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Synthesis and structures of a series of Ge–M (M = C, Si, and Sn) compounds derived from germyllithium containing three 2-(dimethylamino)phenyl groups on germanium

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Abstract

Reactions of {tris[2-(dimethylamino)phenyl]germyl}lithium (**1**) with Group 14 electrophiles afford the corresponding carbogermane, silylgermane, and stannylgermane compounds containing three 2-(dimethylamino)phenyl groups on the germanium atom. X-ray structure analysis of these structures was performed and revealed that: (1) the steric repulsion between the amino groups and the substituents is mainly reflected by the torsion angle M–Ge–C_{ipso}–C_{ortho}; (2) the N···M atomic distances are within the sum of the van der Waals radii; (3) in a series of the silylgermanes, the Ge–Si bond length increases as the size of the silyl group increases: $–SiH_3 \leq SiMe_2H \leq SiMe_3 \leq SiMe_2t$-Bu. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: 2-(Dimethylamino)phenyl group; Germyllithium; Silane; Germane; Stannane; Crystal structure

1. Introduction

Recently, we have reported on the preparation and structure of {tris[2-(dimethylamino)phenyl]germyl}-lithium (**1**) [1a]; the 2-(dimethylamino)phenyl group functioning as the nitrogen donor induces a large distortion of the geometry around the germanium atom. The germyllithium **1** can be an ideal agent [2,3] for constructing the germanium Group 14 element linkage with the {tris[2-(dimethylamino)phenyl]-germyl moiety, which is expected to be a novel tripodal ligand. The skeleton can afford a cavity surrounded by the three amino groups, as shown in Fig. 1 [4].

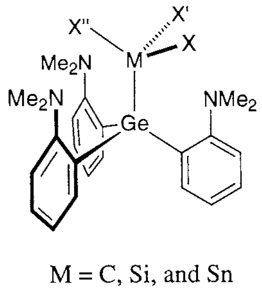
In this context, we report here the reactions of **1** with Group 14 electrophiles and X-ray structure analysis of the obtained Ge–M (M = C, Si, and Sn) compounds [5].

2. Results and discussion

2.1. Preparations

The germyllithium **1** was prepared from tris[2-(dimethylamino)phenyl]germane (**2**) with *tert*-butyllithium in THF as reported previously [1]. The reactions of **1** with Group 14 electrophiles were carried out as shown in Scheme 1.

The reaction of **1** with methyl iodide afforded the methylgermane **3** in 82% yield. The germyllithium **1**



M = C, Si, and Sn

Fig. 1. Ge–M (M = C, Si, and Sn) compounds with three 2-(dimethylamino)phenyl groups.

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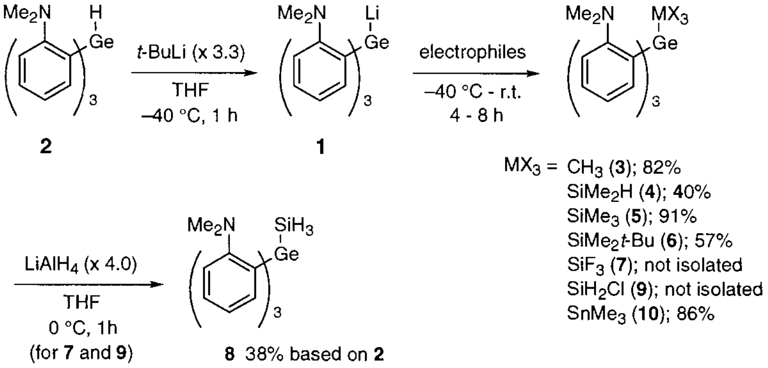

Scheme 1.

also reacted with monochlorosilanes, Me_2HSiCl, Me_3SiCl, and t-$BuMe_2SiCl$ to yield the corresponding silylgermanes **4**, **5**, and **6** in 40, 91, and 57% yields, respectively. The reactions of **1** with silicon tetrafluoride (SiF_4) and dichlorosilane (SiH_2Cl_2) were also successful. Thus, **1** was treated with gaseous silicon tetrafluoride in THF at − 78°C to yield the (trifluorosilyl)germane **7**. Isolation of **7** was unsuccessful, because it was highly moisture sensitive and barely crystallized, but its formation could be confirmed by ^{1}H-, ^{29}Si-, and ^{19}F-NMR spectroscopy. The value of $^{1}J_{Si-F}$ (342 Hz) is reasonable when compared with the reported values [6], e.g. 356 Hz for F_3SiSiH_3 [7]. Furthermore, **7** was characterized by converting it into the corresponding (trihydrosilyl)germane **8** by reduction of the Si–F bonds with $LiAlH_4$ [8]. When **1** was treated with dichlorosilane in THF at − 40°C, the (chlorosilyl)germane **9** was obtained as an oily compound, which could not be purified because of the high moisture sensitivity. Formation of **9** was confirmed by ^{1}H- and ^{29}Si-NMR spectroscopy and its conversion to **8** by reduction of the Si–Cl bonds with $LiAlH_4$ [8]. The reaction of **1** with trimethylstannyl chloride afforded the corresponding stannylgermane **10** in 86% yield.

2.2. Structural studies of *3*, *4*, *5*, *6*, *8*, and *10*

The structures of the obtained Ge–M (M = C, Si, and Sn) compounds **3**, **4**, **5**, **6**, **8**, and **10** were investigated by X-ray diffraction as shown in Figs. 2–7, respectively. Selected bond lengths, bond angles, and torsion angles for **3**, **4**, **5**, **6**, **8**, and **10** are listed in Table 1, and the X-ray diffraction data are shown in Table 2. The following characteristic features should be noted. (1) In all compounds, except **6**, all of the three amino groups are located on the frontal face of the Ge–M (M = C, Si, and Sn) bond. The steric repulsion between the amino groups and the substituents is mainly reflected in the torsion angle M–Ge–C_{ipso}–C_{ortho}. In **6**, due to the bulky t-butyl group on the silicon atom, one amino group occupies the region opposite the Ge–Si bond with a torsion angle of 168°, and another amino group is almost perpendicular to the Ge–Si bond with a torsion angle of − 93°. Due to the steric repulsion, the Si–$C_{t\text{-}Bu}$ bond (1.922(4) Å) is longer than the typical Si–C bond (1.86–1.91 Å) (so called 'long' Si–C bond) [9], and the $C_{t\text{-}Bu}$–Si–Ge bond angle (114.0(1)°) is larger than the tetrahedral angle. (2) In all cases except for the two amino groups in **6**, the N···M interatomic distances are within the sum of the van der Waals radii (N, 1.54; C, 1.85; Si, 2.00; Sn, 2.20 Å) [10]: **3**, 3.19 Å; **4**, 3.39 Å; **5**, 3.48 Å; **6**, 4.56 Å; **8**, 3.13 Å; **10**, 3.42 Å. These data demonstrate that the N···M interatomic distances are influenced by the substituents on M rather than M itself; thus, the average of the distances is less than 3.2 Å for the non-substituted species (Ar_3Ge–MH_3) **3** and **8** and are close to ca. 3.4 Å for the methyl-substituted species (Ar_3Ge–MMe_2R) **4**, **5**, and **10**. (3) Based on the summation of three bond angles ΣC–Ge–C′, the geometries around the germanium atom are slightly deformed from the tetrahedral geometry in all cases. (4)

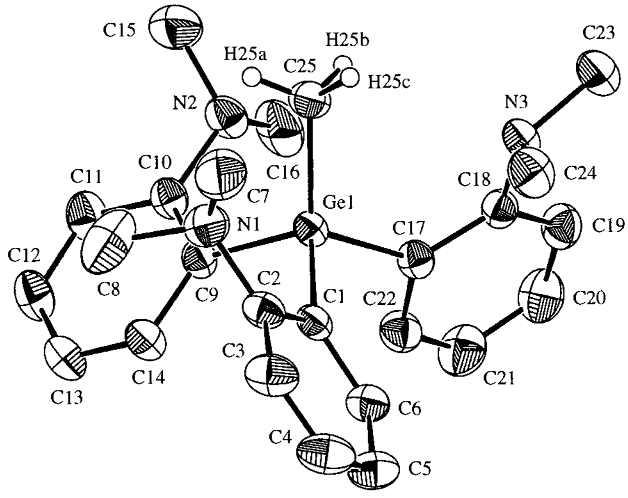

Fig. 2. Molecular structure of **3**. One of the two independent molecules in a unit cell is shown. The thermal ellipsoids are drawn at a 30% probability. Hydrogen atoms, except for H25a, b, and c on C25, are omitted for clarity.

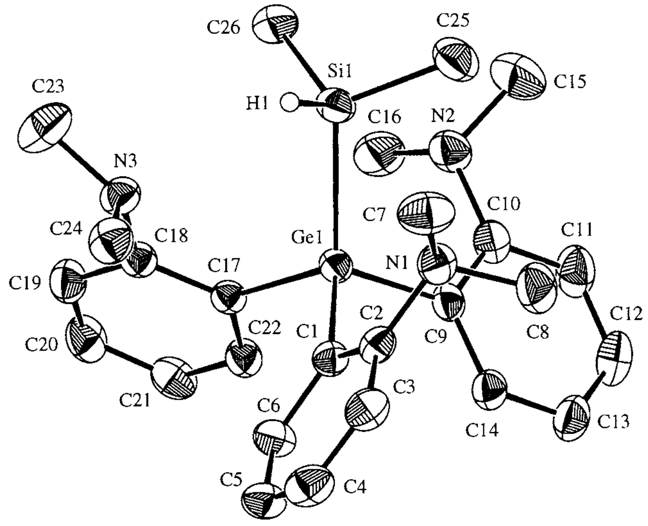

Fig. 3. Molecular structure of **4**. The thermal ellipsoids are drawn at a 30% probability. Hydrogen atoms, except for H1 on the silicon atom, are omitted for clarity.

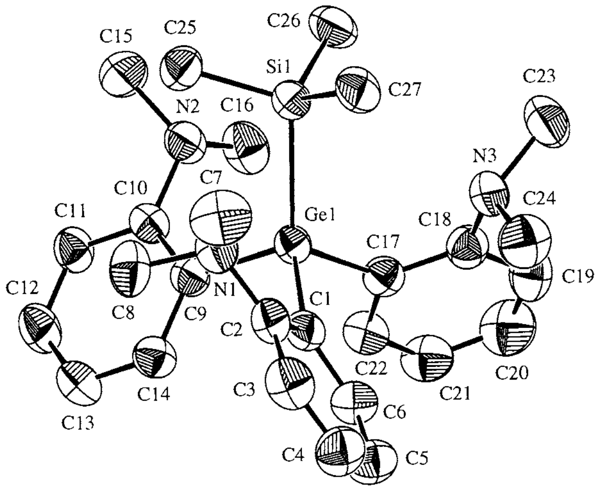

Fig. 4. Molecular structure of **5**. The thermal ellipsoids are drawn at a 30% probability. Hydrogen atoms are omitted for clarity.

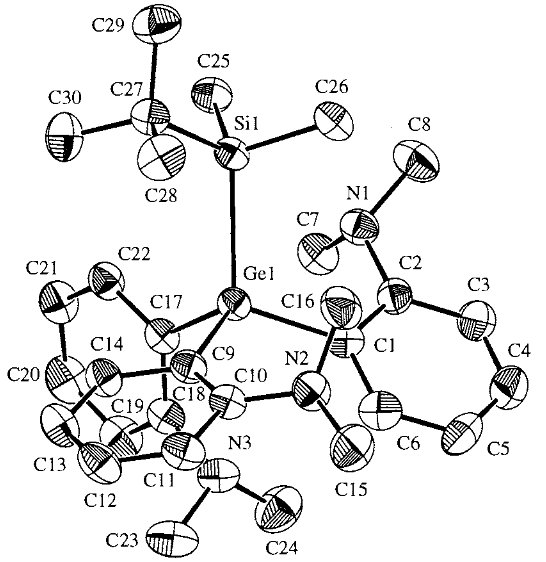

Fig. 5. Molecular structure of **6**. The thermal ellipsoids are drawn at a 30% probability. Hydrogen atoms are omitted for clarity.

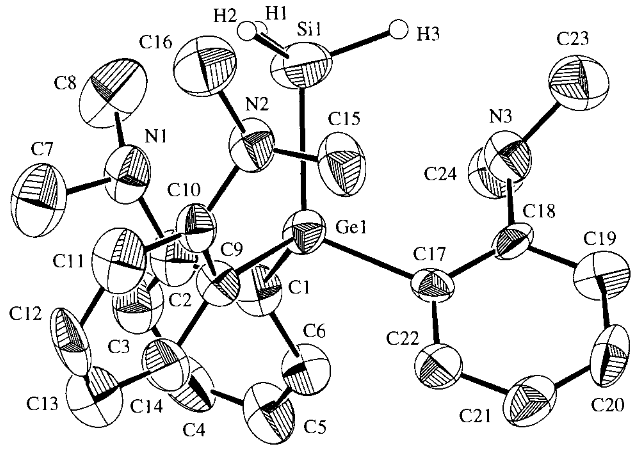

Fig. 6. Molecular structure of **8**. One of the four independent molecules in a unit cell is shown. The thermal ellipsoids are drawn at a 30% probability. Hydrogen atoms, except for H1, 2, and 3 on the silicon atom, are omitted for clarity.

In a series of silylgermanes, the Ge–Si bond length increases as the size of the silyl group increases; $-SiH_3$ (**8**) (2.326(6) Å) ≤ $SiMe_2H$ (**4**) (2.374(1) Å) ≤ $SiMe_3$ (**5**) (2.386(2) Å) ≤ $SiMe_2$*t*-Bu (**6**) (2.445(1) Å). (5) In the stannylgermane **10**, the Ge–Sn bond length (2.573(2) Å) is somewhat shorter than that of $Ph_3GeSnMe_3$ (2.6106(5)–2.652(2) Å) [5d,e] and other Ge–Sn bond lengths (2.596(4)–2.636(1) Å) [5b,c,d,e] reported so far, whereas other corresponding bond lengths and angles are similar to each other.

Whereas the steric interaction dominates the structure factors, the electronic interaction, that is, coordination by the amino groups to the atom M, seems to be much less important, perhaps due to the low Lewis acidity of M. The ^{29}Si resonance of the silylgermanes **4**–**10** and the ^{119}Sn resonance of the stannylgermane **10** were observed in the region for the normal tetracoordinate species [7].

3. Conclusions

The tris[2-(dimethylamino)phenyl]germane moiety can adjust the size of the cavity to accept the substituents by changing the torsion angle M–Ge–C_{ipso}–C_{ortho}. It was found that in all compounds except **6**, all of the three amino groups were located on the frontal face of the Ge–M bond. Under these circumstances, the N···M distances for the parent carbogermane **3** and silylgermane **8** are less than 3.2 Å, while the distances for the methylated silylgermanes and stannylgermane **4**, **5**, and **10** are close to 3.4 Å.

Table 1
Selected bond lengths (Å), bond angles (°), and torsion angles (°) for **3**, **4**, **5**, **6**, **8**, and **10** [a,b]

MX_3 =	CH_3 (**3**)	SiH_3 (**8**)	$SiMe_2H$ (**4**)	$SiMe_3$ (**5**)	$SiMe_2t$Bu (**6**)	$SnMe_3$ (**10**)
Ge–M	1.939(4)	2.326(6)	2.374(1)	2.386(2)	2.445(1)	2.573(2)
Ge–C1	1.967(3)	1.94(2)	1.972(4)	1.975(6)	1.974(4)	1.94(2)
Ge–C9	1.962(4)	1.94(1)	1.977(4)	1.971(5)	1.995(4)	1.99(2)
Ge–C17	1.969(4)	1.97(2)	1.973(4)	1.971(6)	1.975(4)	1.93(2)
M–X	0.90(6)	1.45	1.864(5) [c]	1.874(7)	1.879(4) [c]	2.11(2)
	0.99(5)	1.45	1.866(5) [c]	1.866(8)	1.880(4) [c]	2.13(2)
	1.24(7)	1.46	1.40(3) [d]	1.859(7)1	1.922(4) [e]	2.12(2)
M···N1	3.163(6)	3.31(2)	3.367(4)	3.440(6)	3.417(3)	3.35(2)
M···N2	3.233(6)	3.03(2)	3.419(4)	3.497(5)	4.775(4)	3.43(1)
M···N3	3.221(6)	3.24(1)	3.396(4)	3.513(5)	5.480(4)	3.48(1)
ΣX–M–X′ [f]	320	328	324	326	322	317
ΣC–Ge–C′ [f]	318	318	315	312	323	317
M–Ge–C1–C2	39.5(4)	−45(1)	−37.8(3)	35.1(5)	−42.7(3)	−35(1)
M–Ge–C9–C10	48.2(4)	−26(1)	−38.7(4)	41.9(5)	−93.1(4)	−25(1)
M–Ge–C17–C18	20.1(4)	−33(1)	−35.5(4)	38.9(5)	168.3(3)	−38(1)
Ge–C1–C2–N1	0.3(5)	5(2)	−4.3(5)	5.9(8)	−6.7(5)	−3(2)
Ge–C9–C10–N2	3.8(5)	−11(2)	−2.8(5)	3.3(8)	4.7(6)	−15(2)
Ge–C17–C18–N3	11.2(5)	−1(2)	−3.0(5)	2.0(8)	4.7(5)	−2(2)

[a] Data for one of the two independent molecules are shown.
[b] Data for one of the four independent molecules are shown.
[c] Si–C_{Me}.
[d] Si–H.
[e] Si–$C_{t\text{-}Bu}$.
[f] Summation of the three bond angles.

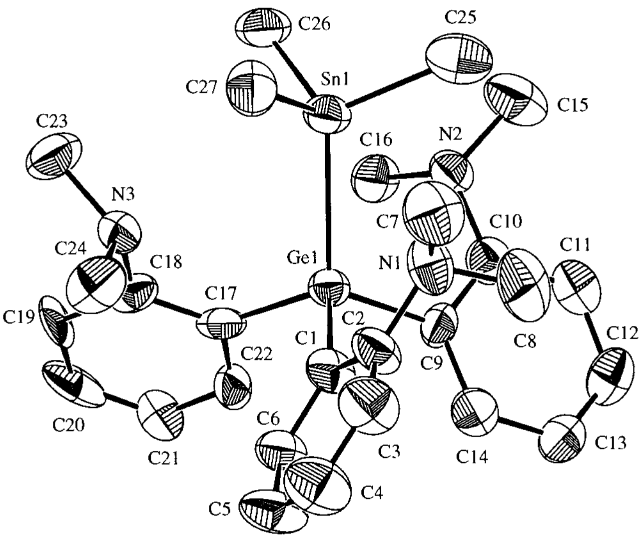

Fig. 7. Molecular structure of **10**. One of the two independent molecules in a unit cell is shown. The thermal ellipsoids are drawn at a 30% probability. Hydrogen atoms are omitted for clarity.

4. Experimental

4.1. General

^{1}H (270 MHz), ^{13}C (67.94 MHz), ^{19}F (254.19 MHz), ^{29}Si (53.67 MHz), and ^{119}Sn (100.68 MHz) NMR spectra were recorded on a Jeol EX-270 spectrometer. ^{1}H and ^{13}C chemical shifts were referenced to internal benzene-d_6 (^{1}H δ 7.200 ppm, ^{13}C δ 128.00 ppm) and $CDCl_3$ (^{13}C δ 77.00 ppm). ^{19}F, ^{29}Si, and ^{119}Sn chemical shifts were referenced to external trichlorofluoromethane (0 ppm), tetramethylsilane (0 ppm), and tetramethylstannane (0 ppm), respectively. Mass spectra were measured at 70 eV on a Jeol JMS-700 mass spectrometer equipped with a MS-SEPU data processing system. Melting points were measured with a Yanaco-MP-S3 apparatus and were uncorrected. IR spectra were recorded on a Jasco IR-810 spectrophotometer. The elemental analyses were performed at the Microanalysis Division of the Institute for Chemical Research, Kyoto University. Analytical samples were purified by recrystallization.

tert-Butyllithium in pentane was purchased from Kanto Chemical Co., Inc. Silicon tetrafluoride was purchased from Nippon Sanso Co., Ltd. Dichlorosilane was kindly donated by Shin-Etsu Chemical Co., Ltd. Hexane was distilled under nitrogen over sodium wire. THF and Et_2O were distilled under nitrogen over sodium benzophenone ketyl, $LiAlH_4$, or sodium–potassium alloy. All reactions were carried out under an inert atmosphere, unless otherwise noted.

4.2. Synthesis of {tris[2-(dimethylamino)phenyl]germyl}lithium (*1*) [1a]

To a solution of tris[2-(dimethylamino)phenyl]germane (**2**) [1b] (220 mg, 0.50 mmol) in THF (1.0 ml) was added *tert*-butyllithium in pentane (1.64 M, 1.00 ml, 1.64 mmol) at −40°C. The reaction mixture was stirred t −40°C for 1h to give a yellow suspension of **1**.

Table 2
Summary of X-ray diffraction data for **3**, **4**, **5**, **6**, **8**, and **10**

	3	**4**	**5**	**6**	**8**	**10**
Chemical formula	$C_{25}H_{33}N_3Ge$	$C_{26}H_{37}N_3SiGe$	$C_{27}H_{39}N_3SiGe$	$C_{30}H_{45}N_3SiGe$	$C_{24}H_{33}N_3SiGe$	$C_{27}H_{39}N_3GeSn$
Formula weight	448.15	492.27	506.30	548.38	464.22	596.91
Crystal size (mm)	0.50 × 0.40 × 0.20	0.40 × 0.30 × 0.50	0.40 × 0.20 × 0.40	0.30 × 0.20 × 0.50	0.50 × 0.50 × 0.50	0.30 × 0.30 × 0.30
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)
a (Å)	16.926(2)	11.076(2)	10.241(4)	10.570(2)	22.51(1)	19.019(4)
b (Å)	17.153(2)	15.070(2)	15.154(3)	15.712(2)	24.197(8)	15.026(4)
c (Å)	8.923(2)	16.037(3)	18.566(2)	9.915(1)	9.432(2)	20.822(4)
α (°)	95.71(1)			93.615(10)	90.01(1)	
β (°)	90.26(1)	91.79(2)	95.27(2)	105.38(1)	89.98(3)	104.25(1)
γ (°)	69.569(7)			71.99(1)	89.95(4)	
V (Å^3)	2414.1(6)	2675.6(7)	2869.0(10)	1509.5(4)	5138(3)	5767(2)
Z	4	4	4	2	8	8
$D_{\mathrm{Calc.}}$ (g cm^{-3})	1.233	1.222	1.172	1.206	1.200	1.375
μ(Cu–K$_\alpha$) (cm^{-1})	18.18	20.99	19.70	19.08	21.57	83.00
Temperature (K)	293	293	293	293	293	293
No. of reflections collected	7450	4395	4725	4762	15724	9427
No. of independent reflections	7168 ($R_{\mathrm{int}} = 0.015$)	4157 ($R_{\mathrm{int}} = 0.067$)	4448 ($R_{\mathrm{int}} = 0.018$)	4481 ($R_{\mathrm{int}} = 0.027$)	15270 ($R_{\mathrm{int}} = 0.072$)	8952 ($R_{\mathrm{int}} = 0.053$)
No. of observed reflections ($I > 3\sigma(I)$)	5595	3167	3150	3749	5410	4746
No. of variables	547	285	446	317	1045	578
R	0.040	0.042	0.055	0.045	0.073	0.079
R_w	0.065	0.055	0.080	0.077	0.097	0.114
Goodness-of-fit	1.12	1.71	1.88	1.33	1.50	1.77

*4.3. Synthesis of tris[2-(dimethylamino)phenyl]methylgermane (**3**)*

Methyl iodide (1.10 ml, 16.5 mmol) was added to a suspension of **1** (prepared from 0.49 mmol of **2**) in THF (1.0 ml) at −40°C, and then the mixture was stirred at room temperature (r.t.) for 4 h. After the solvent was removed under reduced pressure, the residue was diluted with hexane (10 ml). The resulting suspension was filtered and the filtrate was concentrated to give a solid. Recrystallization of the solid from hexane (0.5 ml) yielded **3** as colorless crystals (182 mg, 82% yield based on **2**). M.p.: 109.5–111.0°C. ^{1}H-NMR (C_6D_6): δ 1.59 (s, 3H), 2.45 (s, 18H), 6.98–7.00 (m, 3H), 7.15–7.25 (m, 6H), 7.47–7.49 (m, 3H). ^{13}C-NMR ($CDCl_3$): δ 1.62, 46.24, 120.65, 123.68, 129.24, 137.02, 138.67, 159.91. MS: m/e 449 (M$^+$, 8), 434 (M$^+$–Me, 1), 329 (82), 134 (100). Anal. Calc. for $C_{25}H_{33}N_3Ge$: C, 67.00; H, 7.42; N, 9.38. Found: C, 67.19; H, 7.42; N, 9.39.

*4.4. A typical procedure for reaction of **1** with monochlorosilanes: synthesis of tris[2-(dimethylamino)phenyl](dimethylsilyl)germane (**4**)*

Dimethylchlorosilane (1.80 ml, 16.5 mmol) was added to a suspension of **1** (prepared from 0.50 mmol of **2**) in THF (1.0 ml) at −40°C, and then the mixture was stirred at r.t. for 8 h. After the solvent was removed under reduced pressure, the residue was diluted with benzene (10 ml) under an inert atmosphere. The resulting suspension was filtered, and the filtrate was concentrated to give a solid. Recrystallization of the solid from hexane (2.0 ml) under an inert atmosphere yielded **4** as colorless crystals (97 mg, 40% yield based on **2**). M.p.: 165.5–166.5°C. ^{1}H-NMR (C_6D_6): δ 0.57 (d, 6H, $J = 3.5$ Hz), 2.43 (s, 18H), 4.71 (septet, 1H, $J = 3.5$ Hz), 6.90–6.96 (m, 4H), 7.10–7.24 (m, 4H), 7.46–7.49 (m, 4H). ^{13}C-NMR ($CDCl_3$): δ −3.05, 46.52, 120.14, 123.94, 129.22, 137.72, 139.34, 159.51. ^{29}Si-NMR (C_6D_6): δ −27.6 (dd, $^1J_{\mathrm{Si-H}} = 188$ Hz, $^2J_{\mathrm{Si-H}} = 7$ Hz), IR (KBr, cm^{-1}): ν(Si–H) 2110. MS: m/e 449 (M$^+$, 8), 434 (M$^+$–Me, 1), 329 (82), 134 (100). Anal. Calc. for $C_{25}H_{37}N_3GeSi$: C, 63.43; H, 7.58; N, 8.54. Found: C, 63.35; H, 7.79; N, 8.54.

*4.r5. Tris[2-(dimethylamino)phenyl](trimethylsilyl)germane (**5**)*

This compound was obtained in 45% yield (based on **2**) after recrystallization from hexane. M.p.: 170.0–171.5°C. ^{1}H-NMR (C_6D_6): δ 0.57 (s, 9H), 2.40 (s, 18H), 6.89–6.95 (m, 4H), 7.12–7.20 (m, 4H), 7.44–7.47 (m, 4H). ^{13}C-NMR ($CDCl_3$): δ 1.21, 45.84, 46.74, 120.14, 123.97, 129.18, 138.31, 139.60, 159.75. ^{29}Si-NMR

(C_6D_6): δ −6.41. MS: *m*/*e* 507 (M^+, 0.4), 492 (M^+−Me, 3), 434 (M^+−$SiMe_3$, 77), 120 ($C_6H_4NMe_2$, 100). Anal. Calc. for $C_{27}H_{39}N_3GeSi$: C, 64.05; H, 7.76; N, 8.30. Found: C, 63.67; H, 7.75; N, 8.44.

Table 3
Positional parameters and B_{iso}/B_{eq} for **3**

Atom	*x*	*y*	*z*	B_{eq}
Ge(1)	0.23638(2)	0.22420(2)	0.06578(5)	3.50(1)
Ge(1′)	−0.26292(2)	0.22252(3)	−0.47940(5)	3.80(1)
N(1)	0.3254(2)	0.0290(2)	−0.0062(4)	5.55(9)
N(1′)	−0.1735(2)	0.0266(2)	−0.4820(4)	5.57(9)
N(2)	0.1907(2)	0.3333(2)	−0.1983(4)	4.94(8)
N(2′)	−0.3079(2)	0.3331(2)	−0.1761(4)	5.10(8)
N(3)	0.0471(2)	0.3041(2)	0.2305(4)	4.38(7)
N(3′)	−0.4524(2)	0.2999(2)	−0.6256(4)	4.57(8)
C(1)	0.3094(2)	0.1422(2)	0.1923(4)	3.78(8)
C(1′)	−0.1894(2)	0.1403(2)	−0.6350(4)	3.91(8)
C(2)	0.3442(2)	0.0568(2)	0.1432(5)	4.36(9)
C(2′)	−0.1551(2)	0.0539(2)	−0.6188(5)	4.36(9)
C(3)	0.3920(3)	0.0012(3)	0.2388(6)	5.9(1)
C(3′)	−0.1067(3)	−0.0009(3)	−0.7345(6)	5.9(1)
C(4)	0.4088(3)	0.0285(3)	0.3801(6)	6.4(1)
C(4′)	−0.0891(3)	0.0277(3)	−0.8656(6)	6.4(1)
C(5)	0.3786(3)	0.1121(3)	0.4297(5)	5.8(1)
C(5′)	−0.1195(3)	0.1098(3)	−0.8826(5)	5.9(1)
C(6)	0.3284(3)	0.1681(2)	0.3354(5)	4.59(9)
C(6′)	−0.1695(3)	0.1662(3)	−0.7683(5)	4.88(10)
C(7)	0.2960(4)	−0.0409(4)	−0.0117(7)	8.3(2)
C(7′)	−0.1981(4)	−0.0453(4)	−0.5024(8)	8.7(2)
C(8)	0.3925(5)	0.0129(4)	−0.1159(7)	9.2(2)
C(8′)	−0.1086(5)	0.0128(5)	−0.3739(7)	9.6(2)
C(9)	0.3125(2)	0.2526(2)	−0.0661(4)	3.81(8)
C(9′)	−0.1864(2)	0.2534(2)	−0.3392(4)	4.26(9)
C(10)	0.2810(2)	0.3009(2)	−0.1835(4)	4.12(9)
C(10′)	−0.2182(2)	0.3060(3)	−0.2085(4)	4.63(9)
C(11)	0.3352(3)	0.3163(3)	−0.2825(5)	5.3(1)
C(11′)	−0.1649(3)	0.3297(3)	−0.1115(5)	6.6(1)
C(12)	0.4206(3)	0.2864(3)	−0.2632(5)	5.6(1)
C(12′)	−0.0790(3)	0.3034(4)	−0.1458(6)	7.4(1)
C(13)	0.4529(3)	0.2407(3)	−0.1435(5)	5.3(1)
C(13′)	−0.0465(3)	0.2511(3)	−0.2762(6)	6.1(1)
C(14)	0.4000(2)	0.2235(3)	−0.0482(5)	4.73(10)
C(14′)	−0.1003(3)	0.2276(3)	−0.3704(5)	5.2(1)
C(15)	0.1627(4)	0.3154(4)	−0.3484(6)	7.8(2)
C(15′)	−0.3281(3)	0.3032(4)	−0.0380(6)	7.1(1)
C(16)	0.1533(3)	0.4220(3)	−0.1492(7)	7.6(1)
C(16′)	−0.3501(3)	0.4220(4)	−0.1781(8)	8.2(2)
C(17)	0.1799(2)	0.3274(2)	0.1995(4)	3.76(8)
C(17′)	−0.3193(2)	0.3239(2)	−0.5786(4)	3.86(8)
C(18)	0.0957(2)	0.3566(2)	0.2514(4)	4.00(8)
C(18′)	−0.4026(2)	0.3513(2)	−0.6304(4)	4.19(9)
C(19)	0.0596(3)	0.4387(3)	0.3200(5)	5.2(1)
C(19′)	−0.4359(3)	0.4300(3)	−0.6817(5)	5.7(1)
C(20)	0.1071(4)	0.4891(3)	0.3424(6)	6.4(1)
C(20′)	−0.3866(4)	0.4788(3)	−0.6906(6)	6.9(1)
C(21)	0.1912(4)	0.4598(3)	0.3024(6)	6.6(1)
C(21′)	−0.3051(4)	0.4531(3)	−0.6449(6)	6.4(1)
C(22)	0.2263(3)	0.3798(3)	0.2304(5)	5.0(1)
C(22′)	−0.2728(3)	0.3762(3)	−0.5900(5)	5.1(1)
C(23)	−0.0449(3)	0.3430(3)	0.2533(6)	6.5(1)
C(23′)	−0.5426(3)	0.3390(4)	−0.6455(6)	6.7(1)
C(24)	0.0771(3)	0.2280(3)	0.3048(6)	6.0(1)
C(24′)	−0.4204(3)	0.2211(3)	−0.7212(5)	5.9(1)
C(25)	0.1590(3)	0.1823(3)	−0.0480(6)	4.9(1)
C(25′)	−0.3398(3)	0.1808(4)	−0.3808(7)	5.3(1)

Table 4
Positional parameters and B_{iso}/B_{eq} for **4**

Atom	*x*	*y*	*z*	B_{eq}
Ge(1)	0.19299(4)	0.11562(3)	0.21173(3)	3.32(1)
Si(1)	0.1596(1)	−0.00670(8)	0.12068(8)	4.30(3)
N(1)	0.3459(3)	0.1530(2)	0.0539(2)	4.39(8)
N(2)	0.2877(3)	−0.0554(2)	0.3119(2)	4.95(9)
N(3)	−0.0939(3)	0.1047(2)	0.1723(2)	4.35(8)
C(1)	0.2231(3)	0.2290(3)	0.1546(2)	3.70(9)
C(2)	0.2904(3)	0.2332(3)	0.0831(2)	3.73(9)
C(3)	0.3029(4)	0.3136(3)	0.0417(3)	4.9(1)
C(4)	0.2481(5)	0.3892(3)	0.0700(3)	5.7(1)
C(5)	0.1835(4)	0.3866(3)	0.1408(3)	5.2(1)
C(6)	0.1712(4)	0.3073(3)	0.1892(3)	4.6(1)
C(7)	0.3311(5)	0.1392(4)	−0.0352(3)	6.6(1)
C(8)	0.4734(4)	0.1477(4)	0.0801(3)	6.6(1)
C(9)	0.3344(3)	0.1006(3)	0.2888(2)	3.69(9)
C(10)	0.3645(4)	0.0194(3)	0.3264(3)	4.3(1)
C(11)	0.4693(4)	0.0137(3)	0.3761(3)	5.9(1)
C(12)	0.5421(4)	0.0863(4)	0.3898(3)	6.2(1)
C(13)	0.5124(4)	0.1660(3)	0.3543(3)	5.1(1)
C(14)	0.4096(3)	0.1728(3)	0.3045(3)	4.20(10)
C(15)	0.3504(6)	−0.1407(4)	0.3091(4)	7.9(2)
C(16)	0.1897(5)	−0.0605(3)	0.3697(3)	6.5(1)
C(17)	0.0547(3)	0.1410(2)	0.2826(2)	3.34(8)
C(18)	−0.0658(4)	0.1313(2)	0.2572(2)	3.67(9)
C(19)	−0.1565(4)	0.1448(3)	0.3138(3)	4.9(1)
C(20)	−0.1294(4)	0.1675(3)	0.3949(3)	5.3(1)
C(21)	−0.0120(4)	0.1795(3)	0.4211(3)	5.0(1)
C(22)	0.0789(4)	0.1669(3)	0.3652(2)	4.08(9)
C(23)	−0.2068(5)	0.0578(4)	0.1582(4)	7.5(2)
C(24)	−0.0822(4)	0.1734(3)	0.1096(3)	5.4(1)
C(25)	0.3016(4)	−0.0656(3)	0.0948(3)	5.9(1)
C(26)	0.0518(4)	−0.0894(3)	0.1627(4)	6.2(1)

*4.6. Tris[2-(dimethylamino)phenyl](tert-butyldimethylsilyl)germane (**6**)*

This compound was obtained in 57% yield (based on **2**) after recrystallization from hexane. M.p.: 164.0–165.0°C. ^{1}H-NMR (C_6D_6): δ 0.51 (s, 6H), 1.03 (s, 9H), 2.29 (s, 18H), 7.01–7.06 (m, 6H), 7.20–7.26 (m, 3H), 7.92–7.95 (m, 3H). ^{13}C-NMR ($CDCl_3$): δ −2.69, 20.45, 28.20, 45.86, 119.87, 122.50, 128.64, 137.72, 138.92, 158.92. ^{29}Si-NMR (C_6D_6): δ 1.43. MS: *m*/*e* 549 (M^+, 0.1), 534 (M^+−Me, 0.9), 492 (M^+−*t*-Bu, 4), 434 (M^+−$SiMe_2$*t*-Bu, 100), 134 (99), 120 (98). Anal. Calc. for $C_{30}H_{45}N_3GeSi$: C, 65.71; H, 8.27; N, 7.66. Found: C, 66.03; H, 8.39; N, 7.71.

*4.7. Synthesis of tris[2-(dimethylamino)phenyl](trifluorosilyl)germane (**7**)*

To a suspension of **1** (prepared from 0.50 mmol of **2**) in THF–toluene (1.0 ml/10.0 ml) was introduced at

−78°C with stirring an excess of gaseous silicon tetrafluoride for ca. 5 min through a gas inlet tube from the gas cylinder until the yellow color disappeared and a white precipitate was formed. The mixture was warmed to ambient temperature over 5 h. The formation of **7** was confirmed by means of NMR spectra. ^{1}H-NMR (C_6D_6): δ 2.48 (s, 18H), 6.90–6.96 (m, 3H), 7.07–7.10 (m, 3H), 7.15–7.20 (m, 3H), 7.40–7.43 (m, 3H). ^{13}C-NMR ($CDCl_3$): δ 45.99, 120.74, 124.80, 130.37, 135.96, 136.55, 159.16. ^{29}Si-NMR (C_6D_6): δ −69.64 (q, $^1J_{Si-F} = 342$ Hz). ^{19}F-NMR (C_6D_6): δ −132.2 ($^1J_{Si-F} = 342$ Hz).

*4.8. Synthesis of tris[2-(dimethylamino)phenyl]-(chlorosilyl)germane (**9**)*

Gaseous dichlorosilane was liquidized at −78°C and diluted with THF to make a 1.5 M solution. The solution (1.9 ml, 2.8 mmol) was added to a suspension of **1** (prepared from 0.48 mmol of **2**) in THF (1.5 ml) at −40°C, and was then stirred at r.t. for 8 h. After the solvent was removed under reduced pressure, crude **9** was obtained as oil. The yield was estimated by means of NMR analysis (61%): toluene was used as an internal standard. ^{1}H-NMR (C_6D_6): δ 2.44 (s, 18H), 5.29 (s, 2H), 6.91–6.97 (m, 4H), 7.06–7.15 (m, 4H), 7.44–7.47 (m, 4H). ^{13}C-NMR (C_6D_6): 45.81, 121.05, 125.75, 131.47, 135.06, 136.97, 159.34. ^{29}Si-NMR (C_6D_6): δ −39.27 (dd, $^1J_{Si-H} = 245$ Hz).

Table 5
Positional parameters and B_{iso}/B_{eq} for **5**

Atom	x	y	z	B_{eq}
Ge(1)	0.19299(4)	0.11562(3)	0.21173(3)	3.32(1)
Si(1)	0.1596(1)	−0.00670(8)	0.12068(8)	4.30(3)
N(1)	0.3459(3)	0.1530(2)	0.0539(2)	4.39(8)
N(2)	0.2877(3)	−0.0554(2)	0.3119(2)	4.95(9)
N(3)	−0.0939(3)	0.1047(2)	0.1723(2)	4.35(8)
C(1)	0.2231(3)	0.2290(3)	0.1546(2)	3.70(9)
C(2)	0.2904(3)	0.2332(3)	0.0831(2)	3.73(9)
C(3)	0.3029(4)	0.3136(3)	0.0417(3)	4.9(1)
C(4)	0.2481(5)	0.3892(3)	0.0700(3)	5.7(1)
C(5)	0.1835(4)	0.3866(3)	0.1408(3)	5.2(1)
C(6)	0.1712(4)	0.3073(3)	0.1892(3)	4.6(1)
C(7)	0.3311(5)	0.1392(4)	−0.0352(3)	6.6(1)
C(8)	0.4734(4)	0.1477(4)	0.0801(3)	6.6(1)
C(9)	0.3344(3)	0.1006(3)	0.2888(2)	3.69(9)
C(10)	0.3645(4)	0.0194(3)	0.3264(3)	4.3(1)
C(11)	0.4693(4)	0.0137(3)	0.3761(3)	5.9(1)
C(12)	0.5421(4)	0.0863(4)	0.3898(3)	6.2(1)
C(13)	0.5124(4)	0.1660(3)	0.3543(3)	5.1(1)
C(14)	0.4096(3)	0.1728(3)	0.3045(3)	4.20(10)
C(15)	0.3504(6)	−0.1407(4)	0.3091(4)	7.9(2)
C(16)	0.1897(5)	−0.0605(3)	0.3697(3)	6.5(1)
C(17)	0.0547(3)	0.1410(2)	0.2826(2)	3.34(8)
C(18)	−0.0658(4)	0.1313(2)	0.2572(2)	3.67(9)
C(19)	−0.1565(4)	0.1448(3)	0.3138(3)	4.9(1)
C(20)	−0.1294(4)	0.1675(3)	0.3949(3)	5.3(1)
C(21)	−0.0120(4)	0.1795(3)	0.4211(3)	5.0(1)
C(22)	0.0789(4)	0.1669(3)	0.3652(2)	4.08(9)
C(23)	−0.2068(5)	0.0578(4)	0.1682(4)	7.5(2)
C(24)	−0.0822(4)	0.1734(3)	0.1096(3)	5.4(1)
C(25)	0.3016(4)	−0.0656(3)	0.0948(3)	5.9(1)
C(26)	0.0518(4)	−0.0894(3)	0.1627(4)	6.2(1)

Table 6
Positional parameters and B_{iso}/B_{eq} for **6**

Atom	x	y	z	B_{eq}
Ge(1)	0.17147(4)	0.25371(3)	0.37358(4)	3.871(10)
Si(1)	0.3803(1)	0.29898(7)	0.4540(1)	4.20(2)
N(1)	0.3319(3)	0.1998(2)	0.1355(3)	4.89(8)
N(2)	0.2021(4)	0.0872(2)	0.6036(4)	5.45(8)
N(3)	−0.1109(4)	0.2405(3)	0.1926(4)	5.41(8)
C(1)	0.2103(4)	0.1417(3)	0.2685(4)	4.45(8)
C(2)	0.2897(4)	0.1274(3)	0.1711(4)	4.53(8)
C(3)	0.3236(5)	0.0442(3)	0.1096(5)	6.3(1)
C(4)	0.2793(6)	−0.0228(4)	0.1387(6)	7.1(1)
C(5)	0.1973(6)	−0.0105(3)	0.2267(6)	6.7(1)
C(6)	0.1627(5)	0.0716(3)	0.2909(5)	5.7(1)
C(7)	0.2262(5)	0.2568(3)	0.0237(4)	5.6(1)
C(8)	0.4621(5)	0.1734(4)	0.0984(5)	6.8(1)
C(9)	0.0875(4)	0.2452(3)	0.5283(4)	4.26(8)
C(10)	0.1057(4)	0.1710(3)	0.6134(4)	4.38(8)
C(11)	0.0219(5)	0.1801(3)	0.7035(4)	5.4(1)
C(12)	−0.0738(5)	0.2618(3)	0.7180(5)	6.0(1)
C(13)	−0.0856(5)	0.3345(3)	0.6442(5)	5.8(1)
C(14)	−0.0059(4)	0.3265(3)	0.5512(4)	4.74(9)
C(15)	0.1848(6)	0.0098(3)	0.6546(7)	7.6(1)
C(16)	0.3433(5)	0.0837(3)	0.6245(6)	6.7(1)
C(17)	0.0231(4)	0.3454(3)	0.2467(4)	4.08(8)
C(18)	−0.0952(4)	0.3257(3)	0.1695(4)	4.61(9)
C(19)	−0.1942(5)	0.3863(3)	0.0702(5)	6.0(1)
C(20)	−0.1794(5)	0.4702(3)	0.0530(5)	6.4(1)
C(21)	−0.0683(5)	0.4927(3)	0.1333(5)	5.5(1)
C(22)	0.0320(4)	0.4305(3)	0.2293(4)	4.74(9)
C(23)	−0.2194(6)	0.2501(4)	0.2631(6)	7.5(1)
C(24)	−0.1254(6)	0.1880(4)	0.0697(6)	7.8(1)
C(25)	0.3986(4)	0.3717(3)	0.3215(5)	5.35(10)
C(26)	0.5334(4)	0.1954(3)	0.4839(5)	5.6(1)
C(27)	0.3900(4)	0.3654(3)	0.6241(4)	4.88(9)
C(28)	0.3825(6)	0.3117(4)	0.7447(5)	6.7(1)
C(29)	0.5258(6)	0.3862(4)	0.6660(6)	7.1(1)
C(30)	0.2721(6)	0.4533(3)	0.6017(5)	6.5(1)

*4.9. Reduction of **9** with $LiAlH_4$: synthesis of tris[2-(dimethylamino)phenyl](silyl)germane (**8**)*

A solution of dichlorosilane in THF (2.0 M, 4.0 ml, 8.1 mmol) was added to a suspension of **1** (prepared from 2.0 mmol of **2**) in THF (5.0 ml) at −40°C, and was then stirred at r.t. for 5 h. The mixture was added to a suspension of $LiAlH_4$ (310 mg, 8.1 mmol) in THF (10 ml) at 0°C and stirred for 1 h. The reaction mixture was diluted with THF (60 ml), followed by the successive addition of H_2O (0.3 ml), 15% NaOH aqueous solution (0.3 ml), and H_2O (0.9 ml) at 0°C. The resulting suspension was filtered, and the filtrate was concentrated to give an oily material. Crystallization of the oil from hexane yielded **8** as colorless crystals (350 mg,

Table 7
Positional parameters and B_{iso}/B_{eq} for **8**

Atom	x	y	z	B_{eq}
Ge(1)	0.25861(9)	0.97847(8)	0.6897(2)	5.08(5)
Ge(2)	0.24120(8)	0.47851(8)	0.1897(2)	5.08(5)
Ge(3)	0.01280(8)	0.24658(7)	0.0216(2)	4.77(5)
Ge(4)	0.51297(8)	0.25355(7)	0.4786(2)	4.78(5)
Si(1)	0.2880(3)	0.9029(2)	0.8252(6)	8.7(2)
Si(2)	0.2121(3)	0.4030(2)	0.3257(6)	8.8(2)
Si(3)	−0.0360(3)	0.1784(2)	−0.1098(6)	8.0(2)
Si(4)	0.4640(3)	0.3217(2)	0.6102(6)	7.9(2)
N(1)	0.3902(6)	0.9983(6)	0.762(2)	7.0(5)
N(2)	0.2033(7)	0.9771(7)	0.986(1)	6.6(5)
N(3)	0.2198(7)	0.8698(6)	0.535(1)	6.2(4)
N(4)	0.2961(7)	0.4766(7)	0.489(1)	7.3(5)
N(5)	0.1115(7)	0.4997(7)	0.262(2)	7.3(5)
N(6)	0.2766(8)	0.3682(6)	0.034(1)	6.2(4)
N(7)	−0.1208(6)	0.2713(6)	−0.013(2)	6.7(5)
N(8)	0.0197(7)	0.1319(6)	0.159(1)	5.9(4)
N(9)	0.0644(7)	0.2340(8)	−0.274(1)	7.9(5)
N(10)	0.3768(7)	0.2300(6)	0.514(2)	6.6(5)
N(11)	0.5230(6)	0.3680(6)	0.339(1)	5.6(4)
N(12)	0.5665(8)	0.2692(8)	0.775(1)	7.5(5)
C(1)	0.3206(9)	1.0082(7)	0.568(2)	6.3(6)
C(2)	0.378(1)	1.0168(8)	0.619(2)	6.3(6)
C(3)	0.4195(10)	1.0406(9)	0.539(3)	8.3(7)
C(4)	0.407(1)	1.0565(8)	0.397(3)	8.1(7)
C(5)	0.351(1)	1.0479(8)	0.346(2)	7.9(7)
C(6)	0.3080(8)	1.0238(7)	0.426(2)	5.9(5)
C(7)	0.3983(10)	1.045(1)	0.856(2)	10.8(8)
C(8)	0.436(1)	0.960(1)	0.784(2)	11.3(8)
C(9)	0.2385(7)	1.0413(7)	0.808(2)	4.6(4)
C(10)	0.2183(7)	1.0319(8)	0.948(2)	5.3(5)
C(11)	0.2149(9)	1.079(1)	1.038(2)	8.2(7)
C(12)	0.2284(10)	1.1302(9)	0.993(3)	8.7(7)
C(13)	0.2462(8)	1.1390(9)	0.856(3)	8.0(7)
C(14)	0.2510(8)	1.0946(8)	0.771(2)	6.5(6)
C(15)	0.144(1)	0.9609(8)	0.945(2)	8.7(7)
C(16)	0.211(1)	0.9619(9)	1.134(2)	10.5(8)
C(17)	0.1888(7)	0.9627(7)	0.570(1)	4.3(4)
C(18)	0.1799(8)	0.9125(8)	0.513(2)	4.9(5)
C(19)	0.129(1)	0.9014(8)	0.440(2)	6.6(6)
C(20)	0.0864(9)	0.941(1)	0.423(2)	7.2(6)
C(21)	0.0960(9)	0.9918(10)	0.476(2)	7.4(7)
C(22)	0.1484(10)	1.0034(7)	0.551(2)	6.2(5)
C(23)	0.1988(10)	0.8138(9)	0.553(2)	9.3(7)
C(24)	0.267(1)	0.8686(8)	0.438(2)	9.3(7)
C(25)	0.2610(7)	0.5411(6)	0.311(2)	4.8(5)
C(26)	0.2816(7)	0.5308(8)	0.449(2)	5.5(5)
C(27)	0.2864(9)	0.575(1)	0.541(2)	8.4(7)
C(28)	0.2712(9)	0.6286(9)	0.491(3)	9.3(8)
C(29)	0.2532(9)	0.6383(9)	0.351(3)	8.4(7)
C(30)	0.2472(8)	0.5932(8)	0.267(2)	7.0(6)
C(31)	0.286(1)	0.4616(9)	0.634(2)	11.0(8)
C(32)	0.356(1)	0.4609(9)	0.445(2)	9.1(7)
C(33)	0.1796(7)	0.5078(6)	0.069(2)	5.3(5)
C(34)	0.1254(10)	0.5172(7)	0.116(2)	6.8(6)
C(35)	0.0798(9)	0.5396(9)	0.040(3)	8.3(7)
C(36)	0.092(1)	0.5575(8)	−0.099(3)	9.1(8)
C(37)	0.148(1)	0.5489(8)	−0.154(2)	8.3(7)
C(38)	0.1923(9)	0.5239(7)	−0.072(2)	6.5(6)
C(39)	0.102(1)	0.545(1)	0.358(2)	11.1(8)
C(40)	0.063(1)	0.462(1)	0.282(2)	11.9(9)
C(41)	0.3099(7)	0.4627(8)	0.066(1)	4.3(4)
C(42)	0.3196(9)	0.4112(9)	0.015(2)	5.5(5)
C(43)	0.371(1)	0.4012(8)	−0.057(2)	7.0(6)
C(44)	0.4130(9)	0.442(1)	−0.075(2)	7.7(7)
C(45)	0.4037(9)	0.4926(9)	−0.022(2)	7.1(6)
C(46)	0.3520(10)	0.5031(8)	0.049(2)	5.9(5)
C(47)	0.2300(9)	0.3683(9)	−0.067(2)	9.0(7)
C(48)	0.301(1)	0.3130(8)	0.049(2)	9.9(7)
C(49)	−0.0408(8)	0.2848(7)	0.153(2)	5.5(5)
C(50)	−0.1006(10)	0.2882(7)	0.125(2)	6.1(6)
C(51)	−0.1408(9)	0.3069(9)	0.233(3)	9.0(7)
C(52)	−0.116(2)	0.3257(9)	0.360(2)	9.6(8)
C(53)	−0.058(1)	0.3241(10)	0.386(2)	9.1(7)
C(54)	−0.0223(8)	0.3014(8)	0.284(2)	6.9(6)
C(55)	−0.1815(9)	0.2470(9)	−0.023(2)	10.5(8)
C(56)	−0.1158(9)	0.3130(8)	−0.123(2)	8.6(6)
C(57)	0.0741(7)	0.2161(7)	0.145(1)	4.4(4)
C(58)	0.0725(8)	0.1637(7)	0.199(1)	4.6(4)
C(59)	0.1180(9)	0.1446(7)	0.287(2)	6.0(5)
C(60)	0.1654(9)	0.1772(9)	0.329(2)	6.8(6)
C(61)	0.1682(7)	0.2289(8)	0.276(2)	5.7(5)
C(62)	0.1249(9)	0.2484(7)	0.183(2)	6.0(5)
C(63)	−0.0251(9)	0.1331(9)	0.270(2)	8.7(7)
C(64)	0.0339(10)	0.0757(8)	0.120(2)	9.0(7)
C(65)	0.0477(7)	0.3035(7)	−0.100(2)	5.5(5)
C(66)	0.0689(9)	0.2919(9)	−0.241(2)	7.5(7)
C(67)	0.090(1)	0.334(1)	−0.328(2)	10.2(8)
C(68)	0.093(1)	0.386(1)	−0.283(3)	10.1(9)
C(69)	0.0734(10)	0.3982(8)	−0.147(3)	8.2(7)
C(70)	0.0528(8)	0.3563(9)	−0.059(2)	6.4(5)
C(71)	0.120(1)	0.2048(10)	−0.244(2)	11.7(8)
C(72)	0.043(1)	0.223(1)	−0.424(2)	12.4(9)
C(73)	0.4569(9)	0.2151(6)	0.349(2)	5.2(5)
C(74)	0.3975(9)	0.2126(7)	0.377(2)	5.6(5)
C(75)	0.3582(9)	0.1927(9)	0.271(3)	8.2(7)
C(76)	0.382(1)	0.175(1)	0.143(3)	9.8(9)
C(77)	0.439(1)	0.1763(9)	0.118(2)	8.4(7)
C(78)	0.4778(8)	0.1964(7)	0.217(2)	6.9(6)
C(79)	0.3170(9)	0.2545(10)	0.525(3)	11.4(8)
C(80)	0.3841(9)	0.1872(8)	0.622(2)	8.4(6)
C(81)	0.5767(7)	0.2828(6)	0.357(2)	4.5(4)
C(82)	0.5718(7)	0.3352(7)	0.304(2)	4.7(4)
C(83)	0.6164(9)	0.3572(7)	0.211(2)	6.0(5)
C(84)	0.6626(9)	0.3236(8)	0.174(2)	6.3(6)
C(85)	0.6667(8)	0.2715(8)	0.226(2)	6.0(5)
C(86)	0.6237(9)	0.2514(7)	0.319(2)	5.5(5)
C(87)	0.4750(10)	0.3668(9)	0.233(2)	9.4(7)
C(88)	0.5349(9)	0.4239(8)	0.380(2)	8.8(7)
C(89)	0.5501(7)	0.1983(7)	0.600(2)	5.9(5)
C(90)	0.5693(8)	0.213(1)	0.742(2)	7.0(6)
C(91)	0.590(1)	0.171(1)	0.826(2)	8.8(7)
C(92)	0.5929(10)	0.117(1)	0.784(3)	9.0(8)
C(93)	0.5754(9)	0.1023(8)	0.649(3)	8.2(7)
C(94)	0.5530(7)	0.1427(8)	0.560(2)	6.0(5)
C(95)	0.619(1)	0.299(1)	0.743(2)	11.2(8)
C(96)	0.548(1)	0.280(1)	0.921(2)	13.4(10)

38% yield based on **2**). M.p.: 88.0–90.0°C. ^{1}H-NMR (C_6D_6): δ 2.45 (s, 18H), 4.17 (s, 3H), 6.94–6.98 (m, 3H), 7.08–7.15 (m, 3H), 7.53–7.57 (m, 3H). ^{13}C-NMR ($CDCl_3$): δ 45.99, 120.40, 124.04, 129.45, 136.55, 138.94, 159.26. ^{29}Si-NMR (C_6D_6): δ -81.14 (q, $^{1}J_{Si-H} = 196$ Hz). IR (KBr, cm^{-1}): ν(Si–H) 2140. MS: m/e 465 (M^{+}, 10), 464 (M^{+}–1, 29), 463 (M^{+}–2, 13),

Table 8
Positional parameters and B_{iso}/B_{eq} for **10**

Atom	x	y	z	B_{eq}
Sn(1)	0.08862(6)	0.13464(7)	0.36171(6)	5.84(3)
Sn(2)	0.23829(7)	0.21569(8)	−0.07507(7)	6.81(3)
Ge(1)	0.15340(10)	0.2783(1)	0.41126(8)	4.81(4)
Ge(2)	0.10955(10)	0.2815(1)	−0.10100(9)	5.08(4)
N(1)	0.0306(8)	0.327(1)	0.2865(8)	7.5(4)
N(2)	0.2662(7)	0.1569(9)	0.3553(6)	5.7(3)
N(3)	0.0822(8)	0.1982(9)	0.5211(7)	6.0(4)
N(4)	0.0984(9)	0.0963(10)	−0.1770(7)	7.3(4)
N(5)	0.1668(9)	0.257(1)	0.0566(7)	7.5(4)
N(6)	0.2098(8)	0.424(1)	−0.1479(8)	7.2(4)
C(1)	0.0898(9)	0.382(1)	0.3959(8)	6.0(4)
C(2)	0.037(1)	0.393(1)	0.3389(9)	7.0(5)
C(3)	−0.012(1)	0.462(2)	0.332(1)	9.9(7)
C(4)	−0.007(2)	0.525(2)	0.382(2)	10.7(9)
C(5)	0.048(1)	0.518(1)	0.439(1)	9.6(7)
C(6)	0.0944(10)	0.445(1)	0.4439(9)	6.6(5)
C(7)	−0.044(1)	0.305(2)	0.246(1)	10.8(8)
C(8)	0.071(1)	0.355(2)	0.2410(10)	10.5(8)
C(9)	0.2350(9)	0.313(1)	0.3724(8)	5.5(4)
C(10)	0.2718(9)	0.250(1)	0.3441(9)	6.1(5)
C(11)	0.319(1)	0.280(2)	0.3068(10)	7.5(6)
C(12)	0.331(1)	0.370(2)	0.300(1)	8.2(6)
C(13)	0.298(1)	0.430(1)	0.3291(10)	7.3(5)
C(14)	0.2469(10)	0.401(1)	0.3648(9)	6.5(5)
C(15)	0.285(1)	0.097(1)	0.308(1)	9.6(7)
C(16)	0.303(1)	0.131(1)	0.4245(9)	6.7(5)
C(17)	0.1883(9)	0.2726(9)	0.5064(9)	5.8(4)
C(18)	0.1530(9)	0.2344(10)	0.5490(9)	5.8(4)
C(19)	0.185(1)	0.231(1)	0.6195(7)	8.0(6)
C(20)	0.255(1)	0.270(1)	0.6444(10)	8.6(6)
C(21)	0.289(1)	0.310(1)	0.603(1)	7.4(6)
C(22)	0.257(1)	0.311(1)	0.5353(8)	6.4(5)
C(23)	0.066(1)	0.114(1)	0.549(1)	8.6(6)
C(24)	0.024(1)	0.264(1)	0.521(1)	9.0(7)
C(25)	0.090(1)	0.114(1)	0.262(1)	9.5(7)
C(26)	0.135(1)	0.018(1)	0.413(1)	7.7(5)
C(27)	−0.022(1)	0.131(1)	0.3661(10)	8.0(6)
C(28)	0.0486(9)	0.247(1)	−0.1874(9)	6.4(5)
C(29)	0.051(1)	0.160(1)	−0.216(1)	7.5(6)
C(30)	0.005(1)	0.140(1)	−0.2794(9)	8.4(6)
C(31)	−0.038(1)	0.206(2)	−0.311(1)	9.0(7)
C(32)	−0.043(1)	0.287(2)	−0.287(1)	8.2(7)
C(33)	0.002(1)	0.306(1)	−0.2233(8)	6.6(5)
C(34)	0.135(2)	0.038(2)	−0.217(1)	12.2(9)
C(35)	0.066(1)	0.043(1)	−0.133(1)	10.4(7)
C(36)	0.0597(9)	0.2425(10)	−0.0354(9)	5.5(4)
C(37)	0.093(1)	0.229(1)	0.0325(9)	7.0(5)
C(38)	0.055(1)	0.189(2)	0.075(1)	8.8(7)
C(39)	−0.018(1)	0.166(2)	0.050(1)	9.2(7)
C(40)	−0.052(1)	0.180(2)	−0.015(1)	9.4(7)
C(41)	−0.015(1)	0.219(1)	−0.0567(9)	7.1(5)
C(42)	0.208(1)	0.210(2)	0.1131(9)	11.2(8)
C(43)	0.170(1)	0.354(2)	0.0702(10)	9.0(6)
C(44)	0.1061(8)	0.4114(10)	−0.1014(7)	4.9(4)
C(45)	0.1579(8)	0.465(1)	−0.1176(7)	5.2(4)
C(46)	0.159(1)	0.555(1)	−0.107(1)	7.6(6)
C(47)	0.109(2)	0.594(1)	−0.0834(10)	9.0(7)
C(48)	0.053(1)	0.545(1)	−0.0678(9)	7.5(6)
C(49)	0.0511(9)	0.454(1)	−0.0769(8)	6.2(5)
C(50)	0.280(1)	0.468(2)	−0.135(1)	12.0(9)
C(51)	0.183(1)	0.407(1)	−0.218(1)	8.4(6)
C(52)	0.243(1)	0.087(2)	−0.032(1)	10.4(7)
C(53)	0.317(1)	0.296(2)	−0.011(1)	12.5(9)
C(54)	0.281(1)	0.198(2)	−0.161(1)	10.4(8)

462 (M^+−3, 21), 434 (M^+−SiH_3, 33), 120 ($C_6H_4NMe_2$, 100). Anal. Calc. for $C_{24}H_{33}N_3GeSi$: C, 62.09; H, 7.16; N, 9.05. Found: C, 61.83; H, 7.28; N, 8.95.

*4.10. Synthesis of tris[2-(dimethylamino)phenyl](trimethylstannyl)germane **(10)***

A solution of trimethylchlorostannane (370 mg, 1.86 mmol) in THF (0.50 ml) was added to a suspension of **1** (prepared from 0.49 mmol of **2**) in THF (1.0 ml) at −40°C, and was then stirred at r.t. for 6 h. After the solvent was removed under reduced pressure, the residue was diluted with benzene (10 ml). The resulting suspension was filtered, and the filtrate was concentrated to give a solid. Recrystallization of the solid from hexane (1.0 ml) yielded **10** as colorless crystals (218 mg, 74% yield based on **2**). M.p.: 189.0–190.0°C. ^{1}H-NMR (C_6D_6): δ 0.47 (s, 9H), 2.37 (s, 18H), 6.92 (m, 3H), 7.06–7.08 (m, 3H), 7.53–7.55 (m, 3H). ^{13}C-NMR ($CDCl_3$): δ −5.46, 46.67, 119.59, 123.74, 137.61, 138.63, 159.71. ^{119}Sn-NMR (C_6D_6): δ −78.82. MS: m/e 599 (M^+, 0.1), 584 (M^+−Me, 55), 582 (66), 580 (61), 434 (M^+−$SnMe_3$, 100). Anal. Calc. for $C_{27}H_{39}N_3GeSn$: C, 54.33; H, 6.59; N, 7.04. Found: C, 54.23; H, 6.58; N, 7.04.

*4.11. X-ray structure determinations for **3**, **4**, **5**, **6**, **8**, and **10***

All crystal data and refinement parameters are summarized in Table 2. Data were collected on a Rigaku AFC7R diffractometer with graphite monochromated Cu–K_α radiation using the $\omega - 2\theta$ scan technique ($2\theta_{max} = 120°$). The structure was solved by heavy-atom Patterson methods [11] and expanded using Fourier techniques [12] and refined on $|F|^2$. Empirical absorption corrections based on azimuthal scans of several reflections were applied for all of the compounds except **6**. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms bonded to the carbon atoms were located at the expected positions by a geometrical calculation and fixed at these positions. The hydrogen atoms bonded to silicon atoms in **4** and **8** were found on the difference Fourier map and refined isotropically. The final atomic coordinates and isotropic temperature factors of **3**, **4**, **5**, **6**, **8**, and **10** are listed in Tables 3–8, respectively.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary CCDC nos. 113088–113093. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2

1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@-ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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