dimethylsilylethynyl]silane and -germane were synthesized by the reaction of $BrMgC{\equiv}CSi(CH_2Cl)Me_2$ with $SiCl_4$/$GeCl_4$. Their structures were proved by IR, NMR spectroscopy and X-ray analysis, and compared to the results of MP2/6-311G(d,p) calculations.

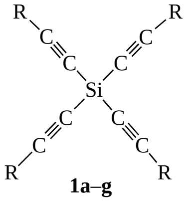
$$HC{\equiv}CSi(CH_2Cl)Me_2 \xrightarrow[SiCl_4\text{ or }GeCl_4]{EtMgBr} M[C{\equiv}CSi(CH_2Cl)Me_2]_4$$

M = Si or Ge

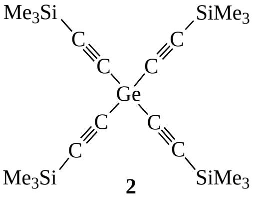
Keywords: organosilicon compounds, organogermanium compounds, alkynes, X-ray analysis, quantum chemical calculations.

Silicon and germanium organic compounds as well as materials on their basis, due to their unique properties, have found wide application in chemistry, technology and medicine.[1] Of special interest are branched structures containing silicon and germanium atoms both in the center and on the periphery. They are used as building blocks for preparation of anisotropic thin films and adsorbates,[2] molecular electronic materials[3] with light-emitting[4] and other properties.[5–7] Highly unsaturated silanes and germanes with several acetylenic fragments are attractive for the synthesis of more complex compounds, including polymers.[1(*b*),8] The structures of tetrakis(ethynyl) silanes **1a**–**g**[9(*a*)–(*c*)] and germane **2**[9(*d*)] were also confirmed by X-ray diffraction.

The functionalization of compounds **1**, **2** is possible *via* involvement of their C≡C bonds. However, if groups R could be functionalized with the C≡C bonds remaining intact, this would open a way to new organosilicon acetylenic dendrimers. In this respect, chloromethyl(dimethyl)silyl group $SiMe_2CH_2Cl$ is promising, as its closest analogue, iodomethyl(dimethyl)silyl group was shown to be a good silylmethylating reagent.[10–12] The goal of the present work was to synthesize the hitherto unknown tetrakis[(chloromethyl)dimethylsilylethynyl]silane and -germane, to investigate their structure and to examine the possibility of further functionalization using terminal chloromethyl groups. Tetraethynyl organosilicon or organogermanium dendrimers are usually prepared by organometallic synthesis in two steps using organolithium[9] or Grignard reagents.[13] The yields vary from moderate to excellent, although the synthesis of ethynylmagnesium bromide may be complicated by bismetallation of acetylene giving BrMgC≡CMgBr.[13,14]


1a–g

a R = $SiMe_3$
b R = Me
c R = H
d R = Ph
e R = 4-MeC_6H_4
f R = 4-$Bu^tC_6H_4$
g R = 4-PhC_6H_4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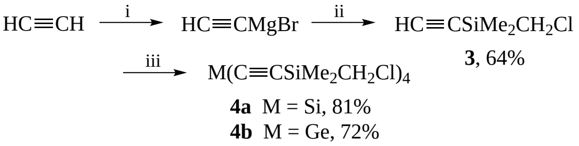
With this in mind, for the synthesis of tetrakis[(chloromethyl)dimethylsilylethynyl]silane or -germane we have used the Grignard synthesis. In the first step, chloro(chloromethyl)dimethylsilane was reacted with ethynylmagnesium bromide to give (chloromethyl)dimethylethynylsilane **3** in 64% yield (Scheme 1). Silane **3** was obtained earlier in 41% yield using sodium acetylenide in nitrobenzene.[15] The subsequent reaction of ethynylsilane **3** with ethylmagnesium bromide and tetrachlorosilane resulted in the formation of tetrakis[(chloromethyl)dimethylsilylethynyl]silane **4a** in 81% yield. When using $GeCl_4$, tetrakis[(chloromethyl)dimethylsilylethynyl]germane **4b** was obtained in 72% yield. Compounds **4a**,**b** are stable and can be stored for several months without decomposition. The synthesis and spectral characteristics of compounds **3** and **4a**,**b** are described in Online Supplementary Materials.

Single crystals of compounds **4a**,**b** suitable for X-ray structural analysis were grown from ether (Figure 1, Table 1).[†] Compounds **4a** and **4b** crystallize in orthorhombic space group


$$HC{\equiv}CH \xrightarrow{i} HC{\equiv}CMgBr \xrightarrow{ii} \underset{\mathbf{3},\ 64\%}{HC{\equiv}CSiMe_2CH_2Cl} \xrightarrow{iii} M(C{\equiv}CSiMe_2CH_2Cl)_4$$

4a M = Si, 81%
4b M = Ge, 72%

Scheme 1 *Reagents and conditions*: i, EtMgBr, abs. THF, 30 °C; ii, $ClCH_2SiMe_2Cl$, abs. THF, 30 °C, 1 h; iii, EtMgBr, $SiCl_4$ or $GeCl_4$, room temperature, 1.5 h.

[†] Crystals of compounds **4a** and **4b** were obtained by recrystallization from diethyl ether.

Crystal data for **4a**. $C_{20}H_{32}Cl_4Si_5$, orthorhombic, space group *Pccn*, M_r = 554.71, *a* = 13.495(3), *b* = 20.148(4) and *c* = 11.322(2) Å, $\alpha = \beta = \gamma = 90°$, *V* = 3078.5(11) Å^3, *Z* = 4, *T* = 293 K, d_{calc} = 1.197 g cm^{-3}, *F*(000) = 1160. Colorless prism-shaped single crystal with dimensions 0.03 × 0.15 × 0.50 mm was selected and intensities of 66634 reflections were measured using a Bruker D8 Venture diffractometer (MoKα radiation, λ = 0.71073, the φ and ω scans, μ = 0.586 mm^{-1}, $2\theta_{max}$ = 60.13°). After merging of equivalents and absorption correction 4504 independent reflections (R_{int} = 0.1114) were

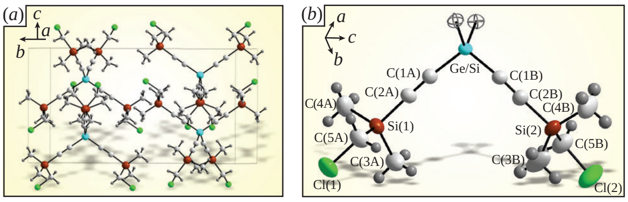


Figure 1 (*a*) Crystal structure of compounds **4a** and **4b** $M(SiC_5H_8Cl)_4$ (M = Si, Ge). (*b*) The atoms in the asymmetric part of the unit cell are labeled. The thermal ellipsoids are drawn at the 50% probability level.

Table 1 The main bond lengths (Å) of compounds $Si(SiC_5H_8Cl)_4$ **4a** and $Ge(SiC_5H_8Cl)_4$ **4b**.

$Si(SiC_5H_8Cl)_4$, **4a**		$Ge(SiC_5H_8Cl)_4$, **4b**	
Si–C(1A)^i	1.819(2)	Ge–C(1A)	1.888(5)
Si–C(1A)	1.819(2)	Ge–C(1A)^i	1.888(5)
Si–C(1B)	1.822(2)	Ge–C(1B)	1.883(5)
Si–C(1B)^i	1.822(2)	Ge–C(1B)^i	1.883(5)
C(1A)–C(2A)	1.206(3)	C(1A)–C(2A)	1.197(7)
Si(1)–C(3A)	1.842(3)	Si(1)–C(3A)	1.837(7)
Si(1)–C(2A)	1.850(2)	Si(1)–C(2A)	1.848(6)
Si(1)–C(4A)	1.842(3)	Si(1)–C(4A)	1.844(6)
Si(1)–C(5A)	1.875(3)	Si(1)–C(5A)	1.873(6)
C(5A)–Cl(1)	1.791(3)	C(5A)–Cl(1)	1.782(6)
C(1B)–C(2B)	1.200(3)	C(1B)–C(2B)	1.206(7)
Si(2)–C(3B)	1.832(3)	Si(2)–C(3B)	1.821(7)
Si(2)–C(4B)	1.837(3)	Si(2)–C(4B)	1.843(8)
Si(2)–C(2B)	1.852(2)	Si(2)–C(2B)	1.850(6)
Si(2)–C(5B)	1.867(3)	Si(2)–C(5B)	1.854(7)
C(5B)–Cl(2)	1.783(3)	C(5B)–Cl(2)	1.783(6)

Pccn with four molecules in the unit cell and half molecule in an asymmetric unit. The molecules have S_4 symmetry. Cell parameters of compounds **4a** and **4b** are very close, but germanium derivative has larger cell size and *a*, *b*, *c* parameters due to the differences in the Si–C and Ge–C bond lengths (~1.82 and 1.88 Å, respectively).

In order to get a better insight into the geometry, electronic structure and spectroscopic properties of compounds **4a**,**b**, we performed MP2/6-311G(d,p) calculations (including frequency calculations),[19] which are very time-consuming but adequately reproduce the experimental structure, and compared the results with the X-ray and IR experiments. The calculated C≡C bond lengths in both structures are very similar, 1.240 ± 0.001 Å, but their polarity, assessed as the difference $\Delta q_{C\equiv C}$, in molecule **4b** (0.05) is notably smaller than in molecule **4a** (0.12). This is consistent with the notably higher Allred–Rochow electronegativity of germanium ($\chi_{Ge} = 2.02$) than that of silicon ($\chi_{Si} = 1.74$) and explains sharply different calculated IR intensities of the C≡C stretching vibrations: 0.22 km mol^{-1} in molecule **4b** and 7.7 km mol^{-1} for more polar triple bond in molecule **4a**.

As mentioned above, one of the goals was to functionalize the obtained dendrimers using terminal chloromethyl groups. However, all our attempts to involve the CH_2Cl group in the intramolecular cyclization on the example of tetrakis[(chloromethyl)dimethylsilylethynyl]silane **4a** by the reaction with amines (methylamine and ethylenediamine) in order to close the ring by the $CH_2N(R)CH_2$ link failed. The amination did truly occur, as proved by the formation of the corresponding amine hydrochloride precipitated from the reaction mixture and the appearance of characteristic signals of the $SiCH_2N$, NCH_2CH_2N and NCH_3 groups in the ^1H NMR spectra at 2.13–2.23, 2.43 and 2.37 ppm, respectively. However, even at high dilution, the isolated product represented an inseparable mixture of oligomers. The formation of only negligible amounts of the product of intramolecular cyclization is, apparently, due to sterically too remote CH_2Cl groups.

All measurements were performed on the analytical equipment of the Baikal Center for Collective Use of Siberian Branch of Russian Academy of Sciences and Krasnoyarsk Center of Collective Use of Siberian Branch of Russian Academy of Sciences. We thank Dr. M. Molokeev (Laboratory of Crystal Physics, Kirensky Institute of Physics) for his very useful help in the X-ray structural analysis.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.05.029.

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used for the structure solution and refinement. Final *R* factors: $R_1 = 0.0469$ [2715 reflections with $I > 2\sigma(I)$], $wR_2 = 0.1047$ (all reflections), GOF = 0.892.

Crystal data for **4b**. $C_{20}H_{32}Cl_4Si_4Ge$, orthorhombic, space group *Pccn*, $M_r = 599.20$, $a = 13.592(6)$, $b = 20.269(8)$ and $c = 11.336(5)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 3123(2)$ Å^3, $Z = 4$, $T = 293$ K, $d_{calc} = 1.274$ g cm^{-3}, $F(000) = 1232$. Colorless block-shaped single crystal with dimensions 0.20 × 0.20 × 0.30 mm was selected and intensities of 21498 reflections were measured using the SMART APEX II single crystal diffractometer (equipped with a CCD-detector, graphite monochromator and MoKα radiation source, $\lambda = 0.71073$, the φ and ω scans, $\mu = 1.483$ mm^{-1}, $2\theta_{max} = 60.13°$). After merging of equivalents and absorption correction 2670 independent reflections ($R_{int} = 0.1385$) were used for the structure solution and refinement. Final *R* factors: $R_1 = 0.0633$ [2043 reflections with $I > 2\sigma(I)$], $wR_2 = 0.0984$ (all reflections), GOF = 1.109.

The structures were solved and refined by direct methods using the SHELX programs set.[16] Data were corrected for absorption effects using the multi-scan method (SADABS). Non-hydrogen atoms were refined anisotropically using SHELX.[16] All hydrogen atoms of the SiC_5H_8Cl ligand were positioned geometrically as riding on their parent atoms with d(C–H) = 0.96–0.97 Å for the C–H bonds and $U_{iso}(H) = 1.2U_{eq}(C)$. The structural tests for the presence of missing symmetry elements and possible voids were produced using the PLATON program.[17] The DIAMOND program [18] was used for the crystal structure plotting.

CCDC 2080893 (**4a**) and 2117144 (**4b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

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