Synthesis and Structure of 1,3-Bis[tris(trimethylsilyl)methyl]-2,4,5-triselena-1,3-digermabicyclo[1.1.1]pentane

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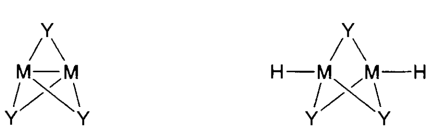
1,3-Bis[tris(trimethylsilyl)methyl]-2,4,5-triselena-1,3-digermabicyclo[1.1.1]pentane **4**, obtained by photodeselenation of the corresponding 2,4,5,6-tetraselena-1,3-digermabicyclo[2.1.1]hexane, shows a short Ge···Ge distance of 2.672 Å; an Se···Se interaction in **4** is observed by ^{77}Se NMR, X-ray analysis and electronic spectroscopy.

In recent years, group IV propellanes **I** and bicyclo [1.1.1]pentanes **II** (M = Y = C, Si, Ge, Sn) have received much attention in the view of the nature of the bridgehead bonds.[1] Pentasila-[1.1.1]propellane has not, as yet, been isolated although a derivative of bicyclo[1.1.1]pentasilane[2] has been synthesized. According to both calculations and experiments, M–M distances in [1.1.1]propellanes (M = C, Si, Ge, Sn, Y = CH_2, SiH_2, GeH_2, SnH_2) are much shorter than that in bicyclo-[1.1.1]pentane except for the tin analogue.[1–3] Theoretically, substitution of electronegative groups (*e.g.* O, CH_2) at the peripheral positions should stabilize the central M–M interaction for M = Si or Ge.[1d] Therefore, the structure of [1.1.1]propellanes of the type M_2Y_3 (M = Si, Ge, Sn; Y = O, S, Se) **I** and the corresponding bicyclo[1.1.1]pentanes $H_2M_2Y_3$ **II** should be very similar.[4] Interestingly, the calculated values of distances between bridgehead atoms of trioxadisila- and trioxadigerma-bicyclo[1.1.1]pentanes are 2.069 and 2.235 Å, respectively, which corresponds to Si–Si triple bond and Ge–Ge double bond values, respectively, despite the absence of a formal M–M bond.[1c,f,3b,4]

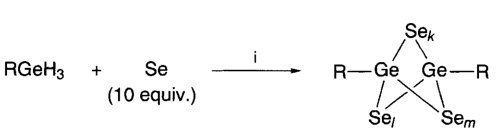
Although in the case of the silicon only one example of group IV trichalcogenadisilabicyclo[1.1.1]pentane derivatives has been demonstrated,[5,6] neither the bicyclo nor the propellane derivatives of the germanium analogue have been experimentally reported. Here, we report the first isolation and structure of 2,4,5-triselena-1,3-digermabicyclo[1.1.1]pentane utilizing the bulky tris(trimethylsilyl)methyl group for kinetic stabilization.

A mixture of tris(trimethylsilyl)methylgermane (1.0 g, 3.25 mmol) and selenium (2.5 g, 32.5 mmol) was heated at 150–160 °C for 18 h in DBU {1,8-diazabicyclo[5.4.0]-7-undecene} (0.5 ml) and decalin (20 ml).† GPC and TLC separation afforded hexaselenadigermabicyclo[3.2.1]octane **1**, pentaselenadigermabicyclo[2.2.1]heptane **2** and tetraselenadigermabicyclo[2.1.1]hexane **3** in 27, 12 and 19% yields, respectively (Scheme 1).‡ The structures of **1**, **2**, and **3** were determined by elemental analysis and ^{1}H, ^{13}C and especially ^{77}Se NMR spectroscopy. There are three possible structures for **1**, hexaselenadigermabicyclo[4.1.1]octane, hexaselenadigermabicyclo[3.2.1]octane and hexaselenadigermabicyclo [2.2.2]-octane, which are plausible from elemental analysis and ^{1}H and ^{13}C NMR spectra. The ^{77}Se NMR spectrum of **1** shows four identical signals at δ 642.4, 443.7, 278.4 and −96.5 in 1 : 2 : 2 : 1 ratio. This indicates that **1** is undoubtedly hexaselenadigermabicyclo[3.2.1]octane. Similarly, the ^{77}Se NMR spectrum of **2** shows signals at δ 427.0 and −10.9 in a 1 : 4 ratio, which indicates that it has a bicyclo[2.2.1]heptane skeleton. Compound **3** has a bicyclo[2.1.1]hexane skeleton as indicated by two signals in its ^{77}Se NMR spectrum. Irradiation ($h\nu$ > 300 nm) of **3** for 70 min in benzene gave 2,4,5-triselena-1,3-digermabicyclo[1.1.1]pentane **4** in 62% yield (Scheme 2). Chromatographic separation and recrysallization from benzene afforded **4** as orange crystals (mp > 300 °C). Compound **4** is the first example of a trichalcogenadigermabicyclo[1.1.1]pentane system. The bicyclo[1.1.1]pentane structure of **4** was deduced on the basis of the following spectroscopic properties: the FAB mass spectrum indicated the M^+ cluster in the range of *m/z* 834–857 in agreement with that calculated for $C_{20}H_{54}Ge_2Se_3Si_6$. Elemental analyses were also in agreement with the calculated values. The ^{1}H, ^{13}C and ^{77}Se NMR spectra were fully consistent with the highly symmetrical structure: ^{1}H NMR (400 MHz, C_6D_6) δ 0.39 (s); ^{13}C NMR (125 MHz, C_6D_6) δ 3.9 (q), 4.7 (s); ^{77}Se NMR (76.4 MHz, C_6D_6) δ 995.0. An absorption maximum at 365 nm (ε = 100 dm^3 mol^{-1} cm^{-1}, hexane), tailing into the visible region (*ca.* 440 nm), was observed in the electronic spectrum. The structure of **4** was unequivocally determined by single-crystal X-ray diffraction analysis.§ The molecule has D_{3h} symmetry, Fig. 1. The bicyclo[1.1.1]pentane skeleton is constructed from three cyclobutanes (at dihedral angles of 120.60, 119.98 and 119.42°, av. 120.0°), and has acute Ge–Se–Ge angles (67.43, 67.64 and 67.29°), which are similar to that of digermathiirane.[7] Interestingly, the atomic distances between the peripheral selenium atoms (3.46–3.47 Å) are within the sum of van der Waals radii of selenium (4.0 Å). The interaction between selenium atoms is observed by ^{77}Se NMR spectroscopy and suggested by the electronic spectrum. The chemical shift of the bridging selenium atoms of **4** appear at extremely low field, δ 995.0 (relative to $SeMe_2$), which can be explained by a Se···Se interaction, namely a stereo compression effect;[8] the absorption maximum at 365 nm also arises from the interaction between selenium atoms. The bridgehead Ge···Ge distance is 2.672 Å, which is slightly longer than typical Ge–Ge single bond lengths (2.41–2.54 Å),[9] but slightly shorter than the longest Ge–Ge single bond so far characterized [in $Bu^t{}_3Ge$–$GeBu^t{}_3$ (2.71 Å)][10] and corresponds to the Ge···Ge distance in tetrakis(2,6-diethylphenyl)digermoxane (2.617 Å).[11] This extremely short Ge···Ge distance results from geometric factors, and is a consequence of the propellane structure.



I **II**

M = C, Si, Ge, Sn
Y = CH_2, SiH_2, GeH_2, SnH_2, O, S, Se

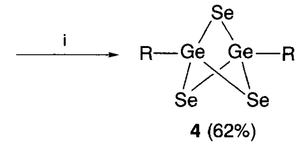


x = k + l + m

	x	Yield (%)	[k. l. m]
1	6	27	[3. 2. 1]
2	5	12	[2. 2. 1]
3	4	19	[2. 1. 1]

Scheme 1 *Reagents and conditions*: i, 150–160 °C, decalin, DBU, 18 h; R = $C(SiMe_3)_3$

3



4 (62%)

Scheme 2 *Reagents and conditions*: i, $h\nu$ (>300 nm), benzene, 70 min; R = $C(SiMe_3)_3$

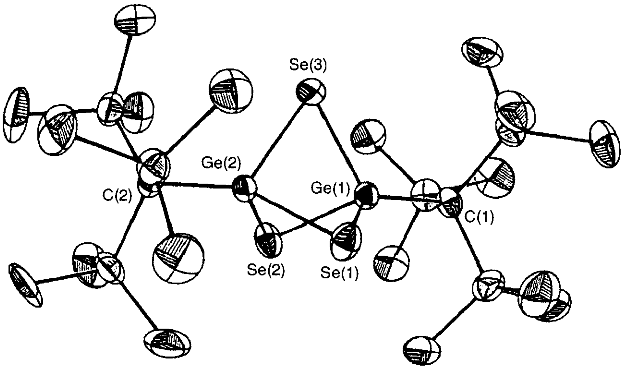


Fig. 1 ORTEP drawing of **4**. Selected bond lengths (Å) and angles (°): Ge(1)–Se(1) 2.407(1), Ge(1)–Se(2) 2.403(1), Ge(1)–Se(3) 2.412(1), Ge(1)–C(1) 1.947(8), Ge(2)–Se(1) 2.407(1), Ge(2)–Se(2) 2.398(1), Ge(2)–Se(3) 2.411(1), Ge(2)–C(2) 1.951(8), Ge(1)···Ge(2) 2.672(1); Ge(1)–Se(1)–Ge(2) 67.43(4), Ge(1)–Se(2)–Ge(2) 67.64(4), Ge(1)–Se(3)–Ge(2) 67.29(4), Se(1)–Ge(1)–Se(2) 92.40, Se(1)–Ge(1)–Se(3) 91.86(4), Se(2)–Ge(1)–Se(3) 92.05(4), Se(1)–Ge(2)–Se(2) 92.52(4), Se(1)–Ge(2)–Se(3) 91.87(5), Se(2)–Ge(2)–Se(3) 92.22(4), Se(1)···Se(2) 3.4717, Se(2)···Se(3) 3.4656, Se(3)···Se(1) 3.4624.

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Footnotes

† $(Me_3Si)_3CGe_3H_3$ was prepared by reduction of $(Me_3Si)_3CGeCl_3$ with LAH in THF in 67% yield; white crystals, mp 257 °C; ^1H NMR (400 MHz, $CDCl_3$, 25 °C, $SiMe_4$) δ 0.19 (s, 27H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, $SiMe_4$) δ 2.70 (q), 3.39 (s); MS (70 eV, EI), *m*/*z* 293 [M^+ − 15].

‡ *Selected data* for **1**: reddish orange crystals, mp > 300 °C; ^1H NMR (300 MHz, $CDCl_3$, 25 °C, $SiMe_4$) δ 0.41 (s); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, $SiMe_4$) δ 4.9 (s), 5.3 (q); ^{77}Se NMR (76.4 MHz, $CDCl_3$, 25 °C, $SeMe_2$) δ −96.5, 278.4, 442.7, 642.4; UV–VIS (hexane) $\lambda_{max}(\varepsilon/dm^3\ mol^{-1}\ cm^{-1})$ 311 (sh, 4900), 421 (sh, 450), 450 nm (sh, 200); MS (FAB) *m*/*z* 1068–1097 [M^+]; $C_{20}H_{54}Ge_2Se_6Si_6$ (1082.10): calc. C, 22.06; H 4.96; found: C 22.77, H 4.46%.

For **2**: reddish brown crystals, mp > 300 °C; ^1H NMR (300 MHz, $CDCl_3$, 25 °C, $SiMe_4$) δ 0.42 (s); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, $SiMe_4$) δ 4.9 (q), 5.5 (s); ^{77}Se NMR (76.4 MHz, $CDCl_3$, 60 °C, $SeMe_2$) δ −6.8, 433.6; UV–VIS (hexane) $\lambda_{max}(\varepsilon/dm^3\ mol^{-1}\ cm^{-1})$ 310 (sh, 2690), 385 (sh, 360), 438 nm (sh, 160); MS (FAB), *m*/*z* 990–1017 [M^+]; $C_{20}H_{54}Ge_2Se_5Si_6$ (1003.14): calc. C 23.81, H 5.36; found: C 23.71, H 5.12.

For **3**: reddish brown crystals, mp > 300 °C; ^1H NMR (300 MHz, $CDCl_3$, 25 °C, $SiMe_4$) δ 0.43 (s); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, $SiMe_4$) δ 4.5 (q), 4.9 (s); ^{77}Se NMR (76.4 MHz, $CDCl_3$, 25 °C, $SeMe_2$) δ 405.6, 478.0; UV–VIS (hexane) $\lambda_{max}(\varepsilon/dm^3\ mol^{-1}\ cm^{-1})$ 278 (sh, 1240), 363 (sh, 190), 415 nm (sh, 40); MS (FAB) *m*/*z* 912–937 [M^+]; $C_{20}H_{54}Ge_2Se_4Si_6$ (924.18): calc. C 25.86, H 5.82; found: C 26.16, H 5.26%).

§ *Crystal data* for **4**: $C_{20}H_{54}Ge_2Se_3Si_6$, M = 845.23, monoclinic, space group $P2_1/c$, a = 15.758(1), b = 13.229 (1), c = 17.612 (2) Å, β = 93.45 (1)°, V = 3664.6 Å^3, Z = 4, μ(Mo-Kα) = 47.7 cm^{-1}, D_c = 1.53 g cm^{-3}. The 4723 independent reflections ($|F_o| > 3\sigma|F_o|$, $\theta < 50°$) were measured on Enraf-Nonius CAD4 diffractometer using Mo-Kα radiation and ω–2θ scan. Structure solved by direct methods and all non-hydrogen atoms refined anisotropically by full-matrix least squares to R = 0.046 and wR = 0.057. Silicon atoms of the tris(trimethylsilyl)methyl group on the one side are disordered over two sites. Refinement of occupancies of these indicated 9 : 1 occupancies. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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