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TETRAHEDRON

Synthesis and Structure of Tris[(2-alkoxymethyl)phenyl]germanes and Tris[(2-methylthiomethyl)phenyl]germane[1]

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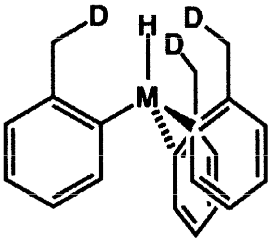
Abstract: Tris[(2-alkoxymethyl)phenyl]germanes and tris[(2-methylthiomethyl)phenyl]germane were prepared and their structures were investigated by means of X-ray crystallographic analysis and ^{73}Ge NMR spectra, which indicated incipient dative bonding between germanium and sulfur or oxygen atoms to make the germanium atom hexavalent and heptavalent, respectively. © 1998 Elsevier Science Ltd. All rights reserved.

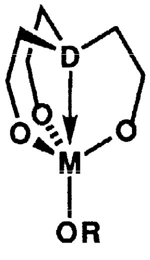
INTRODUCTION

Recently the hypervalency of main group metal elements has attracted considerable attention. Of the hypervalency of group 14 elements, that for the organosilicon compounds has been well investigated[2,3,4] while the hypervalency of organogermanium compounds has not fully been investigated[5] except for some triarylgermanes (A; M = Ge)[6] and germatranes (B; M = Ge)[7]. In the course of a new project on supramolecular organogermanium chemistry[8], we were interested in obtaining further insights into this interesting phenomenon of germanium hypervalency.

Of the systems where hypervalency has been observed, triarylgermanes seems most intriguing since the steric enforcement toward hypervalency is not so strong as that in the case of germatranes because a rotation about C(phenyl)-CH_2 bond will make the donor atoms far apart from the central atom. According to Corriu *et al.*[3], hypervalency is achieved in the case of triarylgermanes and -silanes when the donor D is dimethylamino group.



A



B

M = Si, Ge
D = donor

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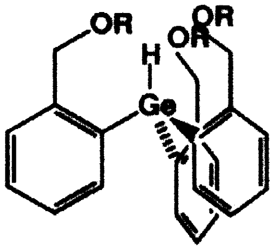
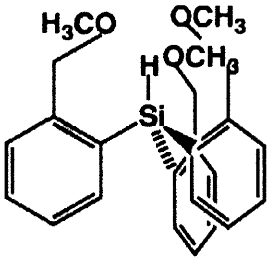
In this paper we discuss the case where the donor atom is an atom other than nitrogen. For this purpose, we chose the following compounds, tris[2-alkoxymethyl)phenyl]germane (**1a-1c**) and tris[2-methylthiomethyl)phenyl]germane (**3**). Their silicon analogs, tris[2-methoxymethyl)phenyl]silane (**2**) and tris[2-methylthiomethyl]phenyl]silane (**4**) were also prepared for comparison.



1a-1c

a; $R = CH_3$-
b; $R = C_2H_5$-
c; $R = (CH_3)_3C$-



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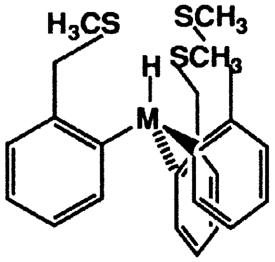
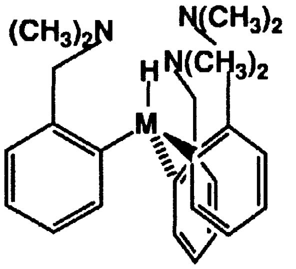


3,4

3; M = Ge
4; M = Si

It is expected that a comparison between these compounds and their nitrogen analogs, tris[dimethylaminomethyl)phenyl]germane(**5**) and -silane(**6**) will cast some light on the possible dative bond formation between germanium (silicon) and oxygen (sulfur) since **5** and **6** were proved to be heptacoordinated[3]. In these heptacoordinated compounds, the three nitrogen atoms of the side chain are coordinated to the central atom, occupying the *trans* position to the aryl group to form "tricapped tetrahedron"[3] (*i.e.*, coordination of three ligands to the tetrahedral central metal or metalloid atom).



5, 6

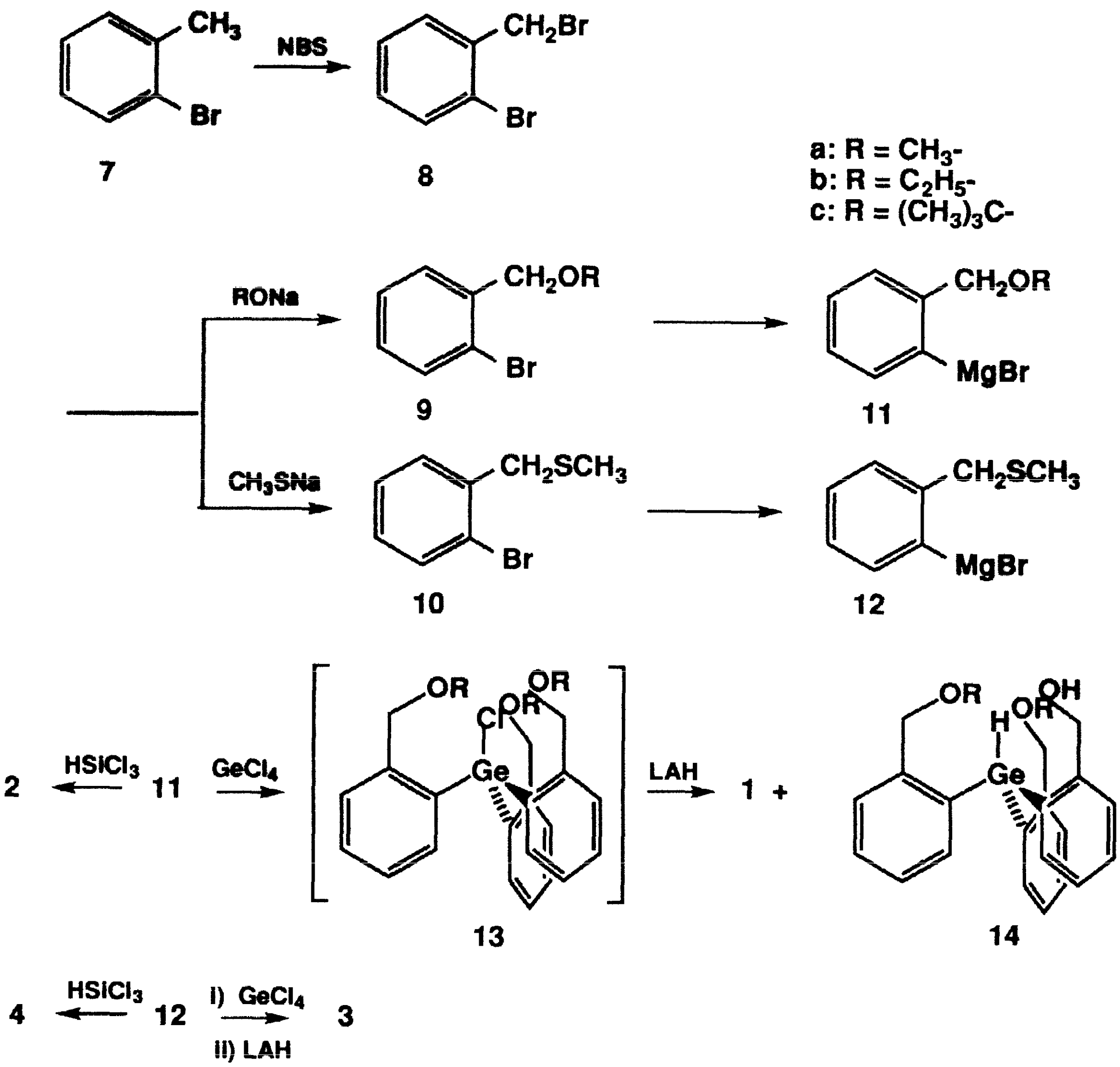
5; M = Ge
6; M = Si

Then it would be interesting to see if compounds **1-4** are also heptacoordinated, *i.e.*, if oxygen or sulfur is a ligand strong enough to cause hypervalency of germanium or silicon in triarylgermanes and -silanes. With this in mind we prepared a series of **1-4** and investigated these by X-ray crystallography and ^{73}Ge NMR spectra.

RESULTS AND DISCUSSION

Preparation of compounds

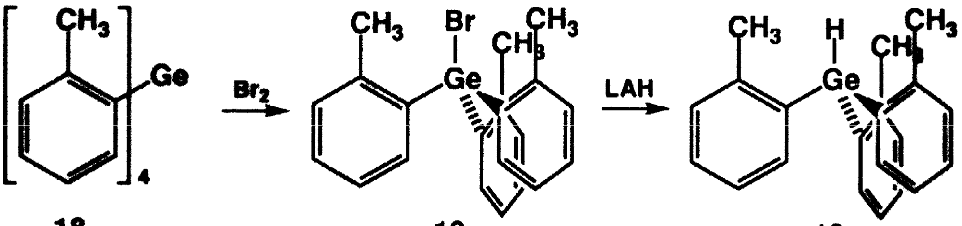
The common precursor for **1-4**, *i.e.*, alkyl *o*-bromobenzyl ether (**9a-c**) or 2-bromobenzyl methyl thioether (**10**) were obtained from *o*-bromotoluene (**7**) *via* 2-bromobenzyl bromide (**8**) by conventional procedures. The chlorotriarylgermane intermediate **13**, obtained form the Grignard reagents **11** and **12**, were not isolated but subsequently treated with lithium aluminum hydride (LAH) to afford the desired triarylgermanes **1a-1c** or **3** in a moderate yield. Treatment of the same Grignard reagents **11** and **12** with trichlorosilane afforded triarylsilanes **2** and **4**.(Scheme 1)



Scheme 1. Preparation of Triarylgermanes and -silanes

It is desirable to obtain the methoxy derivative **1a** or at least the ethoxy derivative **1b** for a better comparison with **5** and **6**. Unfortunately, however, **1a** is liquid and **1b** fails to give good crystals for X ray analysis. Hence we chose **1c**. In the case of thio compounds, the methylthio derivative **3** yielded good crystals. In the case of preparation of **1a** and **1c**, monohydroxy compounds, **14a** and **14c**, respectively, were formed in addition to the desired products.

The reference compound for NMR study, tris(2-methylphenyl)germane (**16**), was prepared from tetrakis(*o*-methylphenyl)germane (**18**), which in turn was prepared from *o*-bromotoluene and $GeCl_4$ (Scheme 2).



18 **19** **16**

Scheme 2. Preparation of Reference Compound

The structure of these compounds was confirmed by IR spectra, ^{1}H, ^{13}C, ^{29}Si and ^{73}Ge NMR spectra, and in some cases by elemental analysis. Some organogermanium or -silicon compounds deteriorated rapidly and gave elemental analyses slightly deviated from the calculated values. The NMR data, however, supported the structures.

Molecular Structure of 1c and 3

Perspective view of **1c** and **3** together with atomic numbering scheme is shown in Figures 1 an 2, respectively.

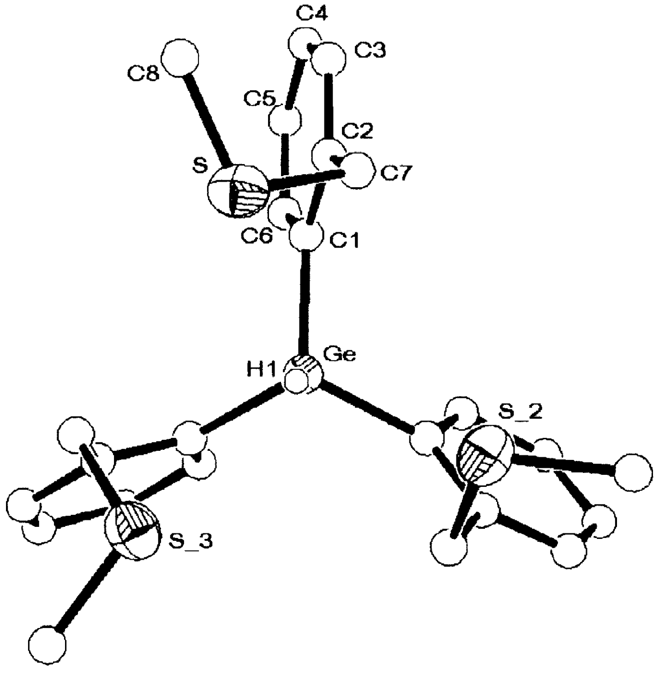


Figure 1. Perspective view of **3**. The numeral in the atom label of S denotes the number of the symmetry operation in the crystal structure. Symmetry operations 2 and 3 are represented as (*-y*, *+x-y*, *+z*) and (*-x+y*. *-x*, *+z*), respectively.

Selected distances(Å) and angles(degrees) for **3** are as follows: Ge-C1, 1.954(5); Ge···S, 3.778(2); C1-Ge-C1_2, 109.4(1); H1-Ge-C1-C6, -160.9(3). Selected distances(Å) and angles(degrees) of **1c** are given in Table 1.

Compound **3** is C_3 symmetric, because the Ge-H bond resides on the crystallographic three fold axis. The carbon atoms of benzyl and methylthio groups are all in the hydrogen side, rather than germanium side of Ge-H bond. This is the case with tris(2-methylphenyl)germane(**16**)[9] and **5**.

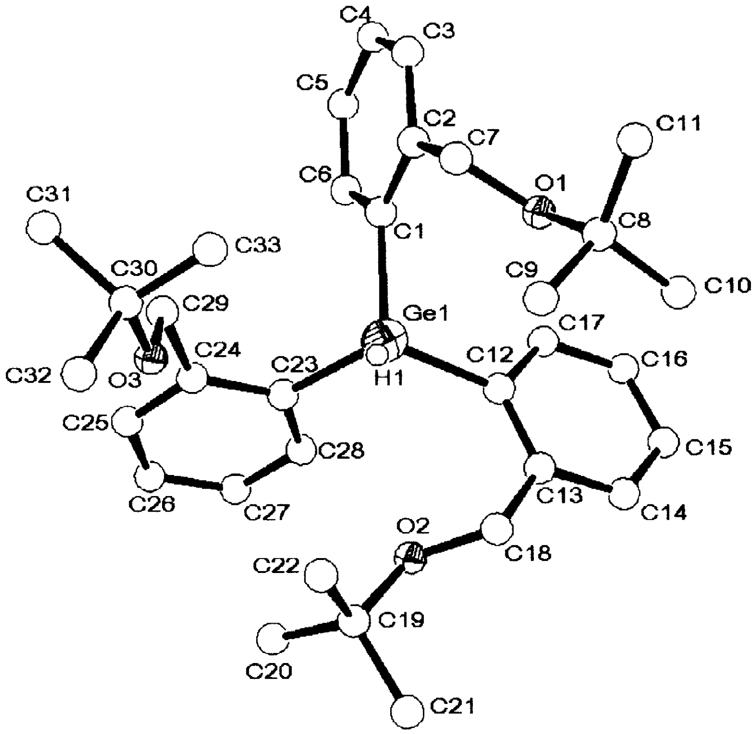


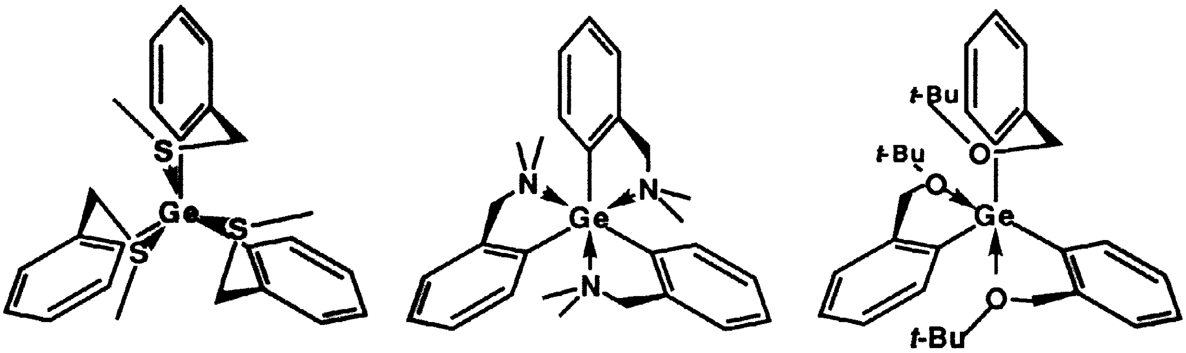
Figure 2. Perspective view of **1c**.

Table 1. Selected distances(Å) and angles(degrees) of **1c**.

Ge-C1	1.966(3)
Ge-C12	1.955(4)
Ge-C23	1.963(4)
Ge···O1	3.277(3)
Ge···O2	3.214(3)
Ge···O3	3.703(3)
C1-Ge1-C12	108.8(1)
C12-Ge1-C23	111.0(2)
C23-Ge1-C1	106.9(1)
H1-Ge-C1-C6	-151(1)
H1-Ge-C12-C17	-139(1)
H1-Ge-C23-C28	-128(2)

The most crucial point, the interatomic distance between sulfur and germanium, is 3.778(2)Å, which is slightly, *e.g.*, *ca.* 0.12 Å(3%) shorter than the sum of van der Waals radii(3.90Å)[10]. It seems that one of the sulfur lone pair is directed to germanium atom. In the case of **5**, the interatomic distance between nitrogen and germanium is 3.66Å, which is 0.60Å(16%) shorter than the sum of van der Waals radii(3.65Å). The twist angle H1-Ge-C1-C6 which corresponds to the deviation from coplanarity of benzene ring with the H-Ge-C1 plane is *ca.* 20°. The average bond angle Ar-Ge-H in **5** is reported to be 112.7°; on the other hand, the same angle for **3** is 109.4(1)°, which is very close to the tetrahedral angle.

A very interesting point is the difference in the position of donor atoms relative to the aromatic ring. If we draw a Newman-type projection along Ge-H bond for **3** and **5** as is shown in Fig. 3, in the former the Ge-Ar bond and Ge···S bond are in a sense eclipsed(quasi-eclipsed) while in the latter the Ge-Ar bond and Ge···N bond are quasi-staggered. In other words, in **5**, the three nitrogen atoms are bound to germanium *anti* while in **3** the three sulfur atoms are bound to germanium *cis*, to the *ipso* carbons of the aromatic rings. This observation might cast some light on the appropriateness to interpret silicon hypervalency as a mimic of nucleophilic substitution.[3]



3 **5** **1c**

Fig. 3 Newman type projection of **1a**, **3** and **5**.

The carbon atoms of benzyl and *t*-butoxy groups of **1c** are all in the hydrogen side, rather than germanium side of Ge-H bond as is the case with **3** and **5**. The structure of **1c** is, however, different from that of **3** and **5** in one important point. This is the three unequal O···Ge interatomic distances (Table 1). Thus, one of the three oxygen atoms is not directed to germanium atom and the relevant interatomic distance, 3.703(3)Å is slightly longer than the sum of van der Waals radii of germanium and oxygen (3.62Å). The interatomic distance for other Ge···O bonds is 3.277 and 3.214Å, which is 0.34Å(9%) and 0.41Å(11%), respectively, shorter than 3.62Å. The difference can be visualized in Fig. 3 where one of the Ge···O bond is not quasi-staggered, but quasi-eclipsed with Ge-C(*ipso*) bond. To sum up, we like to propose that in **1c** the germanium is hexavalent. Nevertheless, all three *t*-butoxy ligands are still confined to the proximity of the germanium atom.

The average Ar-Ge-H angle of **1c** is 108.9°, which is essentially identical with the tetrahedral angle as is the case with **3**. The deviation of coplanarity of three benzene rings to the H-Ge-C1(C12 and C23) plane is different and larger than that for **3**. This is probably, at least in part, due to the bulkiness of *t*-butoxy groups.

The X-ray crystallographic analysis of silicon analogs of **3** and **1c**, *i.e.*, **4** and **2**, was impossible; **2** is a liquid, and **4** very rapidly decomposed during the data collection of X-ray diffraction. So the X-ray powder diffraction was measured for **2** and **4**. Since the powder patterns of two compounds were essentially identical, it seemed that these have nearly the same crystal structures. Thus, we can conclude that silicon analogs have much the same structural features of germanium species.

^{73}Ge NMR Spectra

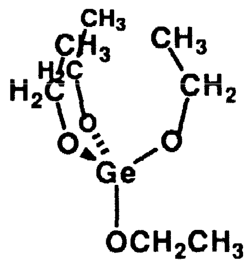
It is generally accepted that multinuclear NMR spectroscopy is a very useful means to prove whether a hypervalent state is involved or not. Thus, hypervalency is often associated with an upfield shift of ^{29}Si signal in the case of silicon compounds. A large line broadening was also reported for germanium hypervalency. We determined ^{73}Ge chemical shifts and linewidth for all compounds we prepared (**1a**-**1c**, **3** and **14**). In addition, we prepared and determined the ^{73}Ge NMR spectra of **5**, triphenylgermane (**15**) and **16** for reference. The results are summarized in Table 2.

Table 2. ^{73}Ge NMR chemical shifts and half-width of triarylgermanes

Compounds	δ	half-width(Hz)
1a	−85	350
1b	−85	350
1c	−84	350
3	−93	270
5	−89	900
14	−85	250
15	−57	20
16	−84	70

Though compounds **1**, **3** and **5** exhibit a substantial upfield shift as compared with **15**, compound **16** shows much the same upfield shift. Hence this upfield shift should be due to γ-effect[11] rather than hypervalency It is interesting to note, however, that there is a rough linear relation($\delta_{Ge} = 0.025\ \delta_{Si} - 0.049$ (R = 0.972)) between the ^{73}Ge chemical shifts of **1a**, **3**, **5**, **15** and ^{29}Si chemical shifts of related silanes, **2** (δ -31.32), **4** (δ -33.34), **6** (δ -35.30[12]) and triphenylsilane (δ -21.1[13]). Such linear relations have long been known between related organogermanium and organosilicon compounds.[14]

On the other hand, the broadening of the signal seems to be always accompanied by the hypervalency. A typical example is the linewidth of ethoxygermatrane (**20**) (165 Hz) *vs.* that of tetraethoxygermane (**21**) (30 Hz)[15] In **15** and **16** the linewidth is narrow, corresponding to the absence of coordination. In the case of **1**, **3** and **5**, the broadening is large, and this is particularly so for **5**, where, as indicated by the interatomic distance, coordination seems stronger.



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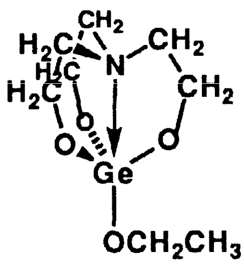

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Thus, both X-ray crystallographic analysis NMR linewidth study support our interpretation that in compound **1**-**4** incipient dative bonding between oxygen(or sulfur) and germanium(and silicon) takes place though it may be weaker than that between nitrogen and germanium in the similar structure **5** and **6**.

EXPERIMENTAL

Syntheses

Mps were obtained using Yanagimoto MP-S3 apparatus and are uncorrected. IR spectra were recorded on Nihon Bunko A202 spectrophotometers. ^{1}H NMR spectra were determined in $CDCl_3$ solution with a JEOL α-500(500 MHz) spectrometer using tetramethylsilane as internal standard. *J* values are in Hz. ^{13}C and ^{29}Si NMR spectra were determined in $CDCl_3$ solution using the same instrument operating at 125.65 MHz, and 99.25 MHz, respectively, using tetramethylsilane as internal standard. ^{73}Ge NMR spectra were determined with the same instrument operating at 17.3 MHz with tetramethylgermane as external standard (condition of measurement; data points, 2048; spectral width, 12500 Hz; acquisition time, 0.1638 sec).

Column chromatography was carried out with Wakogel C-200. High pressure liquid chromatography was carried out with Waters 501 HPLC pump with Waters Differential Refractometer R-401. Liquid chromatography was carried out with Yamazen FFLC 5540 pump and the detector mentioned above.

Tris[2-(methoxymethyl)phenyl]germane (1a) and bis[2-(methoxymethyl)phenyl][2-(hydroxymethyl)phenyl]germane (14a)

The Grignard reagent (**11a**) was prepared by adding a tetrahydrofuran (THF) (28 ml) solution of **9a** (14.00 g, 69.6 mmol) to Mg (1.69 g, 69.5 mmol) in THF (7 ml). Under refluxing, a THF (14 ml) solution of tetrachlorogermane ($GeCl_4$) (4.97 g, 23.2 mmol) was added, and the refluxing was continued for another 10 hrs. After cooling to 0 °C, LAH (0.88 g, 23 mmol) was added and stirred for 15 min. at room temperature. After hydrochloric acid (2 mol l^{-1}) was added, the product was extracted with CH_2Cl_2, which was washed with water, dried over $MgSO_4$ and evaporated. The residue was purified by means of reverse-phase HPLC (medium pressure) chromatography with CH_3CN as the eluent to give tris[2-(methoxymethyl)phenyl]germane (**1a**) (2.53 g, 25.0 %) and, as the by-product, bis[2-(methoxymethyl)phenyl][2-(hydroxymethyl)phenyl]germane (**14a**) (0.94 g, 9.6 %) both as colorless liquid.

(**1a**) IR ($CHCl_3$, ν, cm^{-1}); 2070 (Ge-H). ^{1}H-NMR ($CDCl_3$, δ, r.t.); 3.11 (9H, s, OCH_3), 4.43 (6H, s, $ArCH_2O$) 5.99 (1H, s, GeH), 7.20 (3H, t, *J* = 7.5 Hz, aromatic), 7.24 (3H, dd, *J* = 7.5, 1.5 Hz, aromatic), 7.37 (3H, td, *J* = 7.5, 1.5 Hz, aromatic), 7.43 (3H, d, *J* = 7.5 Hz, aromatic). ^{13}C-NMR ($CDCl_3$, δ, r.t.); 57.72, 74.88, 127.27, 127.92, 129.14, 135.41, 136.07, 143.48. ^{73}Ge-NMR ($CDCl_3$, δ, r.t.) -85.4 ($\nu_{1/2}$ = 350 Hz)

(**14a**) IR ($CHCl_3$, ν, cm^{-1}); 3400 (O-H), 2080 (Ge-H). ^{1}H-NMR ($CDCl_3$, δ, r.t.); 2.98 (6H, s, OCH_3), 4.37 (2H, d, $^2J_{HCH}$ = 11.6 Hz, $ArCH_2OCH_3$), 4.50 (2H, d, $^2J_{HCH}$ = 11.6 Hz, $ArCH_2OCH_3$), 4.61 (2H, s, $ArCH_2OH$), 6.04(1H, s, GeH), 7.20-7.49 (12H, m, aromatic). ^{13}C-NMR ($CDCl_3$, δ, r.t.); 57.32, 64.89, 75.00, 127.27, 127.64, 128.66, 129.03, 129.30, 129.46, 135.68, 135.83, 135.97, 136.07, 143.16, 145.97. ^{73}Ge-NMR($CDCl_3$, δ, r.t.) -84.7 ($\nu_{1/2}$ = 250 Hz).

Tris[2-(ethoxymethyl)phenyl]germane (1b)

The Grignard reagent (**11b**) was prepared by adding a THF(20 ml) solution of **9b** (10.76 g, 50.0 mmol) to Mg (1.22 g, 50.2 mmol) in THF (5 ml). Under refluxing, a THF (10 ml) solution of $GeCl_4$ (3.59 g, 16.7 mmol) was added, and the refluxing was continued for another 40 hrs. After cooling to 0 °C, LAH (0.64 g, 17 mmol) was added and stirred for 15 min. at room temperature. After hydrochloric acid(2 mol l^{-1}) was added, the product was extracted with CH_2Cl_2, washed with water, dried over $MgSO_4$ and evaporated. The residue was purified by recrystallization from CH_3CN to afford tris[2-(ethoxymethyl)phenyl]germane(**1b**) (3.77 g, 47.0 %) as colorless crystal; m.p. 83.5-84.5 °C(from CH_3CN); (Found: C, 67.62 ; H, 7.20%. $C_{27}H_{34}GeO_3$ requires C, 67.68 ; H, 7.15%). IR ($CHCl_3$, ν, cm^{-1}); 2090 (Ge-H). ^{1}H-NMR ($CDCl_3$, δ, r.t.); 0.95 (9H, t, *J* = 7.0 Hz, OCHC*H*$_3$), 3.29(6H, q, *J* = 7.0 Hz, OC CH_3), 4.47 (6H, s, $ArCH_2O$), 6.01 (1H, s, GeH), 7.18 (3H, td, *J* = 7.4, 1.2 Hz, aromatic), 7.23 (3H, dd, *J* = 7.4, 1.2 Hz, aromatic), 7.35 (3H, td, *J* = 7.4, 1.2 Hz, aromatic), 7.44 (3H, dd, *J* = 7.4, 1.2 Hz, aromatic). ^{13}C-NMR; ($CDCl_3$, δ, r.t.); 14.77, 65.59, 73.01, 127.16, 127.96, 129.14, 135.35, 136.11, 143.81. ^{73}Ge-NMR (C_6D_6, δ, r.t.); -85.4 ($\nu_{1/2}$ = 350 Hz).

Tris[2-[(1,1-dimethylethoxy)methyl]phenyl]germane (1c) and bis[2-[(1,1-dimethylethoxy)methyl]phenyl][2-(hydroxymethyl)phenyl]germane (14c)

The Grignard reagent (**11c**) was prepared by adding a THF (20 ml) solution of **9c** (12.17 g, 50.1 mmol) to Mg (1.22 g, 50.2 mmol) in THF (5 ml). Under refluxing, a THF (10 ml) solution of $GeCl_4$ (3.59 g, 16.7 mmol)was added, and the refluxing was continued for another 40 hrs. After cooling to 0 °C, LAH (0.64 g, 17 mmol) was added and stirred for 15 min. at room temperature. After hydrochloric acid (2 mol l^{-1}) was added, the product was extracted with CH_2Cl_2, which was washed with water, dried over $MgSO_4$ and evaporated. The residue was purified by means of reverse-phase HPLC(medium pressure) chromatography with CH_3CN as the eluent to give tris[2-[(1,1-dimethylethoxy)methyl]phenyl]germane (**1c**) (1.29 g, 13.7 %) and bis[2-[(1,1-dimethylethoxy)methyl] [2-(hydroxymethyl)phenyl]germane (**14c**) (1.24 g, 14.6 %) as colorless crystal (**1c**) and colorless liquid (**14c**), respectively.

1c: m.p. 58.0-59.0 °C (from CH_3CN); (Found: C, 70.65 ; H, 8.23 %. $C_{33}H_{46}GeO_3$ requires C, 70.36 ; H, 8.23%). IR ($CHCl_3$, ν, cm^{-1}); 2070 (Ge-H). ^{1}H-NMR ($CDCl_3$, δ, r.t.); 1.05 (27H, s, CH_3), 4.38 (6H, s, $ArCH_2O$), 6.05 (1H, s, GeH), 7.16 (3H, t, *J* = 7.5 Hz, aromatic), 7.24(3H, dd, *J* = 7.5, 1.3 Hz, aromatic), 7.37 (3H, td, *J* = 7.5, 1.3 Hz, aromatic), 7.51 (3H, d, *J* = 7.5 Hz, aromatic). ^{13}C-NMR ($CDCl_3$, δ, r.t.); 27.39, 64.43, 73.41, 126.84, 127.58, 129.39, 134.20, 135.93, 145.18. ^{73}Ge-NMR (C_6D_6, δ, r.t.); -84.0 ($\nu_{1/2}$ = 350 Hz).

14c: IR ($CHCl_3$, ν, cm^{-1}); 3400 (O-H), 2060 (Ge-H). ^{1}H-NMR ($CDCl_3$, δ, r.t.); 1.02 (18H, s, *t*-Bu), 4.38(2H, d, $^2J_{HCH}$ = 10.9 Hz, ArC*H*$_2$O-*t*-Bu), 4.43 (2H, d, $^2J_{HCH}$ = 10.9 Hz, ArC*H*$_2$O-*t*-Bu), 4.52 (2H, s, ArCH2OH), 6.05 (1H, s, GeH), 7.17-7.25 (6H, m, aromatic), 7.36-7.40 (3H, m, aromatic), 7.47-7.48 (3H, m, aromatic). ^{13}C-NMR ($CDCl_3$, δ, r.t.); 27.28, 64.59, 65.68, 73.78, 127.28, 127.42, 128.67, 128.97, 129.56, 135.09, 135.79, 135.85, 136.14, 144.65, 146.39.

Tris[2-(methylthiomethyl)phenyl]germane (3)

The Grignard reagent (**12**) was prepared by adding a THF (80 ml) solution of **10** (21.72 g, 100 mmol) and 1,2-dibromomethane (18.72 g, 100 mmol) to Mg (4.86 g, 200 mmol) in THF (40 ml). Under refluxing, a THF (10 ml) solution of $GeCl_4$ (7.15 g, 33.3 mmol) was added, and the refluxing was continued for another 40 hrs. After cooling to 0 °C, LAH (1.27 g, 33.5 mmol) was added and stirred for 15 min. at room temperature. After hydrochloric acid (2 mol l^{-1}) was added, the product was extracted with CH_2Cl_2, which was washed with water, dried over $MgSO_4$ and evaporated. The residue was purified by means of reverse-phase HPLC (medium pressure) chromatography with CH_3CN as the eluent, and the eluted material was recrystallized from CH_3CN to give tris[2-(methylthiomethyl)phenyl]germane (**3**) (4.08 g, 25.2 %) as colorless crystal. m.p. 116.0-117.0 °C (from CH_3CN). (Found: C, 59.22 ; H, 5.79%. $C_{24}H_{28}GeS_3$ requires C, 59.40 ; H, 5.82%). IR ($CHCl_3$, ν , cm^{-1});. 2090 (Ge-H). ^1H-NMR ($CDCl_3$, δ, r.t.); 1.92(9H, s, SCH_3), 3.75(6H, s, $ArCH_2S$), 6.37 (1H, s, GeH), 7.16 (3H, td, J = 7.3, 1.5 Hz, aromatic), 7.19 (3H, dd, J = 7.3, 1.5 Hz, aromatic), 7.35 (3H, td, J = 7.3, 1.5 Hz, aromatic), 7.42 (3H, d, J = 7.3 Hz, aromatic). ^{13}C-NMR ($CDCl_3$, δ, r.t.); 15.23, 39.27, 126.68, 129.45, 129.54, 135.57, 136.31, 143.60. ^{73}Ge-NMR (C_6D_6, δ, r.t.); -92.7 ($\nu_{1/2}$ = 270 Hz)

Tris[2-(methoxymethyl)phenyl]silane (2)

The Grignard reagent **11a** was prepared by adding a THF (66 ml) solution of **9a** (32.92 g, 163.7 mmol) to Mg (3.98 g, 163 mmol) in THF (17 ml). Under ice-cooling, a THF (30 ml) solution of trichlorosilane ($HSiCl_3$) (7.39 g, 54.6 mmol) was added, and the refluxing was continued for another 40 hrs. After cooling to 0 °C, LAH (1.27 g, 33.5 mmol) was added and stirred for 15 min. at room temperature. Water was added, and the product was extracted with CH_2Cl_2, which was dried over $MgSO_4$ and evaporated. The residue was purified by means of reverse-phase HPLC (medium pressure) chromatography with CH_3CN as the eluent to give tris[2-(methoxymethyl)phenyl]silane (**2**) (18.23 g, 85.1 %) as colorless oil. IR ($CHCl_3$, ν, cm^{-1}); 2160 (Ge-H). ^1H-NMR ($CDCl_3$, δ, r.t.); 3.10 (9H, s, OCH_3), 4.46 (6H, s, $ArCH_2O$), 5.73 (1H, s, SiH), 7.20 (3H, td, J = 7.3, 1.1 Hz, aromatic), 7.25 (3H, dd, J = 7.3, 1.1 Hz, aromatic), 7.39 (3H, td, J = 7.3, 1.1 Hz, aromatic), 7.42 (3H, dd, J = 7.3, 1.1 Hz, aromatic). ^{13}C-NMR ($CDCl_3$, δ, r.t.); 57.70, 74.52, 126.93, 127.52, 129.67, 132.84, 137.04, 144.33. ^{29}Si-NMR ($CDCl_3$, δ, r.t.); -31.32($^1J_{SiH}$ 208 Hz).

Tris[2-(methylthiomethyl)phenyl]silane (4)

The Grignard reagent of **12** was prepared by adding a THF (80 ml) solution of **10** (21.71 g, 100 mmol) to Mg (4.86 g, 200 mmol) in THF (40 ml). Under ice-cooling, a THF (50 ml) solution of $HSiCl_3$ (4.51 g, 33.3 mmol)was added, and the refluxing was continued for another 40 hrs. After cooling to 0 °C, LAH (1.27 g, 33.5 mmol) was added and stirred for 15 min. at room temperature. Water was added, and the product was extracted with CH_2Cl_2, which was washed with water, dried over $MgSO_4$ and evaporated. The residue was purified by means of reverse-phase HPLC (medium pressure) chromatography with CH_3CN as the eluent followed by recrystallization from CH_3CN to give tris[2-(methylthiomethyl)phenyl]silane (**4**) (1.86 g, 12.7 %) as colorless crystal; m.p. 111.5-112.5 °C (from CH_3CN). (Found: C, 65.35; H, 6.33; S, 21.68 %. $C_{24}H_{28}SiS_3$ requires C, 65.40 ; H, 6.40; S, 21.82 %). IR ($CHCl_3$, ν, cm^{-1}); 2170 (Ge-H). ^1H-NMR ($CDCl_3$, δ, r.t.); 1.91 (9H, s, SCH_3), 3.77 (6H, s, $ArCH_2S$), 6.13 (1H, s, SiH), 7.15 (3H, td, J = 7.3, 1.4 Hz, aromatic), 7.19 (3H, dd, J = 7.3, 1.4 Hz, aromatic), 7.38 (3H, td, J = 7.3, 1.4 Hz, aromatic), 7.43 (3H, d, J = 7.3 Hz, aromatic). ^{13}C-NMR ($CDCl_3$, δ, r.t.); 57.70, 74.52, 126.93, 127.52, 129.67, 132.84, 137.04, 144.33. ^{29}Si-NMR ($CDCl_3$, δ, r.t.); -33.34 ($^1J_{SiH}$ = 204 Hz).

Tetrakis(2-methylphenyl)germane (18)

The Grignard solution between *o*-bromotoluene (75.00 g, 438.5 mmol) and $GeCl_4$ (11.00 g, 51.30 mmol), after usual workup, afforded tetrakis(2-methylphenyl)germane (**18**) (11.64g, 52.8%) as colorless crystal. ^1H-NMR ($CDCl_3$, δ, r.t.); 2.03 (12H, s, CH_3), 7.13-7.20 (8H, m, aromatic), 7.30 (4H, td, J = 7.4, 1.3 Hz, aromatic), 7.49 (4H, dd, J = 7.4, 1.3 Hz, aromatic). ^{13}C-NMR ($CDCl_3$, δ, r.t.); 23.52, 125.58, 129.18, 130.21, 135.96, 135.99, 144.03. ^{73}Ge-NMR ($CDCl_3$, δ, r.t.); -33.2 ($\nu_{1/2}$ = 80 Hz).

Tris(2-methylphenyl)germane (16)

A solution of **18** (2.00 g, 458 mmol) and bromine (0.78 g, 4.88 mmol) in $BrCH_2CH_2Br$ (12.2 ml) was refluxed for 30 min. After the solvent was removed, diethyl ether (20 ml) was added and cooled to room temp., to which LAH (0.17 g, 4.5 mmol) was added and stirred for 15 min. Hydrochloric acid (2 mol l^{-1}) was added and the product was extracted with CH_2Cl_2 for 4 times, washed with water and dried over $MgSO_4$. The solvent was removed, and the residue was distilled *in vacuo*. The distillate was chromatographed (medium pressure, reverse phase, CH_3CN) and further recrystallized from CH_3CN to afford tris(2-methylphenyl)germane (**16**) (0.49 g, 31%) as colorless crystal. ^{1}H-NMR ($CDCl_3$, δ, r.t.); 2.33 (9H, s, CH_3), 5.95 (1H, s, GeH), 7.11 (3H, t, J = 7.3 Hz, aromatic), 7.16 (3H, dd, J = 7.3, 1.2 Hz, aromatic), 7.23 (3H, dd, J = 7.3, 1.2 Hz, aromatic), 7.30 (4H, td, J = 7.3, 1.2 Hz, aromatic). ^{13}C-NMR ($CDCl_3$, δ, r.t.); 22.97, 125.49, 129.41, 129.62, 134.63, 135.61, 143.83. ^{73}Ge-NMR ($CDCl_3$, δ, r.t.); -84.0 ($\nu_{1/2}$ = 65 Hz, $^1J_{GeH}$ = 99.6 Hz).

X-ray Data Collection and Reduction

Crystals of **1c** and **3** were obtained *via* slow evaporation of CH_3CN solution at room temperature. X-ray

Table 3. Crystal data for compounds **1c** and 3

Compounds	**3**	**1c**
Formula	$C_{24}H_{28}GeS_3$	$C_{33}H_{46}GeO_3$
Formula weight	485.27	563.32
Crystal system	trigonal	triclinic
Space group	$R3$ (hexagonal setting)	$P\bar{1}$
Crystal color	colorless	colorless
Crystal size (mm)	0.45, 0.30, 0.10	0.2, 0.2, 0.2
a (Å)	14.850(2)	9.877(2)
b (Å)	14.850	18.770(1)
c (Å)	9.166(2)	9.830(2)
α (°)	90	97.59(1)
β (°)	90	118.7(1)
γ (°)	120	85.17(1)
V (Å^3)	1750.3(6)	1584.1(5)
Z	3	2
d_{calcd} (g cm^{-3})	1.38	1.18
λ (Å)	0.71069	1.54184
μ (mm^{-1})	1.56	1.50
$2\theta_{max}$ (°)	55	120
Number of reflections refined	1673	4178
Number of parameters	122	470
R	0.044	0.050
GOF	1.005	0.802

data from the two compounds were collected at room temperature on a Rigaku AFC6A four-circle diffractometer and a Rigaku AFC5 diffractometer, respectively. Intensity data were collected by the $\theta/2\theta$ scan techniques. Structures were solved by direct methods using the programs Shelxs86[16] for **1c** and Shelx76[17] for **3**. Structures were refined based on $|F_o|$ using Xtal3.2[18] for **1c** and Shelx76 for **3**. Final atomic parameters were deposited at the Cambridge Crystallographic Data Centre. The crystallographic data are summarized in Table 3. Perspective views of the molecules (Figs. 1 and 2) were made by the use of ORTEPIII for Windows[19].

REFERENCES AND NOTES

1. Presented at the 8th International Conference on the Organometallic Chemistry of Germanium, Tin and Lead, Sendai, September 1995.
2. Corriu, R. J. P.; Young, J. C. in Patai, S.; Rappoport, Z. ed. *The Chemistry of Organic Silicon Compounds*, part 2, John Wiley & Sons; Chichester, 1989, pp. 1241-1288.
3. Corriu, R. J. P. in Bassindale, A.; Gasper, P. P. ed. *Frontiers of Organosilicon Chemistry*, The Royal Society of Chemistry, London, 1992, pp. 185-196.
4. Chuit, C.; Corriu, R. J. P.; Reyé, C.; Young , J. C. *Chem.Rev.* **1993**, *93*, 1371-1448.
5. Mackay, K. M. in Patai, S. ed. *The Chemistry of Organic Germanium, Tin and Lead Compounds*, John Wiley & Sons; Chichester, 1995, pp. 97-194.
6. Brelière, C.; Carré, F.; Corriu, R. J. P.; Royo. G.; Wong, M. Chi Man.*Organometallics*, **1994**, *13*, 307-314.
7. Verkade, J. G. *Acc. Chem. Res.* **1993**, *26*, 483-489.
8. Aoyagi, S.; Ogawa, K.; Tanaka, K.; Takeuchi, Y. *J. Chem. Soc. Perkin Trans. 2*, **1995**, 355-358.
9. Cameron,T. S.; Mannan, K. M.; Stobart, S. R. *Cryst. Struct. Comm.*, **1975**, *4*, 601.
10. The van der Waals radius of germanium was assumed to be 2.1-2.2 Å[3)] based on: Bondi, A. *J. Phys. Chem.*, **1964**, *68*, 441-451.
11. Takeuchi,Y.; Shimoda, M.; Tanaka, K.; Tomoda, S.; Ogawa,K.; Suzuki, H. *J. Chem. Soc., Perkin Trans. 2*, **1988**, 7-13.
12. Brelière, C.; Carré, F.; Corriu, R. J. P.; Royo. G.*Organometallics*, **1988**, *7*, 1006-1008.
13. Williams, E. A. in Patai, S.; Rappoport, Z. ed. *The Chemistry of Organic Silicon Compounds*, part 1, John Wiley & Sons; Chichester, 1989, pp. 511-554.
14. Liepins,E.; Zicmane, I.; Lukevics, E. *J. Organometal. Chem.*, **1988**, *341*, 315-333.
15. Kupce,E.; Lukevics, E.; Flid, O. D.; Viktorov, N. A.; Gar , T. K. *J.Organomet.Chem.* **1989**, *372*, 187-188.
16. Campbell , J. R. *J.Org.Chem.* **1964**, *29*, 1830-1833.
17. Shelxs86, Sheldrick, G. M. 1986, University of Göttingen, Germany
18. Shelx76, Sheldrick, G. M. 1976, University of Cambridge, England
19. Hall, S. R.; Flack, H. D.; Stewart, J. M. Eds., **1992**, Universities of Western Australia, Geneva, and Maryland.
20. Ortep-3 for Windows, Farrugia, L. J. *J. Appl. Cryst.*, **1997**, 565.