Syntheses and Structural Characterizations of a Novel Bowl-Type Germanol and Its Derivatives

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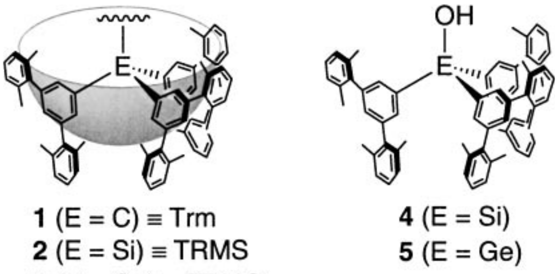
A novel bowl-type triarylgermyl group, tris(2,2″,6,6″-tetramethyl[1,1′:3′,1″-terphenyl]-5′-yl)germyl (denoted as TRMG), was designed, and a germanol and its derivatives bearing this framework were synthesized. X-ray crystallographic analysis of TRMG–OH (**5**) revealed that there is no OH···O hydrogen bonding between adjacent molecules, although the possible presence of a weak intermolecular OH···π interaction was suggested. In sharp contrast to organogermanols known so far, **5** is extremely resistant to self-condensation; no digermoxane was obtained when **5** was subjected to the conditions under which Ph_3GeOH (**8**) affords the corresponding digermoxane. On the other hand, germanol **5** was readily converted to various derivatives. The crystal structure of TRMG–SH (**12**) was also determined.

There have been a great number of reports on the structural features of organosilanols as well as on the weak intermolecular and intramolecular interactions found in their crystal structures.[1] In contrast, only limited information has been accumulated for the structures of analogous organogermanols, presumably because their sensitivity toward self-condensation is higher than that of organosilanols.[2] In the course of our study on the development and application of the bowl-shaped molecules,[3] we have designed a novel triarylmethyl group **1** (denoted as Trm)[4] and a triarylsilyl group **2** (denoted as TRMS)[5,6] shown in Chart 1. In **1** and **2**, the phenyl groups of a Ph_3C and Ph_3Si group are replaced by the radially extended *m*-terphenyl-5′-yl groups, respectively, so that they would form a shallow bowl-shaped cavity. The reactive species bearing the Trm group can be prevented from dimerization or self-condensation effectively, whereas its reactivity towards appropriate molecules is not so much degenerated because there is a relatively large space around it. A stable *S*-nitrosothiol (TrmSNO) was successfully synthesized by taking advantage of the Trm group.[4] We also reported that silanol **4** bearing the TRMS group is extremely resistant to self-condensation.[5] Unlike the usual organosilanols, **4** shows no OH···O hydrogen bonding either in the crystalline state or in solution. It is expected that an analogous germyl group **3** (tris(2,2″,6,6″-tetramethyl[1,1′:3′,1″-terphenyl]-5′-yl)germyl; denoted as TRMG hereafter) will be useful as a novel germyl group possessing the above-mentioned characteristics of the Trm and TRMS groups. Here we report the syntheses, crystal structures, and reactivities of germanol **5** and its derivatives bearing the TRMG group.



1 (E = C) ≡ Trm
2 (E = Si) ≡ TRMS
3 (E = Ge) ≡ TRMG

4 (E = Si)
5 (E = Ge)

Chart 1.

Experimental

Melting points were determined on a Yanaco micro melting point apparatus. All melting points are uncorrected. Et_2O and THF was purified by distillation from sodium diphenylketyl under argon atmosphere before use. Benzene and decalin were distilled from calcium hydride. Dioxane was purchased from Wako Pure Chemical Industries Ltd. and used without purification. Preparative gel permeation liquid chromatography (GPLC) was performed by LC-908 C60 and LC-918 with JAIGEL 1H and 2H columns (Japan Analytical Industry) with chloroform as solvent. Column chromatography was carried out with Wakogel C-200. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX-500 or a JEOL JNM-A500 spectrometer. Infrared spectra were obtained with a JASCO FT-IR420. For measurements of reflectance IR microspectra, an infrared microscope attachment, JASCO IRT-30, was used. Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry, Faculty of Science, the University of Tokyo. The preparations of 5′-bromo-2,2″,6,6″-tetramethyl-1,1′:3′,1″-terphenyl (**6**)[7] and Ph_3GeOH (**8**)[8] have been described in the literature.

Synthesis of Chlorotris(2,2″,6,6″-tetramethyl[1,1′:3′,1″-terphenyl]-5′-yl)germane (TRMG–Cl, 7). To a solution of bromide **6** (1.00 g, 2.74 mmol) in Et_2O (10 mL) was added dropwise *n*-BuLi (1.69 M hexane solution, 1.7 mL, 2.87 mmol) at −78 °C. After stirring at −78 °C for 30 min, the solution was warmed to room temperature and again stirred for 30 min. The solution was cooled to −78 °C again, and then $GeCl_4$ (95 µL, 0.833 mmol) was added dropwise. The reaction mixture was stirred at −78 °C for 1 h and at room temperature overnight. After quenching by saturated aqueous NH_4Cl, the aqueous layer was extracted with $CHCl_3$. The combined organic layer was dried over anhydrous $MgSO_4$,

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and the solvent was removed under reduced pressure. The crude product was purified by GPLC to give **7** (0.515 g, 0.534 mmol, 64%), which was further purified by recrystallization from $CHCl_3$–hexane.

7: colorless crystals, mp 269–270 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.94 (s, 36H), 7.04 (t, $J = 1.7$ Hz, 3H), 7.05–7.14 (m, 18H), 7.42 (d, $J = 1.7$ Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.81 (q), 127.21 (d), 127.29 (d), 131.92 (d), 132.81 (d), 134.99 (s), 135.73 (s), 140.98 (s), 141.54 (s). Found: C, 82.02; H, 6.70%. Calcd for $C_{66}H_{63}ClGe$: C, 82.21; H, 6.59%.

Synthesis of Tris(2,2″,6,6″-tetramethyl[1,1′:3′,1″-terphenyl]-5′-yl)germanol (TRMG–OH, 5). To a solution of **7** (0.380 g, 0.394 mmol) in THF (50 mL) was added NaOH (4.03 g, 0.101 mol) in H_2O (50 mL) and the mixture was heated at reflux temperature. After refluxing overnight, the reaction mixture was extracted with $CHCl_3$. The combined organic layer was dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was recrystallized from $CHCl_3$–hexane to give **5** (0.365 g, 0.385 mmol, 98%).

5: colorless crystals, mp 255–256 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.38 (s, 1H), 1.94 (s, 36H), 7.02 (t, $J = 1.6$ Hz, 3H), 7.04–7.13 (m, 18H), 7.41 (d, $J = 1.6$ Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.79 (q), 127.09 (d), 127.24 (d), 131.49 (d), 132.88 (d), 135.73 (s), 136.08 (s), 141.22 (s), 141.37 (s); IR ν_{OH} 3609 cm^{-1} (microcrystals from C_6H_6–hexane on the metal plate), 3609 cm^{-1} (microcrystals from $CHCl_3$–hexane on the metal plate), 3624 cm^{-1} (5 mM and 20 mM CH_2Cl_2 solution). Found: C, 83.57; H, 7.01%. Calcd for $C_{66}H_{64}GeO$: C, 83.81; H, 6.82%.

Comparison of the Reactivity of Germanols. To a solution of Ph_3GeOH (**8**) (0.100 g, 0.312 mmol) in C_6H_6 (30 mL) was added anhydrous $MgSO_4$ (1.00 g, 8.34 mmol) and the mixture was stirred at reflux temperature for 12 h. The solvent was removed under reduced pressure and the crude product was purified with GPLC to give $Ph_3GeOGePh_3$ (**9**) (0.0871 g, 0.140 mmol, 90%). The reaction of TRMG–OH (**5**) (0.296 g, 0.313 mmol) under the same conditions resulted in the quantitative recovery of **5**. When a solution of **5** (0.150 g, 0.159 mmol) in a mixed solvent of H_2O (9 mL) and dioxane (21 mL) was heated at 110 °C for 12 h in the presence of NaOH (0.43 g, 10.8 mmol), **5** was also recovered quantitatively.

Reaction of 5 with Acetyl Chloride. To the solution of **5** (0.234 g, 0.247 mmol) in C_6H_6 (10 mL) was added dropwise acetyl chloride (1.00 mL, 17.7 mmol) at 50 °C. After stirring at 50 °C overnight, the solvent was removed under reduced pressure. The crude product was recrystallized from $CHCl_3$–hexane to give chlorogermane **7** (0.230 g, 0.238 mmol, 96%).

Reaction of 5 with Hydrochloric Acid. To a solution of **5** (0.200 g, 0.212 mmol) in C_6H_6 (20 mL) was added conc. hydrochloric acid (20 mL) and the mixture was heated at reflux temperature. After refluxing overnight, the reaction mixture was extracted with $CHCl_3$ and the combined organic layer was dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the crude product was recrystallized from $CHCl_3$–hexane to give chlorogermane **7** (0.199 g, 0.207 mmol, 98%).

Synthesis of Bromotris(2,2″,6,6″-tetramethyl[1,1′:3′,1″-terphenyl]-5′-yl)germane (TRMG–Br, 10). To a solution of **5** (0.208 g, 0.220 mmol) in C_6H_6 (20 mL) was added conc. hydrobromic acid (20 mL) and the mixture was heated at reflux temperature. After stirring overnight, the reaction mixture was extracted with $CHCl_3$. The combined organic layer was dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was recrystallized from $CHCl_3$–hexane to give **10** (0.204 g, 0.202 mmol, 92%).

10: colorless crystals, mp 280–284 °C (dec); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.93 (s, 36H), 7.02 (t, $J = 1.6$ Hz, 3H), 7.04–7.14 (m, 18H), 7.41 (d, $J = 1.6$ Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.85 (q), 127.24 (d), 127.33 (d), 131.91 (d), 132.99 (d), 134.96 (s), 135.77 (s), 141.02 (s), 141.55 (s). Found: C, 78.32; H, 6.35%. Calcd for $C_{66}H_{63}BrGe$: C, 78.59; H, 6.30%.

Synthesis of Tris(2,2″,6,6″-tetramethyl[1,1′:3′,1″-terphenyl]-5′-yl)germane (TRMG–H, 11). To a solution of **7** (0.230 g, 0.238 mmol) in THF (5 mL) was added $LiAlH_4$ (78.3 mg, 2.06 mmol) at 0 °C, and the reaction mixture was stirred at room temperature overnight. The resulting mixture was poured into ice water and the aqueous layer was extracted with $CHCl_3$. The combined organic layer was dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure to give **11** (0.223 g, 0.239 mmol, quant.), which was further purified by recrystallization from $CHCl_3$–hexane.

11: white solids, mp 242–243 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.92 (s, 36H), 5.81 (s, 1H), 6.93 (t, $J = 1.6$ Hz, 3H), 7.03–7.12 (m, 18H), 7.30 (d, $J = 1.6$ Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.77 (q), 126.98 (d), 127.19 (d), 130.46 (d), 133.86 (d), 135.63 (s), 135.77 (s), 141.14 (s), 141.48 (s). Found: C, 85.05; H, 7.07%. Calcd for $C_{66}H_{64}Ge$: C, 85.25; H, 6.94%.

Synthesis of Tris(2,2″,6,6″-tetramethyl[1,1′:3′,1″-terphenyl]-5′-yl)germanethiol (TRMG–SH, 12). A solution of **11** (0.613 g, 0.660 mmol) and S_8 (23.5 mg, 0.0916 mmol) in decalin (10 mL) was heated at reflux temperature for 5 d and then the solvent was removed under reduced pressure. The crude product was purified with GPLC to give **12** (0.451 g, 0.468 mmol, 71%), which was further purified by recrystallization from $CHCl_3$–hexane.

12: colorless crystals, mp 263–265 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.21 (s, 1H), 1.92 (s, 36H), 6.99 (t, $J = 2$ Hz, 3H), 7.04–7.13 (m, 18H), 7.37 (d, $J = 2$ Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.79 (q), 127.12 (d), 127.27 (d), 131.26 (d), 133.00 (d), 135.76 (s), 136.60 (s), 141.22 (s), 141.37 (s). Found: C, 82.27; H, 7.00; S, 3.47%. Calcd for $C_{66}H_{64}GeS$: C, 82.41; H, 6.71; S, 3.33%.

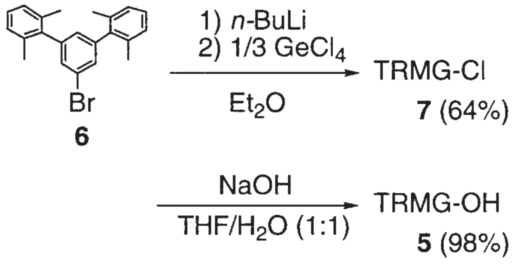
X-ray Crystallographic Analysis of 5a, 5b, and 12. Single crystals of **5b** and **12** were grown in their chloroform/hexane solution, while single crystals of **5a**$\cdot C_6H_{14}$ were grown in their benzene/hexane solution. The intensity data were collected at 120 K on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). Crystallographic and experimental data are listed in Table 1. The structures were solved by the direct method and refined by full-matrix least squares on F^2 using SHELXL 97.[9] The non-hydrogen atoms were refined anisotropically, except for the solvent molecule of **5a**$\cdot C_6H_{14}$ and the minor component of the two disordered 2,6-dimethylphenyl rings of **5b** (0.82:0.18 and 0.83:0.17, respectively). The hydrogen atoms were idealized by using the riding models, except for the OH hydrogens of **5b** and the SH hydrogen of **12**, which were located in the difference Fourier map and then were refined isotropically. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers CCDC 218188–218190.

Results and Discussion

Chlorogermane **7** bearing the TRMG group was prepared by the reaction of tetrachlorogermane with the aryllithium generated from *m*-terphenyl bromide **6** (Scheme 1). The alkaline hydrolysis of **7** in THF/water (1:1) at reflux temperature afforded

Table 1. Crystallographic Data for **5a**•C_6H_{14}, **5b**, and **12**

	5a•C_6H_{14}	**5b**	**12**
Formula	$C_{72}H_{78}GeO$	$C_{66}H_{64}GeO$	$C_{66}H_{64}GeS$
Temperature/K	120	120	120
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$C2/c$	$P2_1/n$	$P2_1/c$
a/Å	31.102(13)	18.220(5)	12.172(4)
b/Å	15.436(6)	24.388(6)	24.854(7)
c/Å	26.603(12)	24.241(6)	17.898(5)
β/deg	110.038(6)	97.893(4)	97.778(3)
V/Å^3	11999(9)	10669(5)	5365(3)
Z	8	8	4
Calculated density/g cm^{-3}	1.143	1.178	1.191
Reflections collected	37516	67998	34140
Unique	10336	18431	9351
R_{int}	0.0387	0.0311	0.0299
F_{000}	4400	4000	2032
Limiting indices	$-29 \le h \le 36$	$-21 \le h \le 20$	$-12 \le h \le 14$
	$-15 \le k \le 18$	$-29 \le k \le 29$	$-29 \le k \le 26$
	$-31 \le l \le 31$	$-26 \le l \le 28$	$-21 \le l \le 21$
Restraints/parameters	0/661	0/1322	0/632
Goodness of fit (F^2)	1.081	1.187	1.103
R indices ($I > 2\sigma(I)$)	$R1 = 0.0603$	$R1 = 0.0457$	$R1 = 0.0474$
	$wR2 = 0.1473$	$wR2 = 0.1131$	$wR2 = 0.1054$
R indices (all data)	$R1 = 0.0673$	$R1 = 0.0552$	$R1 = 0.0527$
	$wR2 = 0.1522$	$wR2 = 0.1179$	$wR2 = 0.1082$



Scheme 1.

germanol **5** almost quantitatively. The IR spectrum of **5** (CH_2Cl_2) shows an absorption at 3624 cm^{-1}, which is assignable to a free OH. This band was found to be concentration-independent, indicating that germanol **5** has a monomeric structure in solution. In the ^{1}H NMR spectrum of **5**, the OH resonance was observed at $\delta = 1.38$. The equivalency of all the methyl protons of the 2,6-dimethylphenyl groups at room temperature shows that the Ge–C bonds rotate rapidly on the NMR time-scale.

The structure of **5** was established by X-ray crystallographic analysis. In large cavity-shaped compounds, the growth of single crystals often depends on the solvent utilized for recrystallization. Two different types of single crystals of **5** were obtained from different solvents, **5a** (from a mixture of benzene and hexane) and **5b** (from a mixture of chloroform and hexane). The crystal structures of **5a** and **5b** are shown in Figs. 1 and 2, respectively. The selected bond lengths and angles for **5a** and **5b** are given in Table 2. In both structures, the OH group is located in the center of a shallow bowl-shaped cavity formed by three *m*-terphenyl units.

The crystal structure of **5a** is isomorphous with that of TRMS–OH (**4**)[5] obtained from the same solvent system (benzene–hexane); it belongs to the monoclinic space group $C2/c$ with $Z = 8$ and one molecule of hexane is included in the asymmetric unit. The most important feature to be noticed is the absence of any OH···O hydrogen bonding. It is well-recognized that germanols have a strong tendency to form intermolecular OH···O hydrogen bonding to give oligomeric structures in the crystalline state.[2] For example, Ph_3GeOH (**8**) was reported to have a tetrameric structure with the intermolecular O···O distances between 2.60 and 2.66 Å.[2b] In sharp contrast, the shortest O···O distance of **5a** is 7.77 Å. There have been a few examples of the germanols which have no intermolecular OH···O hydrogen bridge in the crystalline state.[2c,10] In these

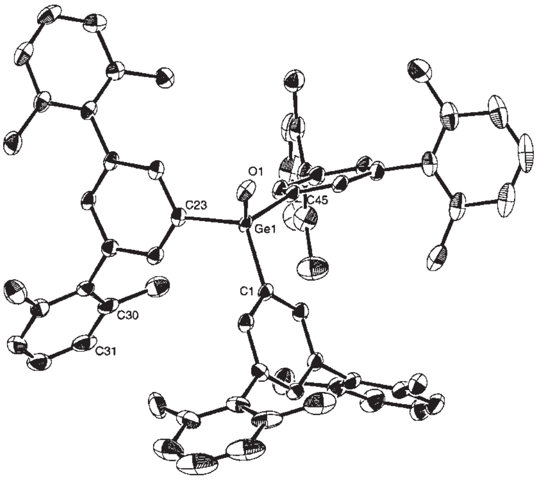


Fig. 1. ORTEP drawing of germanol **5a** (50% probability). The sovlent molecule is omitted for clarity.

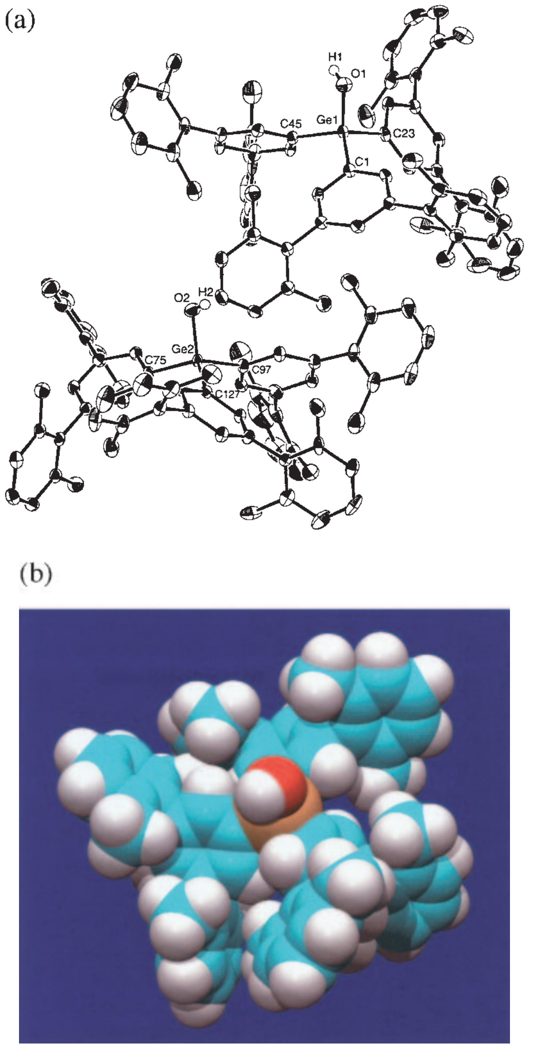


Fig. 2. (a) ORTEP drawing of germanol **5b** (50% probability). The disordered aromatic rings are omitted for clarity. (b) Space filling model of the crystal structure of **5b** (one of two independent molecules).

cases, however, *intra*molecular hydrogen bonding to heteroatoms such as nitrogen[2c] or *intra*molecular OH···π interaction between the GeOH group and an aromatic ring in the same molecule[10] was observed. For several sterically hindered silanols including TRMS–OH (**4**),[5] an *inter*molecular OH···π interaction between the SiOH group and the aromatic ring of the adjacent molecule was observed.[11] Examination of the crystal structure of germanol **5a** suggested the possible presence of the same type of intermolecular OH···π interaction as that observed for silanol **4**. Although the OH hydrogen atom of **5a** could not be unequivocally located, the oxygen atom lies above the C(30)–C(31) bond of the aromatic ring in the adjacent molecule. This arrangement is almost the same as that observed in the crystal structure of silanol **4**. The distances of O(1)···C(31) and O···C(30) are 3.29 and 3.34 Å, respectively, which are similar to the corresponding atomic distances in silanol **4** (3.27 and 3.37 Å).[5]

The crystal structure of **5b** shows that it belongs to the monoclinic space group $P2_1/n$ with $Z = 8$. There are two independent molecules of TRMG–OH in the asymmetric unit, whereas no solvent molecule is included. For **5b**, the OH hydrogen atoms were located in the difference Fourier map and refined isotropically. The shortest O···O distance of **5b** is 9.21 Å, indicating that there is no OH···O hydrogen bonding also for **5b**. As for the intermolecular OH···π interaction, the situation for **5b** is more delicate. In both fragments of **5b**, the O–H bond is directed towards the region above one of the C–C bonds of the aromatic ring in the adjacent molecule (Fig. 3). However, the OH···C distances are 2.86 (H(1)···C(83)), 2.80 (H(1)···C(84)), 2.91 (H(2)···C(17)), and 3.06 Å (H(2)···C(18)), which seem somewhat long for OH···π interaction.[11] Concomitantly, the corresponding O···C distances of between 3.45 and 3.77 Å are longer than those of **5a**. The IR microspectroscopy measurements for the microcrystals of both **5a** and **5b** showed the OH band at 3609 cm^{-1}, which is only 15 cm^{-1} lower than that in solution. These results indicate that the presence of the intermolecular OH···π interactions in the crystals of **5a** and **5b** cannot be ruled out, but they are very weak if they are present at all.

The crystal structures of **5a** and **5b** suggest that the bowl-shaped framework of the TRMG group sterically prevents the

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **5a** and **5b**

5a		**5b**			
		Bond lengths			
		O(1)–H(1)	0.70(3)	O(2)–H(2)	0.77(3)
Ge(1)–O(1)	1.786(2)	Ge(1)–O(1)	1.7852(18)	Ge(2)–O(2)	1.7853(17)
Ge(1)–C(1)	1.939(3)	Ge(1)–C(1)	1.935(2)	Ge(2)–C(75)	1.938(2)
Ge(1)–C(23)	1.931(3)	Ge(1)–C(23)	1.943(2)	Ge(2)–C(97)	1.945(2)
Ge(1)–C(45)	1.946(3)	Ge(1)–C(45)	1.951(2)	Ge(2)–C(127)	1.949(2)
		Bond angles			
		Ge(1)–O(1)–H(1)	114(3)	Ge(2)–O(2)–H(2)	113(2)
O(1)–Ge(1)–C(1)	111.61(11)	O(1)–Ge(1)–C(1)	105.68(9)	O(2)–Ge(2)–C(75)	104.54(9)
O(1)–Ge(1)–C(23)	105.96(11)	O(1)–Ge(1)–C(23)	109.58(9)	O(2)–Ge(2)–C(97)	108.91(9)
O(1)–Ge(1)–C(45)	110.67(12)	O(1)–Ge(1)–C(45)	108.83(9)	O(2)–Ge(2)–C(127)	108.54(8)
C(1)–Ge(1)–C(23)	112.76(13)	C(1)–Ge(1)–C(23)	112.63(9)	C(75)–Ge(2)–C(97)	113.94(9)
C(23)–Ge(1)–C(45)	109.43(12)	C(23)–Ge(1)–C(45)	108.52(9)	C(97)–Ge(2)–C(127)	108.20(8)
C(45)–Ge(1)–C(1)	106.46(12)	C(45)–Ge(1)–C(1)	111.51(9)	C(127)–Ge(2)–C(75)	112.51(9)

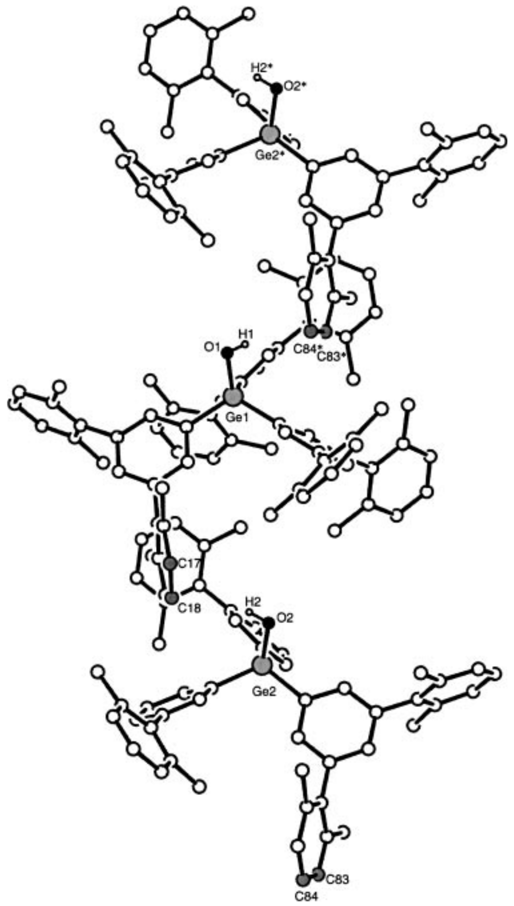
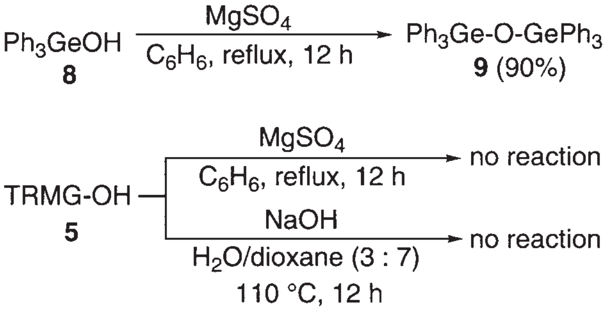


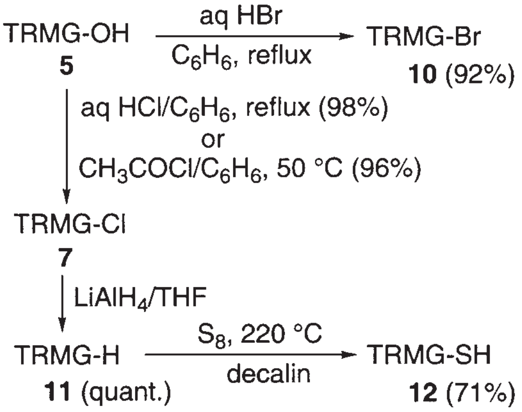
Fig. 3. Diagram of an array of germanol **5b** in the crystals.

formation of the OH···O hydrogen bonding. Unlike usual bulky substituents, however, the TRMG group does not increase the steric congestion around the GeOH center of **5a** and **5b** so much in comparison with Ph_3GeOH (**8**) because there is no ortho-substituent on the aromatic rings connected to the germanium atom in **5**. The mean values of C–Ge–C bond angles are 109.6° for **5a** and 110.9° and 111.6° for two fragments of **5b**, respectively, which are similar to that of **8** (111.6°, a mean value of eight fragments)[2b] and much smaller than that of Mes_3GeOH in $Mes_3GeOH \cdot Mes_3GeNCO$ (Mes = 2,4,6-trimethylphenyl) adduct (114.7°).[12] In germanol **5** bearing a dendritic framework, the molecular size is enlarged in comparison to **8** without increasing steric repulsions among the three aryl groups.

Usually, organogermanols show high sensitivity towards self-condensation. Actually, when a benzene solution of Ph_3GeOH (**8**) was stirred in the presence of anhydrous $MgSO_4$ for 12 h at reflux temperature, **8** was converted to digermoxane **9** almost quantitatively (Scheme 2). In sharp contrast to **8**, no condensation product was obtained when TRMG–OH (**5**) was treated under the same conditions. Upon heating at 110 °C in the presence of NaOH in water/dioxane, **5** also underwent no self-condensation. In spite of such high stability towards condensation, **5** can readily be converted to various derivatives. Treatment of **5** with hydrochloric or hydrobromic acid in benzene afforded the corresponding chlorogermane **7** or bromogermane **10**, respectively, in almost quantitative yields (Scheme 3).



Scheme 2.



Scheme 3.

Chlorogermane **7** was also obtained by the reaction of **5** with acetyl chloride. Reduction of **7** with $LiAlH_4$ afforded hydrogermane **11**, which was further converted to germanethiol **12** in a good yield by heating with elemental sulfur in decalin. These results demonstrate that the bowl-shaped framework of the TRMG group prevents the self-condensation reaction effectively without diminution of the reactivity of the central functional group towards appropriate reagents.

The molecular structure of germanethiol **12** was determined by X-ray crystallography to be as shown in Fig. 4. Selected bond lengths and angles are listed in Table 3. Structural analyses of a triorganogermanethiol are few: only the crystal structure of tricyclohexylgermanethiol (**13**)[13] has been reported so

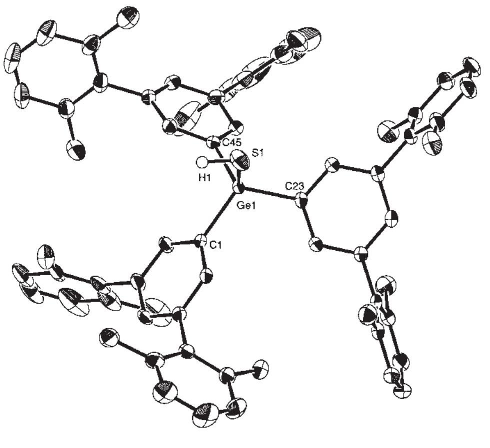


Fig. 4. ORTEP drawing of germanethiol **12** (50% probability).

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **12**

Bond lengths		Bond angles	
S(1)–H(1)	1.13(4)	Ge(1)–S(1)–H(1)	95(2)
Ge(1)–S(1)	2.2284(9)	S(1)–Ge(1)–C(1)	109.14(7)
Ge(1)–C(1)	1.951(2)	S(1)–Ge(1)–C(23)	103.79(8)
Ge(1)–C(23)	1.939(2)	S(1)–Ge(1)–C(45)	110.19(8)
Ge(1)–C(45)	1.944(2)	C(1)–Ge(1)–C(23)	112.93(10)
		C(23)–Ge(1)–C(45)	112.10(10)
		C(45)–Ge(1)–C(1)	108.59(9)

far, and that of **12** is the first example for a triarylgermanethiol. The Ge–S bond length of 2.2284(9) Å in **12** is very close to that in **13** (2.253(2) Å).[13] The mean value of the C–Ge–C bond angles in **12** is 111.2°, which is similar to that of germanol **5**.

Conclusion

A novel bowl-type germyl group **3**, a TRMG group, was designed as the germanium analogue of the Trm and TRMS groups, and a germanol and its derivatives bearing this framework were synthesized. In the crystal structure of germanol **5**, no OH···O hydrogen bonding was observed, although the possible presence of a weak intermolecular OH···π interaction was suggested. In sharp contrast to organogermanols known so far, **5** is extremely resistant to self-condensation; no digermoxane was obtained when **5** was subjected to the conditions under which Ph_3GeOH (**8**) affords the corresponding digermoxane. On the other hand, germanol **5** as well as its derivatives readily reacted with appropriate reagents. Further investigations are underway on the application of the TRMG group to the steric protection of reactive species as well as on the syntheses of the metal complexes using germanol **5** and germanethiol **12** as novel-type of bulky ligands.

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