Reaction of {Tris[2-(dimethylamino)phenyl]germyl}lithium with Elemental Selenium: Formation of 2,2,4,4-Tetrakis[2-(dimethylamino)phenyl]-1,3,2,4-diselenadigermetane

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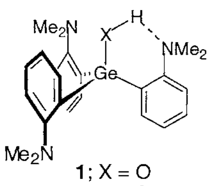
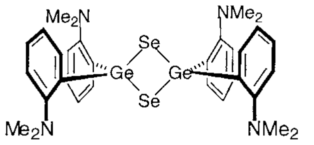
The reaction of {tris[2-(dimethylamino)phenyl]germyl}-lithium with elemental selenium gives 2,2,4,4-tetrakis[2-(dimethylamino)phenyl]-1,3,2,4-diselenadigermetane. The crystal structure of this heterocyclic compound has been determined by X-ray diffraction. The reaction mechanism is discussed based on the NMR monitoring.

The chemistry of compounds containing germanium–Group 16 elements bonds has been extensively investigated from both synthetic and structural view points.[1] Recently, we reported the preparation and structure of tris[2-(dimethylamino)phenyl]germanol (**1**), which contains the germanium–oxygen bond and exhibits intramolecular hydrogen bonding between the hydroxyl group and one of the amino groups.[2] This finding prompted us to prepare and isolate a heavier Group 16 element analog, germaneselenol **2**.[3,4] The Se–H bond is usually so labile that selenols are easily oxidized in air to diselenides. We anticipated that the Se–H bond in **2** would be stabilized through the hydrogen bonding with the amino group(s) in a manner similar to the O–H bond in **1**. We report here the attempted preparation of the germaneselenol, which resulted in the unexpected formation of the four-membered heterocyclic compound, 2,2,4,4-tetrakis[2-(dimethylamino)phenyl]-1,3,2,4-diselenadigermetane **3**.[5]



1; X = O
2; X = Se



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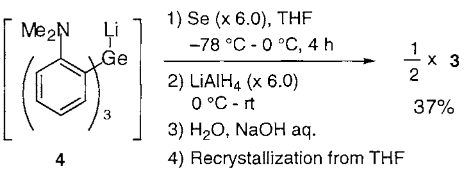
In order to prepare the selenol **2**, we selected the reaction of the germyllithium **4** and elemental selenium, as shown in Scheme 1.[3] The germyllithium **4** was prepared by lithiation of the corresponding hydrogermane[2] **5** with *tert*-butyllithium (3.3 mol amt.) in THF at –40 °C for 1 h.[6] The solution of **4** was allowed to successively react with selenium powder and with lithium aluminum hydride, followed by hydrolysis. Crystallization of the product from THF did not afford **2** but unexpectedly produced the diselenadigermetane **3** in 37 % yield.[7] The crystals were extremely unstable when separated from the mother liquor, and changed rapidly into a powder, suggesting the inclusion of solvent molecule(s).



Scheme 1.

However, the molecular structure of **3** was successfully determined by X-ray diffraction by coating the crystal with mineral oil at a low temperature, as shown in Figure 1.[5,8] The crystals of **3** indeed include three THF molecules in a unit cell. The center of the symmetry lies on the center of the planar four-membered ring. The Se-Ge-Se angle is 96.12(3)° and the Ge-Se-Ge angle is 83.88(3)°. The Ge-Se bond lengths are 2.3678(6) and 2.3716(9) Å, which are among the normal Ge-Se single bond lengths (2.337–2.421 Å).[9] The intramolecular Ge···Ge distance is 3.168(1) Å. The ratio of the Ge···Ge nonbonding distance (NBD) to the Ge-Se bond length (BL) is 1.34, which is in good agreement with the values of the approximate homology rule proposed by Kabe and Masamune:[10] the NBD/BL for the four-membered cyclic compounds consisting of Group 14 elements were reported to be 1.32 to 1.40. The intramolecular Ge···N distances are 2.910(4) and 2.910(6) Å, which are shorter than the sum of the van der Waals radii (Ge, 2.10; N, 1.54 Å).[11]

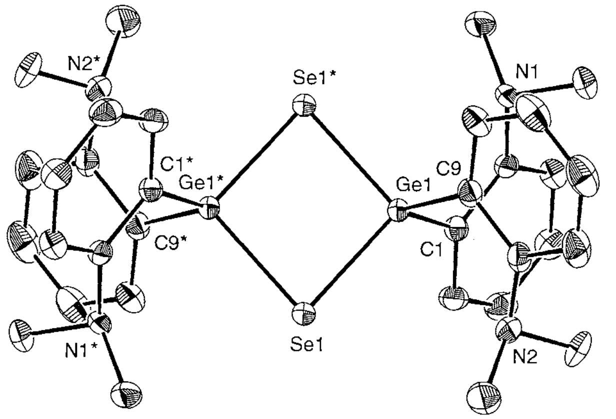
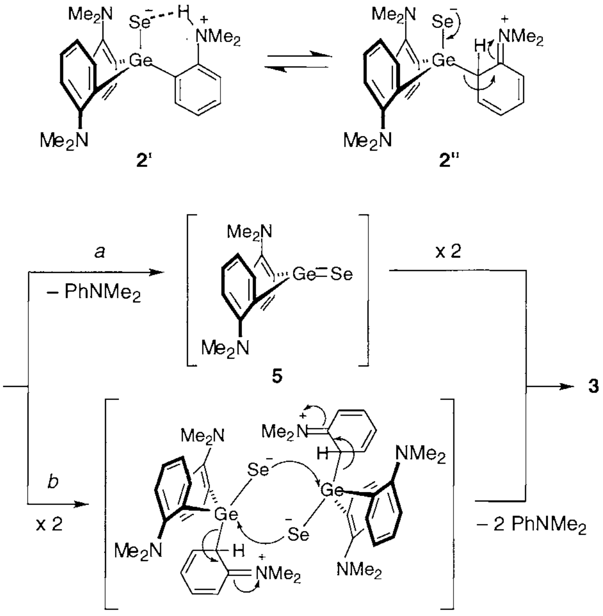


Figure 1. Molecular structure of **3**•3THF with 30% probability ellipsoids. The three THF molecules and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Se1-Ge1 = 2.3678(6), Se1-Ge1* = 2.3716(9), Ge1-C1 = 1.951(4), Ge1-C9 = 1.949(6), Se1-Ge1-Se1* = 96.12(3), Ge1-Se1-Ge1* = 83.88(3), Se1-Ge1-C1 = 110.6(2), Se1-Ge1-C9 = 113.6(1), Se1-Ge1*-C1 = 113.1(2), Se1-Ge1*-C9 = 110.4(2), C1-Ge1-C9 = 112.0(2).

The mechanism of the formation of **3** is still unclear, but **3** turned out to be the secondary product not the primary product, as indicated by the ^{1}H NMR results. The ^{1}H NMR spectra of the reaction mixture just after hydrolysis display none of the signals of **3** but a signal at 5.92 (1H) together with a set of signals for the 2-(dimethylamino)phenyl groups at δ 2.28 (methyl, 18H) and at δ 8.12–8.22 (3,6-protons of the phenyl groups, 6H).[12] These signals may be assigned not to the neutral selenol **2** but rather to the zwitterionic species **2'** (Scheme 2); the signal at δ 5.92 is at a much lower field compared to that of the ordinary selenol proton

($\delta < 0$)[13] and close to that of the ammonium proton (δ 6–9).[14] This contrasting feature of **2'** to that of the germanol **1** can be attributed to the fact that the selenol proton is more acidic than the alcohol proton.[3] After recrystallization from THF under an argon atmosphere, **3** was isolated as crystals; the signals of **2'** even disappeared in the mother liquor. This clearly indicates that **2'** has been converted into **3** during recrystallization.



Scheme 2.

One plausible mechanism is as follows: the zwitterionic species **2'** undergoes intra- (path *a*) and/or intermolecular (path *b*) protodegermylation via another species **2''**, which is formed by the proton shift from the nitrogen to the germanium-bonded ipso-carbon atom of the (amino)phenyl group, as shown in Scheme 2.[1,15] While the intramolecular pathway involves the formation of the germaneselone **5** and its formal head-to-tail [2+2] cycloaddition,[16] the intermolecular reaction proceeds through the nucleophilic attack of the selenide ion on the germanium atom in another molecule. Thus the nitrogen donor intramolecularly activates the selenol proton, inducing a novel type of reaction for the formation of the heterocyclic compound.

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7 Preparation of **3**. To a solution of **5** (434 mg, 1.00 mmol) in THF (6.0 mL) was added *tert*-butyllithium in pentane (1.64 M, 2.0 mL, 3.3 mmol) at –40 °C, and the reaction mixture was stirred for 1 h at the same temperature. To the resulting yellow suspension of **4** was added selenium (powder) (480 mg, 6.1 mmol) in one portion at –78 °C and the mixture was warmed to 0 °C over 4 h. The reaction mixture was diluted with THF (4.0 mL), followed by the addition of lithium aluminum hydride (240 mg, 6.2 mmol) at 0 °C. After stirring at room temperature for 1.5 h, the reaction mixture was again diluted with THF (30 mL) followed by the successive addition of H_2O (0.23 mL), 15% NaOH aqueous solution (0.23 mL), and H_2O (0.69 mL) at 0 °C. The resulting suspension was filtered and the filtrate was concentrated to give a yellow powder. Recrystallization of the powder from THF at 0 °C gave **3**•3THF as colorless crystals, which were unstable without the mother liquor. For the analyses, the THF molecules were completely removed in vacuo to yield **3** (146 mg, 37% yield based on **5**). mp: 274.0–274.5 °C (decomp.). ^1H NMR (C_6D_6): δ 2.24 (s, 24H), 6.88–6.91 (m, 4H), 7.09–7.19 (m, 8H), 8.45–8.49 (m, 4H). ^{13}C NMR (C_6D_6): 46.47, 121.96, 126.31, 130.68, 134.43, 141.71, 158.12. ^{77}Se NMR (C_6D_6): –67.3. Anal. Found: C, 49.03; H, 5.06; N, 6.94%. Calcd for $C_{32}H_{40}N_4Ge_2Se_2$: C, 49.03; H, 5.14; N, 7.15%.

8 Crystal data of **3**•3THF: $C_{44}H_{64}N_4Ge_2Se_2O_3$; FW = 1000.11; Rigaku RAXIS-IV; coated with a mineral oil; crystal size 0.40 x 0.30 x 0.20 mm; triclinic, space group $P\bar{1}$ (# 2), $Z = 1$; a = 12.010(1) Å, b = 12.871(1) Å, c = 8.6692(7) Å; α = 102.526(7), β = 107.447(7)°, γ = 108.151(5); V = 1141.5(2) Å^3, D_{calcd} = 1.455 g/cm^3; μ = 29.52 cm^{-1} (Mo-Kα, λ = 0.71070 Å); $F(000)$ = 512.00; T = 143 K; $2\theta_{max}$ = 55.1°. The structure analysis is based on 4442 reflections, 3607 observed ($I > 3.00\sigma(I)$), and 234 parameters. The structure was solved by direct methods (SIR92) and refined by full-matrix least-squares on $|F|^2$. R = 0.058, R_W = 0.084; goodness of fit indicator = 1.73. One of the three THF molecules was solved using the rigid group model because of its disordering.

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12 The 4,5-protons of the phenyl groups cannot be correctly assigned due to the complexity of the spectra in the region.

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