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Communications

Tetramesitylgermasilene: The First Relatively Stable Germasilene and Its Rearrangement to a Silylgermylene

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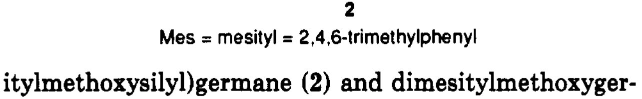
Summary: **The thermolysis of hexamesitylsiladigermirane (1) in the presence of triethylsilane at 105 °C yields mesityl(triethylsilyl)(trimesitylsilyl)germane (3) and dimesityl(triethylsilyl)germane (4). Photolysis of 1 at −78 °C in the presence of triethylsilane gave tetramesitylgermasilene, which upon warming rearranged by a 1,2-aryl shift to mesityl(trimesitylsilyl)germylene, which was then trapped by the silane.**

Recently, we provided convincing evidence for the formation of an intermediate germasilene (a molecule containing a double bond between a silicon and a germanium atom) by the regioselective thermal cleavage of a siladigermirane.[1] Thermolysis of hexamesitylsiladigermirane (1) in the presence of methanol yielded dimesityl(dimesitylmethoxysilyl)germane (2) and dimesitylmethoxygermane, the formation of which is clearly consistent with methanol trapping of the intermediate tetramesitylgermasilene and dimesitylgermylene, respectively. We anticipated that thermolysis of compound 1 in the presence of a reagent capable of trapping the germylene, but unreactive toward the doubly bonded species, would be a viable method of generating the germasilene for further characterization and study. In this communication, we report on the thermolysis and photolysis studies of hexamesitylsiladigermirane in the presence of triethylsilane. Triethylsilane has long been known to be an efficient silylene trap and has recently been shown to trap dimesitylgermylene effectively.[2] However, silanes are unreactive towards doubly bonded silicon compounds.



Mes = mesityl = 2,4,6-trimethylphenyl

The thermolysis of a toluene solution of hexamesitylsiladigermirane (1) for 7 h at 105 °C under argon in the presence of triethylsilane cleanly yields mesityl(triethylsilyl)(trimesitylsilyl)germane[3] (3) and dimesityl(triethylsilyl)germane[2] (4) in a 1:1 ratio by ^{1}H NMR spectroscopy. The identification of compound 3 was relatively straightforward. In the ^{1}H NMR spectrum of 3, signals for the triethylsilyl group, three equivalent mesityl groups, one slowly rotating mesityl group, and a metalloid–H signal at 4.77 ppm were clearly present. The signal at 4.77 ppm was assigned to a germane hydrogen on the basis of the infrared data and the ^{29}Si–^{1}H coupled NMR spectrum of 3, which showed no evidence for a silicon–hydrogen one-bond coupling. A ^{29}Si–^{1}H shift correlated spectrum supports the proposed structure. The ^{29}Si signal at −19.85 ppm correlates with the ^{1}H signal at 4.77 ppm as well as the aryl hydrogen resonances, whereas the ^{29}Si signal at 6.95 ppm correlates with the ^{1}H signal at 4.77 ppm and the resonances from the ethyl hydrogen atoms. These data

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[1] Baines, K. M.; Cooke, J. A. *Organometallics* **1991**, *10*, 3419.

[2] Baines, K. M.; Cooke, J. A.; Vittal, J. J. *J. Chem. Soc., Chem. Commun.*, in press.

[3] Characterization data for 3: white solid; 68%; mp 152–154 °C; IR (thin film) 2037 cm^{-1} (Ge–H); ^{1}H NMR (C_6D_6, δ) 0.7–1.0 (m, 15 H, SiEt$_3$), 1.92 (s, 3 H, Me), 2.09 (s, 12 H, *p*-Me), 2.34 (s, 18 H, *o*-Me), 2.40 (s, 3 H, Me), 4.77 (s, 1 H, Ge–H), 6.64 (s, 1 H, Mes CH), 6.70 (s, 6 H, Mes CH), 6.78 (s, 1 H, Mes CH) (although the signals at 1.92, 2.40, 6.64, and 6.78 broadened, no coalescence was observed between room temperature and 80 °C); ^{13}C NMR ($CDCl_3$, δ) 5.42 (CH_2), 8.11 (Me), 20.90, 25.63, 25.94, 27.05, (Mes Me), 127.52, 128.34, 129.15 (Mes CH), 135.83, 135.99, 138.14, 140.03, 143.02, 143.93, 144.97, (Mes C); ^{29}Si NMR (C_6D_6, δ) −19.85 (bm, SiMes$_3$), 6.95 (m, SiEt$_3$); MS (CI isobutane; *m*/*e* (%)) 693 (2, M$^+$ − H), 578 (24, GeSiMes$_4$), 458 (15, GeSiMes$_3$ − H), 385 (100, SiMes$_3$), 267 (99, SiHMes$_2$), 266 (96, SiMes$_2$), 147 (62, SiMes), 115 (52, SiEt$_3$), 87 (56, HSiEt$_2$); high-resolution MS (*m*/*e*) calcd for ($^{74}GeSi_2C_{42}H_{60}$ − H) 693.3419, found 693.3367. Anal. Calcd for $C_{42}H_{60}GeSi_2$: C, 72.71; H, 8.73 Found: C, 71.79; H, 8.63.

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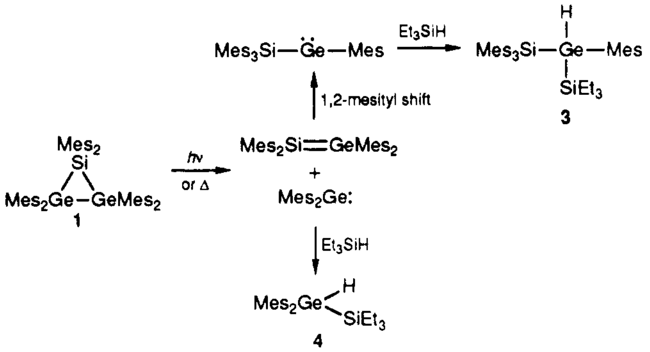
Scheme I

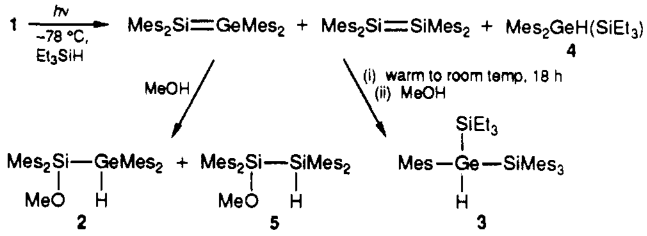


are similar to those of (Mes$_3$Ge)(Et$_3$Si)GeHMes, the structure of which has been unequivocally determined by X-ray crystallography.[2]

The most reasonable explanation for the formation of compounds **3** and **4** begins with the selective thermal cleavage of hexamesitylsiladigermirane to give tetramesitylgermasilene and dimesitylgermylene, which inserts into the Si–H bond of triethylsilane to give compound **4**. A 1,2-mesityl shift converts the germasilene to mesityl(trimesitylsilyl)germylene, which is then trapped by the silane. The selective migration of a mesityl group from germanium to silicon to give a silylgermylene is not surprising, considering the relative stabilities of isomers of the parent hydride (GeSiH$_4$) determined by ab initio calculations.[4,5] The thermodynamically most stable isomer is the singlet silylgermylene (H$_3$SiGeH), with the trans-bent germasilene (H$_2$Si=GeH$_2$) lying 3.2 kcal/mol higher in energy;[4] the singlet germylsilylene (H$_3$GeSiH) lies 16.2 kcal/mol higher in energy.[5] The relative ease of the germasilene-to-silylgermylene isomerization is consistent with the low barrier to isomerization (13.0 kcal/mol) determined by ab initio methods for the parent hydride.[4] The isomerization of the germasilene by a 1,2-aryl shift differs remarkably from the behavior of tetraaryldisilenes, which undergo dyotropic 1,2-diaryl shifts,[6] but is similar to the chemistry of tetramesityldigermene, which undergoes a 1,2-mesityl shift to give a germylgermylene.[2]

Since the germasilene rearranges under thermal conditions, we turned our attention to the photolysis of the siladigermirane at low temperature. The photolytic cleavage of cyclotrisilanes and cyclotrigermanes is a well-known route to disilenes and digermenes, respectively.[7] A solution of **1** in toluene-d_8 at −78 °C was photolyzed (254 nm[8]) in the presence of triethylsilane to give a bright yellow solution. The reaction was monitored by ^{29}Si NMR spectroscopy at −70 °C. Two signals were observed in the downfield region of the spectrum typical for doubly bonded silicon atoms:[9] one at 80.6 ppm and a much lower intensity signal at 63.1 ppm. The signal at 80.6 ppm is assigned to tetramesitylgermasilene and constitutes the first direct observation of a relatively stable germasilene. The signal at 63.1 ppm is attributed to tetramesityldisilene.[10] These assignments were supported by trapping experiments with methanol. Adding methanol to the cold solution, followed by warming to room temperature, removing the solvent, and analyzing by ^{1}H NMR spectroscopy, showed four products. The two major products were identified as dimesityl(dimesitylmethoxysilyl)germane[1] (**2**) and dimesityl(triethylsilyl)germane[2] (**4**) (1:1.4 ratio) with minor amounts of 1,1,2,2-tetramesitylmethoxydisilane[11] (**5**) (5%), 1,1,2,2-tetramesitylmethoxydigermane[1,12] (5%), and 1,1,1-triethyl-2,2-dimesitylsilane (**6**) (trace). The formation of tetramesityldisilene and the triethylsilane-trapped dimesitylsilylene is particularly interesting. Apparently, under photochemical conditions, cleavage of the siladigermirane is less regioselective, generating small amounts of the silylene. We are continuing to investigate the mechanism for the formation of the disilene.

Scheme II



If, instead of quenching the cold photolysate with methanol, the mixture is warmed to room temperature over several hours and then methanol is added, the major products formed are compounds **3** and **4**.[13] Thus, the germasilene–silylgermylene rearrangement is indeed quite facile.

Further evidence for germasilene formation was obtained by UV/vis spectroscopy. A dilute solution of **1** (1 × 10^{-3} M) in cyclohexane was photolyzed at −78 °C for 1 min in the presence of triethylsilane (0.25 M). The UV/vis spectrum of the photolysis mixture at room temperature had an absorption maximum at 414 nm, which can be ascribed to tetramesitylgermasilene. The absorption maximum of the germasilene falls between those of tetramesityldisilene (420 nm in hexane)[10] and tetramesityldigermene (410 nm in cyclohexane).[14] The 414-nm absorption gradually disappeared at room temperature, consistent with the isomerization of the germasilene.[15]

In summary, we have provided the first direct evidence of a relatively stable germasilene, tetramesitylgermasilene, and have shown that the germasilene undergoes a facile 1,2-aryl migration to give a silylgermylene regioselectively.

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(6) Yokelson, H. B.; Siegel, D. A.; Millevolte, A. J.; Maxka, J.; West, R. *Organometallics* **1990**, *9*, 1005.

(7) Tsumuraya, T.; Batcheller, S. A.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 902.

(8) Although these experiments were conducted using 254-nm radiation, we have preliminary results which indicate that 350-nm radiation is just as effective.

(9) West, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201. Brook, A. G.; Baines, K. M. *Adv. Organomet. Chem.* **1986**, *25*, 1.

(10) West, R.; Fink, M. J.; Michl, J. *Science (Washington, D.C.)* **1981**, *214*, 1343.

(11) De Young, D. J.; Fink, M. J.; West, R.; Michl, J. *Main Group Met. Chem.* **1987**, *10*, 19.

(12) Compound **1** is contaminated with minor amounts of hexamesitylcyclotrigermane,[1] which gives tetramesityldigermene upon photolysis. Addition of methanol produces the methoxydigermane.

(13) Minor amounts of **5**, **6**, and 1,1,1,2-tetramesityl-2-(triethylsilyl)digermane were also detected.

(14) Ando, W.; Tsumuraya, T. *J. Chem. Soc., Chem. Commun.* **1989**, 770.

(15) There was no evidence for the formation of tetramesityldisilene or tetramesityldigermene in the UV/vis spectrum.