A Facile Digermene-to-germylgermylene Rearrangement; Bulky Germylene Insertion into the Si–H Bond

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The thermolysis of hexamesitylcyclotrigermane **1** in the presence of triethylsilane at 105 °C yields dimesityl(triethylsilyl)germane **2** and 1,1,1,2-tetramesityl(2-triethylsilyl)digermane **3**; the molecular structure of **3** has been determined by X-ray crystallography.

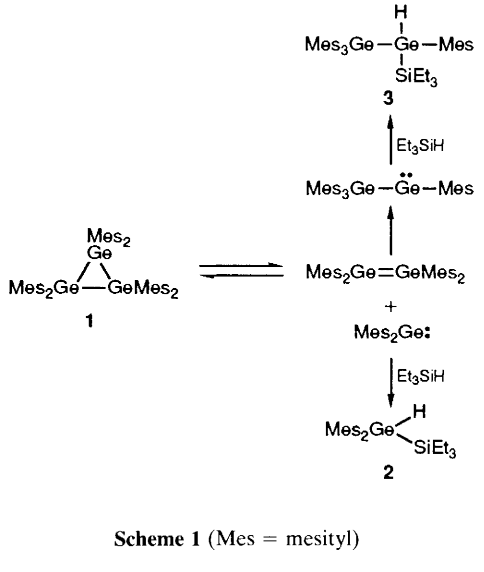
The thermal conversion of hexaaryl-substituted cyclotrigermanes [aryl = 2,4,6-trimethylphenyl (mesityl) and/or 2,6-diethylphenyl] into digermenes is well-established[1] and has been used for the synthesis of a variety of novel small-ring systems containing a germanium–germanium bond.[2] In general, the thermolysis of the cyclotrigermane is carried out in the presence of the appropriate reagent, which then reacts directly with the digermene as it is formed. We have found that tetramesityldigermene, if generated in the absence of a compound reactive towards the Ge=Ge bond, undergoes a 1,2-mesityl shift to give mesityl(trimesitylgermyl)germylene (germanediyl), which can be trapped with triethylsilane.

The thermolysis of a toluene solution of hexamesitylcyclotrigermane **1** for 15 h at 105 °C under argon in the presence of triethylsilane, a known trapping reagent for silanediyl (silylenes), cleanly yields dimesityl(triethylsilyl)germane[†] **2** and 1,1,1,2-tetramesityl(2-triethylsilyl)digermane[‡] **3** in a 1:1 ratio by NMR spectroscopy. Compounds **2** and **3** were separated by chromatography and identified by spectroscopic techniques. The structure of compound **3** was confirmed by X-ray crystallography.[§]

The Ge–Ge bond distance [2.527(2) Å] in compound **3** is similar to the Ge–Ge bond distances observed in the molecular structures of various hexaaryl-substituted cyclotrigermanes[1] and hexamesitylcyclotrigermane [mean distance 2.538(2) Å].[3] The Si–Ge bond distance [2.440(4) Å] is significantly longer than the Si–Ge distances observed in $Ph_3Si–GeMe_3$ [2.394(1) Å][4] and $Me_3Si–GePh_3$ [2.384(1) Å].[5] The Ge–H bond distance [1.70(10) Å] is much longer than that observed in simple germanium hydrides[6] (*i.e.* not substituted with very bulky substituents), but is similar to the Ge–H distance in tri-*o*-tolylgermane (1.700 Å).[7] The Ge–C distances range from 2.005(8) to 2.046(7) Å. The lengthening of the bond distances in **3** is probably because of steric congestion of the bulky substituents.

The products formed in this reaction are intriguing for two reasons. Both compounds appear to be derived from the insertion of a germylene into the Si–H bond of triethylsilane. Insertion reactions of this type, although not unknown, are not common.[8] High yield insertion of a sterically crowded germylene into an Si–H bond is unprecedented. Furthermore, an initial 1,2-mesityl shift in tetramesityldigermene to give mesityl(trimesitylgermyl)germylene, which then inserts into the Si–H bond of triethylsilane, provides a reasonable explanation for the formation of compound **3**. A digermene-to-germylgermylene rearrangement has not previously been reported.

Additional evidence for the digermene-to-germylgermylene rearrangement was obtained in the following experiment. Photolysis[1] (254 nm) of **1** for 4 h at room temperature in cyclohexane under argon, followed by immediate addition of methanol, yielded 1,1,2,2-tetramesityl-1-methoxydigermane[9] as the major product with some unreacted **1** (as determined by ^1H NMR spectroscopy) demonstrating the intermediacy of tetramesityldigermene. However, similar photolysis of **1** followed by triethylsilane addition yielded **3** as the major product after 16 h at room temperature. Subsequent addition of methanol to this sample showed virtually complete conversion of the digermene at room temperature; only traces of the methoxydigermane were observed (as determined by ^1H NMR spectroscopy). Thus, the digermene-to-germylgermylene rearrangement occurs under very mild conditions. This behaviour is in sharp contrast to that of tetraaryldisilenes, which undergo dyotropic 1,2-diaryl rearrangements at room temperature but not 1,2-aryl shifts.[10]



Scheme 1 (Mes = mesityl)

[†] *Spectroscopic data* for **2**: 75%; white solid; IR (thin film) ν/cm^{-1} 2004 (Ge–H); ^1H NMR (C_6D_6) δ 0.8–1.0 (m, 15 H, $SiEt_3$), 2.12 (s, 6 H, *p*-Me), 2.44 (s, 12 H, *o*-Me), 5.29 (s, 1 H, Ge–H), 6.77 (s, 4 H, Mes-H); ^{13}C NMR ($CDCl_3$) δ 5.07 (CH_2), 8.21 (CH_2CH_3), 20.98 (*p*-Me), 24.70 (*o*-Me), 128.23 (Mes-CH), 135.56, 137.33, 143.36 (Mes-C); ^{29}Si NMR (C_6D_6, external $SiMe_4$) δ 4.06; MS [EI, 70 eV, *m*/*z* (%)] 427 (<1, $M^+ - H$), 399 (1, $M^+ - Et$), 312 (100, Mes_2Ge), 192 (57, MesGe − 1); high-resolution MS (*m*/*z*) calc. for $^{74}Ge^{28}SiC_{24}H_{38} - H$ 427.1876, found 427.1831.

[‡] *Spectroscopic data* for **3**: 60%; white solid; m.p. 135–7 °C; IR (thin film) δ/cm^{-1} 2014 (Ge–H); ^1H NMR (C_6D_6) δ 0.7–1.0 (m, 15 H, $SiEt_3$), 2.02 (br s, 3 H), 2.07 (s, 3 H), 2.09 (s, 9 H, *p*-Me), 2.33 (br s, 3 H), 2.39 (s, 18 H, *o*-Me), 4.92 (s, 1 H, Ge–H), 6.60 (br s, 1 H, Mes–CH), 6.71 (s, 6 H, Mes–CH), 6.76 (br s, 1 H, Mes–CH); ^{13}C NMR ($CDCl_3$) δ 5.47, 8.08 ($SiEt_3$), 20.81, 20.88, 25.34, 25.72, 26.51 (Mes–Me), 127.39, 128.28, 128.94 (Mes–CH), 136.33, 137.26, 139.00, 140.78, 143.02, 143.64, 143.85 (Mes–C); ^{29}Si NMR ($CDCl_3$, external $SiMe_4$) δ 7.87; MS [CI: isobutane, *m*/*z* (%)] 738 (1, M^+, $^{74}Ge^{72}Ge$), 622 (24, $Mes_4{}^{74}Ge^{72}Ge$), 431 (85, Mes_3Ge), 312 (71, Mes_2Ge), 192 (36, MesGe − 1), 115 (42, $SiEt_3$) 87 (100, $HSiEt_2$).

[§] *Crystal data*: (from CH_2Cl_2–pentane) $Ge_2Si_1C_{42}H_{60}$. $M = 738.21$, triclinic, space group $P\bar{1}$. $a = 13.713(2)$, $b = 13.740(3)$, $c = 12.377(3)$ Å, $\alpha = 106.02(1)$, $\beta = 110.17(2)$, $\gamma = 102.42(1)°$, $V = 1976.0(8)$ Å^3, $Z = 2$, $D_c = 1.241$ g cm^{-3}, $T = 296$ °K, μ(Mo-K$\bar{\alpha}$) = 15.13 cm^{-1}. $R = 0.072$, $R_w = 0.077$ for 3031 [$I \geqslant 3\sigma(I)$] observations and 237 parameters. The remaining details for the X-ray structure determination can be found in the supplementary material. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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