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A New Approach to the Synthesis of Unsymmetrical Disilenes and Germasilene: Unusual ^{29}Si NMR Chemical Shifts and Regiospecific Methanol Addition

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Summary: The reaction of dilithiosilanes $(^{i}Pr_3Si)_2SiLi_2$ *(**1a**) and* $(^{t}Bu_2MeSi)_2SiLi_2$ *(**1b**) with diaryldichlorosilanes [*Ar_2SiCl_2*, Ar = Mes (2,4,6-trimethylphenyl) and Tip (2,4,6-triisopropylphenyl)] quantitatively produced the corresponding unsymmetrical 1,1-diaryl-2,2-bis(trialkylsilyl)disilenes,* $Ar_2Si{=}Si(SiR_3)_2$ *(**2**,* $R_3Si = {}^{i}Pr_3Si$*; **3**,* $R_3Si = {}^{t}Bu_2MeSi$*). A stable germasilene,* $Mes_2Ge{=}Si(SiMe^{t}Bu_2)_2$ *(**4**), was also synthesized by the reaction of **1b** with dimesityldichlorogermane. These compounds reveal unusual* ^{29}*Si NMR shifts and regioselective methanol additions.*

Since tetramesityldisilene was first isolated as a stable Si═Si doubly bonded compound in 1981,[1] many other stable disilenes bearing various substituents such as alkyl-, aryl-, silyl-, and heteroatom-containing groups have been synthesized and characterized.[2,3] Almost all stable disilenes have been synthesized by three methods: (A) photolysis of linear trisilanes such as $(Me_3Si)_2SiAr_2$ and consequent dimerization of the intermediate silylene, Ar_2Si:; (B) photochemical cleavage of cyclotrisilanes; and (C) reductive coupling of dihalosilanes. These general methods allow the preparation of disilenes of the type $A_2Si{=}SiA_2$ and ABSi═SiAB. Of course, disilenes having differently substituted silicon atoms, such as $A_2Si{=}SiB_2$, are also accessible by these methods; however, the resulting disilene $A_2Si{=}SiB_2$ is usually produced in a statistical mixture together with $A_2Si{=}SiA_2$ and $B_2Si{=}SiB_2$.[3c,4] Methods for the selective synthesis of unsymmetrically substituted disilenes are currently very limited.[5] For a germasilene, a regiospecific generation of $^{t}Bu_2Si{=}GeMes_2$ (Mes = 2,4,6-trimethylphenyl) is reported by the photochemical reaction of Si,Si′-di-*tert*-butyltetramesitylsiladigermirane.[6] Recently, we have reported the successful preparation and isolation of bis(triisopropylsilyl)dilithiosilane (**1a**) by the reaction of 3,3-bis(triisopropylsilyl)-1,2-bis(trimethylsilyl)-3-silacyclopropene with lithium metal in THF.[7] We have also described some reactions of dilithiosilane with electrophiles such as chlorosilanes, and dilithiosilane was found to be a promising reagent for the synthesis of a variety of organosilicon compounds.[7,8] We report here the reaction of dilithiosilane **1b** with dihalosilanes as electrophiles, which provides a new, highly effective route for the selective synthesis of unsymmetrical disilenes[4,5] and germasilene.[6,9] The un-

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(4) Unsymmetrical tetraaryldisilenes of the $A_2Si{=}SiB_2$ type were generated by cophotolysis of two individual trisilane precursors: See ref 3c and Yokelson, H. B.; Siegel, D. A. Millevolte, A. J.; Maxka, J.; West, R. *Organometallics* **1990**, *9*, 1005.

(5) Unsymmetrical disilenes have been prepared by the reductive dehaloganation of the corresponding dihalodisilane derivatives. For $Mes_2Si{=}SiTip_2$, see: (a) Weidenbruch, M.; Pellmann, A.; Pan, Y.; Pohl, S.; Saak, W. *J. Organomet. Chem.* **1993**, *450*, 67. (b) For $(^{t}BuMe_2Si)_2Si{=}Si(SiMe^{i}Pr_2)_2$, see ref 3k.

(6) Kolleger, G. M.; Stibbs, W. G.; Vittal, J. J.; Baines, K. M. *Main Group Met. Chem.* **1996**, *19*, 317.

(7) Sekiguchi, A.; Ichinohe, M.; Yamaguchi, S. *J. Am. Chem. Soc.* **1999**, *121*, 10231.

(8) (a) Tokitoh, N.; Hatano, K.; Sadahiro, T.; Okazaki, R. *Chem. Lett.* **1999**, 931. (b) Hatano, K.; Tokitoh, N.; Takagi, N.; Nagase, S. *J. Am. Chem. Soc.* **2000**, *122*, 4829.

(9) (a) Baines, K. M.; Cooke, J. A. *Organometallics* **1991**, *10*, 3419. (b) Baines, K. M.; Cooke, J. A. *Organometallics* **1992**, *11*, 3487. (c) Baines, K. M.; Cooke, J. A Dixon, C. E.; Liu, H. W.; Netherton, M. R. *Organometallics* **1994**, *13*, 631. Quite recently, we have reported the synthesis of 1,1,2,3-tetrakis[di-*tert*-butyl(methyl)silyl]-4-phenyl-1,2-disila-3-germacyclopenta-2,4-diene, which has a silole-type structure with Si═Ge and C═C double bonds; see: (d) Lee, V. Ya.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2000**, *122*, 12604. For 2-disilagermirene with a Si═Ge double bond, see ref 3q.

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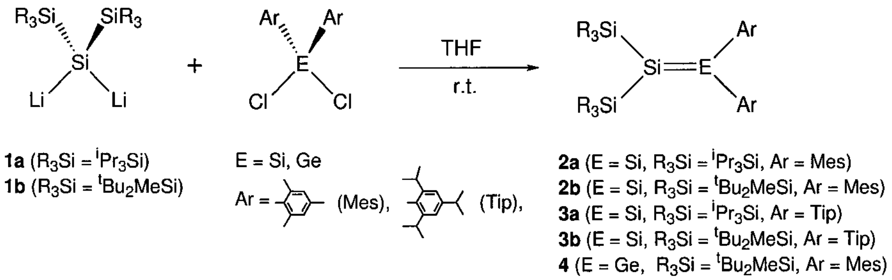
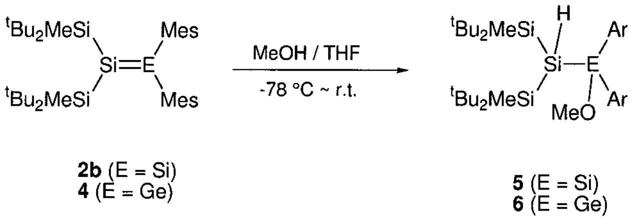
Scheme 1



Scheme 2



usual ^{29}Si NMR chemical shift of the sp^2 silicon atoms and the regiospecific addition of methanol are also presented.

Dry oxygen-free THF was introduced by vacuum transfer to a mixture of bis[di-*tert*-butyl(methyl)silyl]-dilithiosilane (**1b**)[10] and dichlorodimesitylsilane, and the reaction mixture was stirred for 1.5 h at room temperature. The color of the reaction mixture immediately changed to red due to the formation of 1,1-dimesityl-2,2-bis[di-*tert*-butyl(methyl)silyl]disilene (**2b**), which was isolated quantitatively as a red-brown oil (Scheme 1).[11] In a similar manner, 1,1-diaryl-2,2-bis(trialkylsilyl)-disilenes (**2a**, **3a**, and **3b**) were also prepared by the reaction of **1b** with the corresponding diaryldichlorosilanes in 92−96% yield. The germasilene **4** with a Si═Ge double bond was also synthesized by the reaction of the dilithiosilane **1b** with dimesityldichlorogermane in 94% yield.[12]

The structures of **2**−**4** were determined by mass, ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopies[11−13] as well as by product analysis of the reaction with methanol (vide infra).

These unsymmetrical disilenes are quite stable even in solution, and over a couple of months at room temperature no isomerization has been observed. This is in contrast to the behavior of both unsymmetrical tetraaryl- and tetrasilyl-substituted disilenes of the $A_2Si{=}SiB_2$ type, which isomerize at room temperature to give an equilibrium mixture of the *E*- and *Z*-isomers of the ABSi═SiAB type.[3c,k,4] The germasilene **4** is also quite stable in solution, in constrast to the facile germasilene-to-silylgermylene rearrangement by a 1,2-mesityl shift of tetramesitylgermasilene.[9b]

In the ^{29}Si NMR spectrum of **2b**, measured by an inverse-gate pulse sequence, three signals are observed at +8.2, +24.1, and +148.6 ppm with relative intensities of 1:2:1. On the basis of 2D Si−H NMR spectroscopy, the largest signal at +24.1 ppm is assigned to the ^{t}Bu$_2$Me*Si* groups; the other two signals having equal intensity at +8.2 and +148.6 ppm are assigned to the silyl- and aryl-substituted sp^2 silicon atoms, respectively. The other disilenes also show similar ^{29}Si NMR chemical shifts of the sp^2 silicon atoms: +152.3 (**2a**), +137.2 (**3a**), +142.0 ppm (**3b**) for the aryl-substituted sp^2 silicon atoms; −0.8 (**2a**), +14.0 (**3a**), +14.9 ppm (**3b**) for the silyl-substituted sp^2 silicon atoms. The germasilene also exhibits a ^{29}Si NMR resonance of the ^{t}Bu$_2$MeSi-substituted sp^2 silicon atom at +22.4 ppm, which supports the validity of the above assignments. The tetraaryldisilenes and tetrakis(trialkylsilyl)disilenes are reported to give signals of the sp^2 silicon atoms around 53−66[1,3d,4] and 131−156 ppm[3j,k], respectively. The resonances of sp^2 silicon atoms substituted by the aryl groups in **2** and **3** are largely downfield shifted relative to that of tetraaryldisilene; in contrast, the chemical shifts of sp^2 silicon atoms substituted by ^{i}Pr$_3$Si or ^{t}Bu$_2$MeSi groups are largely upfield shifted relative to that of tetrakis(trialkylsilyl)disilene. The reason for such unusual large upfield and downfield shifts of the sp^2 silicon atoms is not clear, but similar trends are reproduced by a GIAO-B3LYP calculation of the model compound $(Me_3Si)_2Si{=}SiMes_2$; the chemical shift of the Me$_3$Si-substituted silicon atom (47.8 ppm) is far more upfield shifted than that of the mesityl-substituted one (156.1 ppm).[14]

The disilenes and germasilene undergo regioselective additions of methanol.[15] Disilene **2b** readily reacted with methanol in THF to give the corresponding adduct **5** as

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[10] Dilithiosilane **1b** was prepared from 3,3-bis[di-*tert*-butyl(methyl)silyl]-1,2-bis(trimethylsilyl)-3-silacyclopropene in a manner similar to that for **1a**. See ref 7.

[11] Procedure for synthesis of **2b**: Dry oxygen-free tetrahydrofuran (ca. 2 mL) was introduced by vacuum transfer to a mixture of 3,3-bis-[di-*tert*-butyl(methyl)silyl]-1,2-bis(trimethylsilyl)-3-silacyclopropene (98 mg, 0.19 mmol) and lithium metal (ca. 10 mg, 1.4 mmol), and then the reaction mixture was stirred at room temperature for 1.5 h to give a red solution of bis[di-*tert*-butyl(methyl)silyl]dilithiosilane (**1b**). After the removal of solvent and bis(trimethylsilyl)acetylene in vacuo, **1b** was obtained as a pale yellow powder. In a glovebox, the lithium metal pieces were removed and then dichlorodimesitylsilane (62 mg, 0.19 mmol) was added. Dry oxygen-free tetrahydrofuran (ca. 2 mL) was introduced into the glass reaction vessel containing **1b** and dichlorodimesitylsilane, and then the reaction mixture was stirred at room temperature for 1 h to give a red-brown solution of **2b**. The solvent was removed in vacuo and then dry oxygen-free C_6D_6 (0.6 mL) was introduced into the reaction mixture. After filtration of the resulting lithium salt, the solvent was removed in vacuo to give pure **2b** as a red-brown oil (118 mg, 99%): ^{1}H NMR (C_6D_6, δ) 0.09 (s, 6 H), 1.18 (s, 36 H), 2.06 (s, 6 H), 2.80 (s, 12 H), 6.72 (s, 4 H); ^{13}C NMR (C_6D_6, δ) −3.5, 21.1, 22.1, 26.0, 30.4, 128.7, 137.8, 139.4, 144.1; ^{29}Si NMR (C_6D_6, δ) 8.2, 24.1, 148.6; HRMS *m*/*z* calcd for $C_{36}H_{64}Si_4$ 608.4085, found 608.4089; UV−vis (hexane) $\lambda_{max/nm}$ (ϵ) 289 (6700), 437 (3200).

[12] Spectroscopic data for **4**: 94% yield; ^{1}H NMR (C_6D_6, δ) 0.12 (s, 6 H), 1.16 (s, 36 H), 2.08 (s, 6 H), 2.71 (s, 12 H), 6.74 (s, 4 H); ^{13}C NMR (C_6D_6, δ) −3.7, 21.0, 21.9, 26.1, 30.3, 128.8, 137.5, 142.4, 145.2; ^{29}Si NMR (C_6D_6, δ) 22.4, 25.1; HRMS *m*/*z* calcd for $C_{36}H_{64}GeSi_3$ 654.3536, found 654.3535; UV−vis (hexane) $\lambda_{max/nm}$ (ϵ) 285 (7400), 424 (3200).

[13] For the spectral data of **2a**, **3a**, and **3b**, see the Supporting Information.

[14] The GIAO-B3LYP calculation was carried out using the Gaussian 98 program with basis sets 6-311G(3d) for Si and 6−311(d) for C and H. Geometry optimization was performed at the B3LYP/6-31G(d) level.

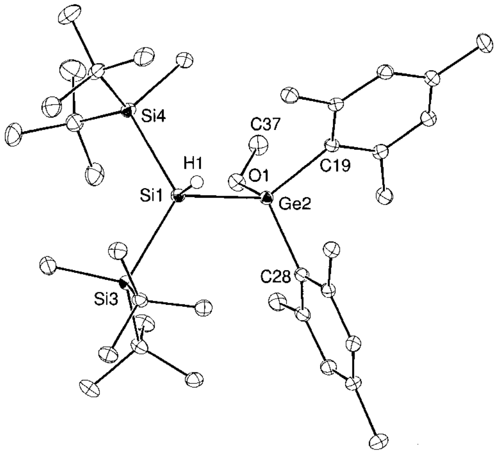

Figure 1. Molecular structure of **6** with thermal ellipsoids drawn at the 30% level (hydrogen atoms are omitted for the clarity). Selected bond distances [Å]: Si1−Ge2 2.4614(8), Si1−Si3 2.423(1), Si1−Si4 2.431(1), Ge2−O1 1.804(2), Ge2−C19 2.003(3), Ge2−C28 1.986(3), Selected bond angles [deg]: Ge2−Si1−Si3 106.1(0), Ge2−Si1−Si4 120.7(0), Si3−Si1−Si4 120.9(0), Si1−Ge2−O1 97.6(1), Si1−Ge2−C19 124.6(1), Si1−Ge2−C28 112.0(1), O1−Ge2−C19 107.8(1), O1−Ge2−C28 110.9(1) C19−Ge2−C28 103.7(1).

a single product in quantitative yield, the structure of which was determined by spectroscopic and X-ray crystallographic methods.[16] The methoxy group is regioselectively bonded to the silicon atom substituted by the two mesityl groups. In the unsymmetrical disilenes, the sp^2 silicon atom connected to the two mesityl groups is more positive than the other sp^2 silicon atom, due to the difference in electronegativity of Si and C. Actually, the calculated natural atomic charges on sp^2 silicon atoms in the model $(Me_3Si)_2Si{=}SiMes_2$ are −0.355 for $(Me_3Si)_2\mathit{Si}$ and +0.958 for $Mes_2\mathit{Si}$ at the B3LYP/6-31(d) level. Thus, the methoxy group is attached to the more positive silicon atom with mesityl substituents.

The germasilene **4** also reacted with methanol to give a single product, **6**,[17] in which the methoxy group is unexpectedly bonded to the germanium atom, as shown in Figure 1. This result shows regioselectivity opposite that of tetramesitylgermasilene, which gives [dimesityl-(methoxy)silyl]dimesitylgermane, in which the methoxy group is attached to the silicon atom.[9a,b] The regioselectivity in **4** can be well understood in terms of the polarized $Si^{\delta-}{=}Ge^{\delta+}$ double bond, caused by the difference in electronegativity of the substituents, as found in the methanol addition to the disilenes **2** and **3**. The calculated atomic charges (−0.332 for $(Me_3Si)_2\mathit{Si}$ and +0.834 for $Mes_2\mathit{Ge}$) in the model $(Me_3Si)_2Si{=}GeMes_2$ at the B3LYP/6-31G(d) level also support the experimental result.

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Supporting Information Available: Tables giving the details of the X-ray structure determination, thermal ellipsoid plots, fractional atomic coordinates, anisotropic thermal parameters, bond lengths, and bond angles for **5** and **6**, ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR charts of **2b**, and spectral data of **2a**, **3a**, and **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) For the mechanistic investigation of the addition of alcohols to disilenes, see: Sakurai, H. *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; John Wiley & Sons Ltd.: New York, 1998; Vol. 2, Chapter 15, and references cited therein.

(16) Spectroscopic data for **5**: Mp 203−204 °C; ^{1}H NMR (C_6D_6, δ) 0.35 (s, 6 H), 1.12 (s, 18 H), 1.17 (s, 18 H), 2.09 (s, 6 H), 2.47 (s, 12 H), 3.35 (s, 3 H), 3.78 (s, 1 H), 6.70 (s, 4 H); ^{13}C NMR (C_6D_6, δ) −1.7, 21.8, 25.5, 30.3, 30.4, 51.8, 129.8, 135.5, 138.8, 143.9; ^{29}Si NMR (C_6D_6, δ) −107.1, 5.4, 19.1. Anal. Calcd for $C_{37}H_{68}OSi_4$: C, 69.30; H, 10.69. Found: C, 69.61; H, 10.37. Crystal data of **5**: $C_{37}H_{68}OSi_4$, fw = 641.27, triclinic, space group $P\bar{1}$, a = 10.9930(8) Å, b = 11.2640(5) Å, c = 18.314(1) Å, α = 103.009(4)°, β = 97.239(3)°, γ = 113.272(4)°, V = 1970.4(2) Å^3, Z = 2, d_{calc} = 1.081 g·cm^{-3}, temperature 120 K, R = 0.0557 ($I > 2\sigma(I)$), R_w = 0.1634 (all data), GOF = 1.026.

(17) Spectroscopic data for **6**: Mp 177−178 °C; ^{1}H NMR (C_6D_6, δ) 0.38 (s, 6 H), 1.11 (s, 18 H), 1.17 (s, 18 H), 2.08 (s, 6 H), 2.52 (s, 12 H), 3.53 (s, 3 H), 4.08 (s, 1 H), 6.70 (s, 4 H); ^{13}C NMR (C_6D_6, δ) −1.9, 21.7, 23.0, 30.22, 30.24, 53.2, 129.7, 138.4, 139.3, 143.3; ^{29}Si NMR (C_6D_6, δ) −92.9, 19.7. Anal. Calcd for $C_{37}H_{68}GeOSi_3$: C, 64.80; H, 9.99. Found: C, 64.94; H, 9.94. Crystal data of **6**·(toluene)$_{0.5}$: $C_{37}H_{68}OSi_4\cdot(C_7H_8)_{0.5}$, fw = 731.89, triclinic, space group $P\bar{1}$, a = 11.0570(7) Å, b = 11.2600(9) Å, c = 18.539(1) Å, α = 81.261(4)°, β = 85.511(4)°, γ = 67.188(4)°, V = 2102.4(3) Å^3, Z = 2, d_{calc} = 1.083 g·cm^{-3}, temperature 120 K, R = 0.0520 ($I > 2\sigma(I)$), R_w = 0.1389 (all data), GOF = 0.944.