Synthesis and Structures of Tris[2-(dimethylamino)phenyl]silane and -germane Compounds

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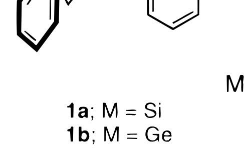
Tris[2-(dimethylamino)phenyl]silane and -germane compounds (**1** and **2**) were synthesized and characterized by X-ray crystallography. Three 2-(dimethylamino)phenyl groups in the hydrosilane (**1a**) and hydrogermane (**1b**) encapsulate the hydrogen atom bonded to silicon and germanium, which results in the short Si−H and Ge−H bonds and an increase in the s character of the bonds. The silanol (**2a**) and germanol (**2b**) exist as monomers through the intramolecular hydrogen bonding between the hydroxy group and one of the amino groups.

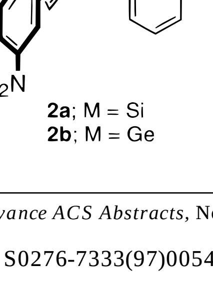
Introduction

The ligands in which three coordinating arms are attached to the central atom have attracted much attention since they highly stabilize the metal and metalloid complexes.[1] We were interested in the synthesis, structures, and reactivities of group 14 compounds with three 2-(dimethylamino)phenyl substituents, in which the dimethylamino donor sites are linked through the *ortho*-phenylene skeleton to the central atom possessing an M−X functionality (M = Si, Ge; X = heteroatoms, metals), as shown in Chart 1. It is noted that the amino groups are located at a position where they can interact not with the central atom (M), but with the neighboring atom (X). This is different from the structural aspects of the well-studied 2-[(dimethylamino)methyl]phenyl analogs,[2,3] in which the amino group can coordinate with the central atom rather than the neighboring atom.

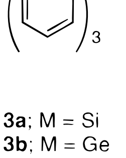
In our synthetic studies of such ligands, we have obtained some related compounds with M−H and M−OH functionalities, that is, tris[2-(dimethylamino)phenyl]silane (**1a**), -germane (**1b**), -silanol (**2a**), and -germanol (**2b**), and found their structural aspects exerted by the amino groups interesting. Herein, we report the full details of the synthesis and structures of **1** and **2**, focused on the fact that (1) the hydrosilane **1a** and hydrogermane **1b** contain the compressed Si−H and Ge−H bonds and (2) the silanol **2a** and germanol **2b** exist as monomers in the solid states through the intramolecular hydrogen bondings. These aspects are compared with those of the parent Ph_3SiX and the 2-(aminomethyl)phenyl analogs **3**.[2,3]



1a; M = Si
1b; M = Ge

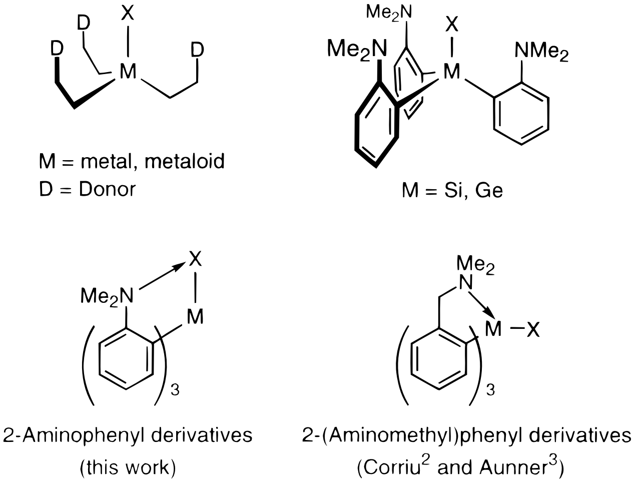


2a; M = Si
2b; M = Ge



3a; M = Si
3b; M = Ge

Chart 1



2-Aminophenyl derivatives
(this work)

2-(Aminomethyl)phenyl derivatives
(Corriu[2] and Aunner[3])

Results and Discussion

Synthesis of Tris[2-(dimethylamino)phenyl]silane (1a) and -germane (1b). Introduction of three (dimethylamino)phenyl groups into the silicon and germanium centers was achieved by use of ortholithiated (dimethylamino)aniline (**4**), which can be prepared by two methods, orthometalation[4] of (dimethylamino)aniline with *n*-BuLi or the halogen−metal exchange[5] of 2-(dimethylamino)bromoaniline with *n*-BuLi. As shown in Scheme 1, the reaction of tetramethoxysilane with an excess of **4** (5.3 molar amounts) in the presence of TMEDA in THF at −78 °C gave crude tris[2-(dimethylamino)phenyl]methoxysilane (**5a**).[5b] Compared to this, some attempted reactions of chlorosilanes,

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[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1997.

(1) For recent examples, see: (a) Gossage, R. A.; McLennan, G. D.; Stobart, S. R. *Inorg. Chem.* **1996**, *35*, 1729. (b) Ray, M.; Golombek, A. P.; Hendrich, M. P.; Young, V. G., Jr.; Borovik, A. S. *J. Am. Chem. Soc.* **1996**, *118*, 6084 and references cited therein.

(2) (a) Brelière, C.; Carré, F.; Corriu, R. J. P.; Royo, G. *Organometallics* **1988**, *7*, 1006. (b) Brelière, C.; Carré, F.; Corriu, R. J. P.; Royo, G.; Man, M. W. C.; Lapasset, J. *Organometallics* **1994**, *13*, 307.

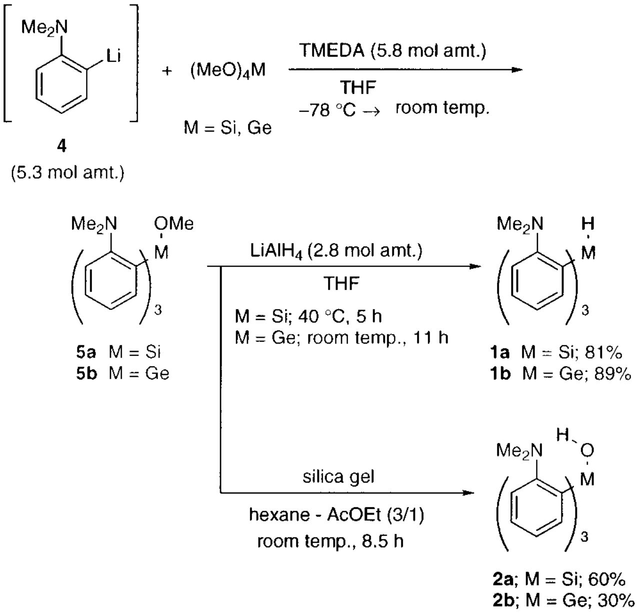
(3) Auner, N.; Probst, R.; Hahn, F.; Herdweck, E. *J. Organomet. Chem.* **1993**, *459*, 25.

(4) (a) Aslandis, P.; Grobe, J. *Z. Naturforsch.* **1983**, *38b*, 280. (b) Tacke, R.; Wiesenberger, F.; Lopez-Mras, A.; Sperlich, J.; Mattern, G. *Z. Naturforsch.* **1992**, *47b*, 1370.

(5) (a) Tidwell, J. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 11797. (b) Zhang, D.; Liebeskind, L. S. *J. Org. Chem.* **1996**, *61*, 2594. (c) Bailey, W. F.; Jiang, X.-L. *J. Org. Chem.* **1996**, *61*, 2596.

S0276-7333(97)00548-7 CCC: $14.00

Scheme 1



such as silicon tetrachloride and trichlorosilane, with **4** under similar conditions afforded complex mixtures. The reaction of tetramethoxygermane with **4** under similar conditions gave crude tris[2-(dimethylamino)phenyl]-methoxygermane (**5b**). Since the methoxy derivatives **5** were converted into the hydroxy derivatives with silica gel (*vide infra*), these compounds were used in the next reactions without purification.

The reduction of methoxysilane **5a** with $LiAlH_4$ in THF at 40 °C afforded the corresponding hydrosilane **1a** in 81% yield (Scheme 1). Reduction of methoxygermane **5b** proceeded even at room temperature to give hydrogermane **1b** in 77% yield. Both compounds were recrystallized from hexane to give colorless crystals, which are stable in air.

Structures of 1a and 1b. X-ray crystallographic analysis of **1a** reveals its unique structure, as shown in Figure 1. The selected bond lengths and angles are listed in Table 1. As expected, all of the amino groups are located on the frontal face of the Si1–H1 bond, but they are highly distorted away from the C_3 symmetry by having the symmetry axis through the Si–H bond. The three amino groups encapsulate the H1 atom with the N···H atomic distances of 2.87(2)–2.97(2) Å, being only 0.1–0.2 Å longer than the sum of the van der Waals radii (H, 1.20 Å; N, 1.55 Å).[6] Although the atomic distances N···Si1 (2.975–3.196(2) Å) are shorter than the sum of the van der Waals radii (3.65 Å), the lone pair electrons on the nitrogens do not direct toward the silicon. The Si1–H1 bond length of 1.32(2) Å in **1a** is short due to the encapsulation of the H1 atom by the amino groups, being 0.17 Å shorter than that of Ph_3SiH (1.491(28) Å)[7] and 0.11 Å shorter than the average value of 1.425 Å for the 450 literature data on Si–H bonds.[8] This value is close to 1.29 Å for the Si–H bond observed in the silane-containing *in*-cyclophane[9] in which the hydrogen atom bonded to the silicon is enclosed with the cyclophane skeleton.

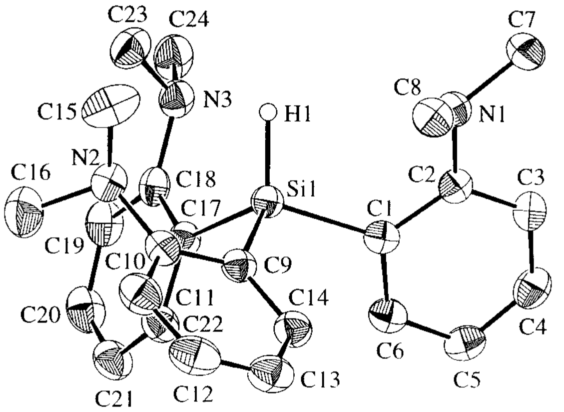


Figure 1. Molecular structure of **1a**. The thermal ellipsoids are drawn at the 30% probability. Hydrogen atoms, except for H1 on silicon which is represented by spheres of arbitrary radius, are omitted for clarity.

Table 1. Selected Interatomic Distances (Å), Bond Angles (deg), and Torsion Angles (deg) for 1a and 1b

	1a (M = Si)	**1b** (M = Ge)
Bond Distances		
M1–H1	1.32(2)	1.42(3)
N1···H1	2.87(2)	2.89(3)
N2···H1	2.97(2)	3.12(3)
N3···H1	2.97(2)	2.94(3)
C1–M1	1.886(2)	1.951(3)
C9–M1	1.883(2)	1.958(3)
C17–M1	1.884(2)	1.960(3)
Bond Angles		
C1–M1–H1	109.0(8)	108(1)
C9–M1–H1	110.4(8)	114(1)
C17–M1–H1	114.0(8)	112(1)
Torsion Angles		
C2–C1–M1–H1	1.32(2)	1.42(3)
C10–C9–M1–H1	1.32(2)	1.42(3)
C18–C17–M1–H1	1.32(2)	1.42(3)
N1–C2–C1–M1	10.2(2)	11.2(4)
N2–C10–C9–M1	−2.2(2)	−1.2(4)
N3–C18–C17–M1	−8.6(2)	−7.3(4)

This structural feature of **1a** is also reflected in the infrared spectra. There is a ν(Si–H) absorption at 2225 cm^{-1}, which is shifted to higher frequency by 100 cm^{-1} relative to that of Ph_3SiH (2125 cm^{-1})[10] and by ca. 50 cm^{-1} relative to that of **3** (2177 or 2189.5 and 2173.3 cm^{-1}).[2,3] This result is consistent with the observed short Si–H bond.

In the ^1H and ^{29}Si NMR spectra of **1a**, the proton bonded to silicon resonates at δ 6.37 and the silicon resonates at δ −31.5 ($^1J_{Si-H}$ = 226 Hz). The deshielding of the ^1H and the shielding of the ^{29}Si compared to those of Ph_3SiH (^1H NMR δ 5.77; ^{29}Si NMR δ −17.8; $^1J_{Si-H}$ = 199 Hz)[10] can be explained by the van der Waals effect;[11] the steric repulsion between the hydrogen and the dimethylamino groups causes a decrease in the electron density on the hydrogen and an increase in the electron density on the silicon atom. Thus, the ^{29}Si chemical shift is close to that of **3** in which the silicon center is [4 + 3] hypercoordinated (^1H NMR δ 5.8; ^{29}Si NMR δ

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(6) Pauling, L. In *The Nature of The Chemical Bond*, 3rd ed.; Cornell University Press: New York, 1960.

(7) Allemand, J.; Gerdil, R. *Cryst. Struct. Commun.* **1979**, *8*, 927.

(8) Cambridge Structural Database, Update April 1996; *QUEST 3D* and *VISTA* Version 2.0.

(9) L'Esperance, R. P.; West, A. P., Jr.; Engen, D. V.; Pascal, R. A. *J. Am. Chem. Soc.* **1991**, *113*, 2672.

(10) The data were obtained in this work.

(11) Günter, H. In *NMR Spectroscopy: Basic Principles, Concepts, and Applications in Chemistry* 2nd ed.; Wiley: Chichester, England, 1995; pp 94–97.

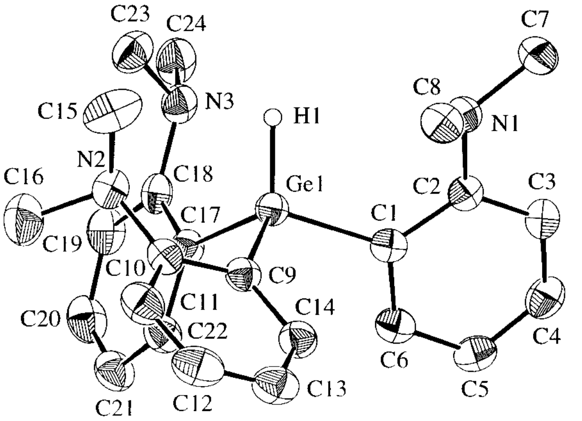


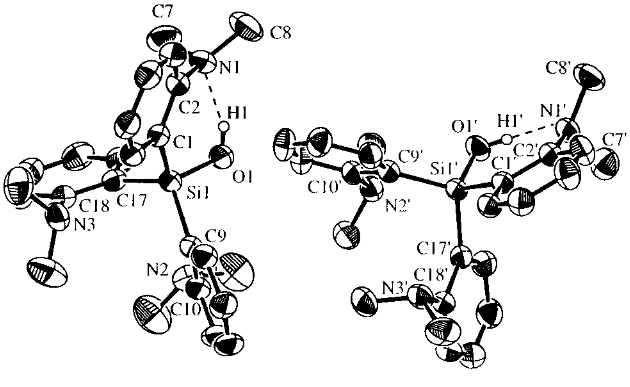
Figure 2. Molecular structure of **1b**. The thermal ellipsoids are drawn at the 30% probability. Hydrogen atoms, except for H1 on germanium which is represented by spheres of arbitrary radius, are omitted for clarity.

−34.9; $^{1}J_{\text{Si-H}} = 226.4$ Hz).[3] The Si−H coupling constant of **1a** is larger than that of Ph_3SiH ($^{1}J_{\text{Si-H}} = 199$ Hz),[10] which indicates an increase in the s character of the Si−H bond. The PM3 calculation is consistent with the NMR data.[12] Thus, the natural bond orbital analysis shows that the s character of the silicon orbital involved in the Si−H bond in **1a** (28.2%) is 4.6% higher than that of the Si−H bond in Ph_3SiH (23.6%).

The X-ray crystallographic analysis of the germanium analog **1b** displays a structure isomorphous to that of **1a**, as shown in Figure 2 and Table 1.[13] Thus, similar structural aspects are observed; the Ge1−H1 bond length of 1.42(3) Å is rather short among the 18 data reported for Ge−H bonds (1.15−1.70 Å; the mean value 1.526 Å).[8,14] Interestingly, tris(*o*-tolyl)germane,[15] where the methyl groups instead of dimethylamino groups are bonded to the *ortho* carbon, has the longest Ge−H bond of 1.700 Å among the reported data.[8]

The short Ge−H bond has also been demonstrated by other spectroscopic data. The infrared spectrum exhibits a ν(Ge−H) at 2140 cm^{-1}, which is 100 cm^{-1} higher in frequency than that of Ph_3GeH (2037 cm^{-1})[16a] and 60 cm^{-1} higher in frequency than that of **3b** (2080 cm^{-1}).[2] The proton bonded to germanium resonates at δ 6.72 in the ^{1}H NMR spectra, which is deshielded in comparison with the shift of Ph_3GeH (δ 5.69)[16b] and that of **3b** (δ 6.05).[2]

Synthesis of Tris[2-(dimethylamino)phenyl]silanol (2a) and -germanol (2b). These silanol and germanol compounds were readily obtained from the methoxysilane and -germane **5**, as shown in Scheme 1. Thus, treatment of **5a** with a suspension of silica gel in hexane/ethyl acetate (3/1) at room temperature for 8.5 h gave the corresponding silanol **2a** in 60% yield.[17] The methoxygemane **5b** was similarly converted into the germanol **2b** in 30% yield.[17] Recrystallization of **2a** and **2b** from hexane gave colorless crystals.



2a **2a'**

Figure 3. Molecular structure of **2a** and **2a′** which are found as independent molecules in a unit cell. The thermal ellipsoids are drawn at the 30% probability. Hydrogen atoms, except for H1 on oxygen which is represented by spheres of arbitrary radius, are omitted for clarity.

Structures of 2a and 2b. X-ray crystallographic analysis of **2a** shows two independent molecules in the asymmetric unit, as shown in Figure 3; the other structure is named **2a′**. The selected bond lengths and angles are listed in Table 2. Since these data for **2a** and **2a′** are similar to each other, the discussion will be presented for **2a** only. The most striking feature in the structure of **2a** is the intramolecular hydrogen bonding between the hydroxy group and one of the amino groups. Due to the intramolecular hydrogen bonding, **2a** is monomeric, which is in sharp contrast to the tetrameric form of Ph_3SiOH through the intermolecular hydrogen bondings.[18] The N1···H1 distance is 1.94(4) Å, and the N1···H1−O1 interatomic distance is 2.713(4) Å, which is within the normal distance of hydrogen bonding (N···H−O 2.62−2.93 Å).[19] The N1···H1−O1 angle is 157(4)° and the Si1−O1−H1 angle is 106(3)°. An electrostatic directionality is another parameter characteristic of the hydrogen bonding. Thus the lone-pair electrons on N1 clearly point toward H1, that is, the N1···H1 vector is nearly in line with the vector of the lone pair electrons; three C−N1···H1 angles are close to the tetrahedral values (C2−N1···H1 = 100(1)°, C7−N1···H1 = 104(1)°, C8−N1···H1 = 113(1)°). It is also noted that one of the amino groups occupies the region opposite to the Si−O bond due to the electronic repulsion of the lone-pair electrons on the oxygen atom. Such an arrangement of the amino groups is quite different from that observed in the hydrosilane **1a**.

The infrared spectra of **2a** shows no well-defined absorption assigned to the O−H stretching, diagnostic of the strong intramolecular hydrogen bonding,[6] whereas

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[12] *SPARTAN* Version 4.0: Hehre, W. J.; Huang, W. W.; Burke, L. D.; Shusterman, A. J. *A SPARTAN Tutorial* Version 4.0; Wavefunction: Irvine, CA, 1995. The geometry of calculated structure of **1a** was based on the X-ray crystallographic data.

[13] Such isomorphism between silicon and germanium compounds has been reported by Corriu et al.[2] and Brook et al., see: Brook, A. G.; Peddle, G. J. D. *J. Am. Chem. Soc.* **1963**, *85*, 1869.

[14] The shortest (1.15(9) Å) and the second shortest (1.37(7) Å) Ge−H bonds have been found in $C_5H_5GeH_3$, see: Barrow, M. J.; Ebsworth, E. A. V.; Marjorie, M. H.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1980**, 603.

[15] Cameron, T. S.; Mannan, K. M.; Stobart, S. R. *Cryst. Struct. Commun.* **1975**, *4*, 601.

[16] (a) Cross, R. J.; Glockling, F. *J. Organomet. Chem.* **1965**, *3*, 146. (b) Cross, R. J.; Glockling, F. *J. Chem. Soc.* **1964**, 4125.

[17] For reviews for silanols and germanols, see: (a) Birkofer, L.; Stuhl, O. In *The Chemistry of Organosilicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; Chapter 10. (b) Armitage, D. A. In *Comprehensive Organometallic Chemistry II*; Davies, A. G., Ed.; Elsevier Science: Oxford, U.K., 1995; Chapter 1. Riviere, P.; Riviere-Baudet, M.; Satge, J. In *Comprehensive Organometallic Chemistry II*; Davies, A. G., Ed.; Elsevier Science: Oxford, U.K., 1995; Chapter 5.

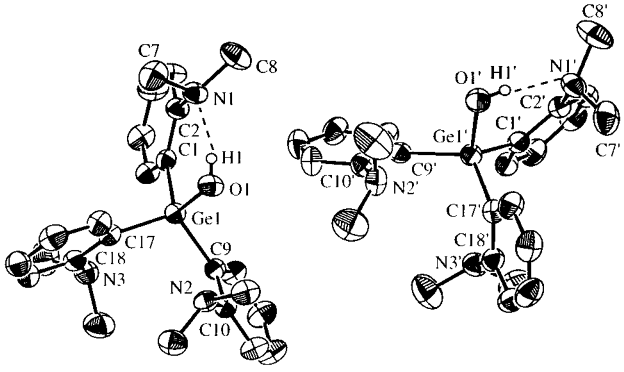
[18] Bourne, S. A.; Nassimbeni, L. R.; Skobridis, K.; Weber, E. *J. Chem. Soc., Chem. Commun.* **1991**, 282.

[19] Stout, G. H.; Jensen, L. H. In *X-ray Structure Determination*, Macmillan: New York, 1968, p 303.

Table 2. Selected Interatomic Distances (Å), Bond Angles (deg), and Torsion Angles (deg) for 2a, 2a′, 2b and 2b′

	M = Si		M = Ge	
	2a	**2a′**[a]	**2b**	**2b′**[a]
	Bond Distances			
O1−H1	0.82(4)	0.79(4)	0.73(7)	0.77(6)
N1···H1	1.94(4)	1.91(4)	2.06(7)	2.06(6)
N1···H1−O1	2.713(4)	2.654(4)	2.734(5)	2.798(6)
O1−M1	1.642(3)	1.629(2)	1.783(3)	1.791(4)
M1−C1	1.905(4)	1.893(4)	1.969(5)	1.983(5)
M1−C9	1.882(3)	1.870(3)	1.941(5)	1.948(5)
M1−C17	1.873(4)	1.873(4)	1.956(5)	1.945(5)
	Bond Angles			
N1−H1−O1	157(4)	156(4)	154(8)	159(6)
H1−O1−M1	106(3)	109(3)	107(6)	101(5)
O1−M1−C1	105.1(2)	105.5(1)	105.8(2)	105.0(2)
O1−M1−C9	106.2(1)	109.0(1)	106.9(2)	104.2(2)
O1−M1−C17	107.3(2)	109.1(2)	107.3(2)	105.1(2)
C2−N1···H1	100(1)	103(1)	106(2)	102(2)
C7−N1···H1	104(1)	99(1)	98(2)	101(2)
C8−N1···H1	113(1)	118(1)	115(2)	114(2)
	Torsion Angles			
H1−O1−M1−C1	19.32	15.53	11.25	21.38
O1−M1−C1−C2	19.7(3)	−10.5(3)	−11.3(5)	19.5(5)
O1−M1−C9−C10	−72.2(3)	61.4(3)	61.2(4)	−73.4(4)
O1−M1−C17−C18	−178.1(3)	−176.6(3)	−176.0(4)	−179.0(4)
M1−C1−C2−N1	8.0(5)	−2.7(5)	−2.7(7)	10.4(7)
M1−C9−C10−N2	−1.3(4)	1.2(4)	−0.1(6)	−2.9(7)
M1−C17−C18−N3	−1.6(5)	0.1(5)	0.6(6)	−1.5(6)

[a] All atom labels should be primed (′), as shown in Figures 3 and 4.



2b **2b'**

Figure 4. Molecular structure of **2b** and **2b′** which are found as independent molecules in a unit cell. The thermal ellipsoids are drawn at the 30% probability. Hydrogen atoms, except for H1 on oxygen which is represented by spheres of arbitrary radius, are omitted for clarity.

Ph_3SiOH, for comparison, exhibits an intense absorption around 3270 cm^{-1}.[10]

The X-ray crystallographic analysis of **2b** shows it to be isomorphous with **2a**. Two independent molecules are present in the unit cell (Figure 4 and Table 2); the other structure is named **2b′**. A similar intramolecular hydrogen bonding N···HO−Ge is observed. The N···H bond length and the N···H−O interatomic distance in **2b** are 2.06(7) and 2.734(5) Å, respectively. The infrared spectra of **2b** similarly showed no well-defined absorption assigned to the O−H stretching.

In conclusion, we have obtained tris[2-(dimethylamino)phenyl]silane and -germane which have the compressed Si−H and Ge−H bonds. We have also succeeded in the introduction of the hydroxy group in the tris[2-(dimethylamino)phenyl]silane and -germane skeletons. The resulting intramolecular hydrogen bonding between the hydroxy group and the amino group leads to the monomeric forms, which is in sharp contrast to the widely observed oligomeric forms of silanols.

Experimental Section

General Remarks. ^1H (270 MHz), ^{13}C (67.94 MHz), and ^{29}Si (53.67 MHz) NMR spectra were recorded on a JEOL EX-270 spectrometer. ^1H and ^{13}C chemical shifts were referenced to internal benzene-d_6 (^1H, δ 7.200 ppm) and $CDCl_3$ (^{13}C, δ 77.00 ppm). ^{29}Si chemical shifts were referenced to external tetramethylsilane (0 ppm). 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. Infrared spectra were recorded on a JASCO IR-810 spectrophotometer. The elemental analyses were performed at the Microanalysis Division of Institute for Chemical Research, Kyoto University. Analytical samples were purified by recrystallization.

N,N-Dimethyl-2-bromoaniline was prepared from 2-bromoaniline and iodomethane.[2] *n*-Butyllithium in hexane was purchased from Wako Pure Chemical Industries. *N,N,N′,N′*-Tetramethylethylenediamine (TMEDA) was distilled from *n*-butyllithium in hexane (50 mL of a 1.6 M solution per 300 mL of TMEDA). Hexane was distilled under nitrogen from sodium wire. THF and Et_2O were distilled under nitrogen from sodium benzophenone ketyl or lithium aluminium hydride. Tetramethoxysilane was purchased from Shin-Etsu Chemical Co., Ltd., and distilled before use.[20] Tetramethoxygermane was purchased from Gelest, Inc. Silica gel was purchased from Merck (Kieselgel 60, 70−230 mesh). All reactions were carried out under an inert atmosphere, unless otherwise noted.

Tris[2-(dimethylamino)phenyl]methoxysilane (5a) and -germane (5b). To a solution of *N,N*-dimethyl-2-bromoaniline

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(20) Tetramethoxysilane is a rather toxic compound; its vapors can cause irreversible blindness. See, for example: (a) *Hazards in the Chemical Laboratory*, 5th ed.; Luxon, S. G., Ed.; The Royal Society of Chemistry: Cambridge, England, 1992; p 603. (b) Stokinger, H. E. In *Patty's Industrial Hygiene and Toxicology*, 3rd ed.; Clayton, G. D., Clayton, F. E., Eds.; John Wiley and Sons, Inc.: New York, 1981; Vol. 2B, pp 3036−3038.

Table 3. Summary of X-ray Diffraction Data

	1a	**1b**	**2a**	**2b**
empirical formula	$C_{24}H_{31}N_3Si$	$C_{24}H_{31}N_3Ge$	$C_{24}H_{31}N_3OSi$	$C_{24}H_{31}N_3OGe$
fw	389.61	434.12	405.61	450.12
color, habit	colorless, prismatic	colorless, prismatic	colorless, prismatic	colorless, prismatic
cryst size (mm)	0.40 × 0.30 × 0.20	0.50 × 0.40 × 0.30	0.50 × 0.50 × 0.50	0.50 x 0.40 × 0.20
cryst syst	triclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a (Å)	9.256(1)	9.350(1)	10.693(2)	10.798(2)
b (Å)	17.066(2)	17.075(3)	27.750(2)	27.820(2)
c (Å)	7.744(1)	7.787(1)	15.635(1)	15.638(1)
α (deg)	92.67(1)	92.81(1)	90.0	90.0
β (deg)	114.173(10)	114.451(9)	92.22(1)	92.22(1)
γ (deg)	84.423(9)	84.28(1)	90.0	90.0
V (Å^3)	1110.7(2)	1126.0(3)	4635(1)	4694.0(9)
Z	2	2	8	8
D(calcd) (g/cm^3)	1.165	1.280	1.162	1.274
μ (cm^{-1})	10.21	19.33	10.31	19.07
temp (K)	293	293	293	293
no. of refns collcd	3538	3579	7494	7582
no. of indep refns	3305 (R_{int} = 0.015)	3346 (R_{int} = 0.034)	7073 (R_{int} = 0.028)	7159 (R_{int} = 0.024)
no. of obsd reflns, $I > 3\sigma(I)$	3048	3069	4879	4766
no. of variables	378	378	760	532
R	0.038	0.043	0.054	0.044
R_w	0.066	0.069	0.088	0.067
goodness of fit	1.89	1.34	1.49	1.08

(1.90 g, 9.4 mmol) in Et_2O (9.5 mL) was added *n*-butyllithium in hexane (1.69 M, 6.2 mL, 10.4 mmol) at −78 °C. The reaction mixture was stirred at −78 °C for 2 h to give a solution of 2-(dimethylamino)phenyllithium (**4**). To the solution of **4** was added TMEDA (1.6 mL, 10.4 mmol) at −78 °C, and then the mixture was warmed to room temperature. The resulting solution was added to a solution of tetramethoxysilane (0.26 mL, 1.77 mmol) in THF (19 mL) at −78 °C. The reaction mixture was warmed to ambient temperature over 12 h. After removal of the solvent, the residue was diluted with benzene (ca. 10 mL) and filtered. The filtrate was concentrated to give crude **5a** (1.70 g). The use of tetramethoxygermane (5.7 mL, 38.7 mmol) in place of tetramethoxysilane gave **5b**. These compounds were used in the next step without further purification. **5a**: ^{1}H NMR (C_6D_6) δ 2.40 (s, 18H), 3.73 (s, 3H), 7.06−7.31 (m, 9H), 7.88−7.91 (m, 3H); ^{29}Si NMR (C_6D_6) δ −13.6; MS *m/e* 419 (M^+, 35), 388 (M^+ − OMe, 15), 387 (39), 299 (31), 266 (100), 134 (90), 120 ($Me_2NC_6H_4$, 58). **5b**: ^{1}H NMR (C_6D_6) δ 2.42 (s, 18H), 3.77 (s, 3H), 7.04−7.30 (m, 9H), 8.01−8.03 (m, 3H); FABMS *m/e* 466 (M^+ + 1, 2), 434 (M^+ − OMe, 28), 134 (100), 120 ($Me_2NC_6H_4$, 58).

Tris[2-(dimethylamino)phenyl]silane (1a). A THF (1.5 mL) solution of **5a** obtained above was added to a suspension of lithium aluminum hydride (190 mg, 4.9 mmol) in THF (5 mL) at 0 °C. The reaction mixture was heated at 40 °C for 5 h. After the reaction mixture was cooled to room temperature, it was diluted with THF (10 mL), followed by successive addition of H_2O (0.19 mL), 15% NaOH aqueous solution (0.19 mL), and H_2O (0.57 mL) at 0 °C. The resulting suspension was filtered, and the filtrate was concentrated to give a solid. Recrystallization from hexane gave **1a** as a colorless crystal (557 mg, 81% yield based on tetramethoxysilane). Mp: 91.5−92.5 °C. ^{1}H NMR (C_6D_6): δ 2.59 (s, 18H), 6.38 (s, 1H), 6.94−6.99 (m, 3H), 7.07−7.10 (m, 3H), 7.20−7.30 (m, 3H), 7.35−7.39 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 45.73, 119.26, 123.32, 129.96, 133.62, 137.32, 160.49. ^{29}Si NMR (C_6D_6): δ −31.5 ($^1J_{Si-H}$ = 226 Hz). IR (KBr, cm^{-1}): ν(Si−H) 2225. MS: *m/e* 389 (M^+, 13), 268 (82), 134 (65), 120 ($Me_2NC_6H_4$, 100). Anal. Calcd for $C_{24}H_{31}N_3Si$: C, 73.99; H, 8.02; N, 10.79. Found: C, 73.87; H, 8.14; N, 10.80.

Tris[2-(dimethylamino)phenyl]germane (1b). This compound was obtained from tetramethoxygermane in 89% yield in essentially the same manner as above except that the reduction was carried out at room temperature for 11 h. Mp: 96.5−97.5 °C. ^{1}H NMR (C_6D_6): δ 2.57 (s, 18H), 6.72 (s, 1H), 6.94−6.99 (m, 3H), 7.07−7.10 (m, 3H), 7.20−7.28 (m, 3H), 7.40−7.43 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 45.70, 119.30, 123.40, 129.49, 135.58, 136.55, 159.42. IR (KBr, cm^{-1}): ν(Ge−H) 2140. MS: *m/e* 435 (M^+, 0.1), 314 (25), 120 ($Me_2NC_6H_4$, 100). Anal. Calcd for $C_{24}H_{31}N_3Ge$: C, 66.40; H, 7.20; N, 9.68. Found: C, 66.31; H, 7.23; N, 9.66.

Tris[2-(dimethylamino)phenyl]silanol (2a). Crude **5a** (2.47 g) was diluted with hexane/ethyl acetate (3/1, 35 mL). To the solution was added silica gel (30 mL) in one portion, and the suspension was stirred at room temperature for 8.5 h in the air. The suspension was filtered with ethyl acetate and THF, and then the filtrate was concentrated to give a solid. Recrystallization from hexane gave **3** as a colorless crystal (564 mg, 60% yield based on tetramethoxysilane). Mp: 77.0−77.5 °C. ^{1}H NMR (C_6D_6): δ 2.48 (s, 18H), 7.03−7.11 (m, 6H), 7.20−7.29 (m, 3H), 7.77−7.80 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 46.20, 120.32, 123.81, 130.14, 134.86, 137.18, 160.38. ^{29}Si NMR (C_6D_6): δ −13.5. MS: *m/e* 405 (M^+, 45), 388 (M^+ − OH, 14), 285 (100), 134 (96), 120 ($Me_2NC_6H_4$, 71). Anal. Calcd for $C_{24}H_{31}N_3OSi$: C, 71.07; H, 7.70; N, 10.36. Found: C, 71.27; H, 7.77; N, 10.38.

Tris[2-(dimethylamino)phenyl]germanol (2b). In a similar manner, **2b** was obtained from tetramethoxygermane in 30% overall yield. Mp: 97.0−98.0 °C. ^{1}H NMR (C_6D_6): δ 2.42 (s, 18H), 5.19 (s, 1H), 7.04−7.12 (m, 6H), 7.20−7.25 (m, 3H), 7.95−7.99 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 46.17, 120.29, 124.01, 129.96, 136.12, 136.17, 159.07. MS: m/e 451 (M^+, 0.1), 434 (M^+ − OH, 14), 134 (89), 120 ($Me_2NC_6H_4$, 100). Anal. Calcd for $C_{24}H_{31}N_3OGe$: C, 64.04; H, 6.94; N, 9.33. Found: C, 63.97; H, 7.00; N, 9.27.

X-ray Structure Determinations for 1a, 1b, 2a, and 2b. All crystal data and refinement parameters are summarized in Table 3. Data were collected on a Rigaku AFC7R diffractometer with graphite-monochromated Cu Kα radiation using the $\omega-2\theta$ scan technique ($2\theta_{max}$ = 120°). The structure was solved by heavy-atom Patterson methods,[21] expanded using Fourier techniques,[22] and refined on $|F|^2$. Empirical absorption corrections based on azimutual scans of several reflections

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[21] *PARTY*: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. The DIRDIF program system. Technical Report of the Crystallography Laboratory; University of Nijmegen: Nijmegen, The Netherlands, 1992.

[22] *DIRDIF92*: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. The DIRDIF program system. Technical Report of the Crystallography Laboratory; University of Nijmegen: Nijmegen, The Netherlands, 1992.

were applied for the germanium compounds **1b** and **2b**. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms bonded to carbon atoms were located at the expected positions by a geometrical calculation and fixed at these positions. The hydrogen atoms bonded to Si in **1a**, Ge in **1b**, and O in **2a** and **2b** were found on the difference Fourier map and refined isotropically.

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Supporting Information Available: Text giving the experimental details of the X-ray crystallography, tables of experimental details, bond distances and angles, torsion angles, atomic coordinates and *B* values, and anisotropic thermal parameters, and ORTEP diagrams of **1a**, **1b**, **2a**, **2a′**, **2b**, and **2b′** (98 pages). Ordering information is given on any current masthead page.

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