Letters to the Editor

1,2-Disila-3-germacyclopenta-2,4-dienes: cyclopentadiene analogs based on heavier group 14 elements*

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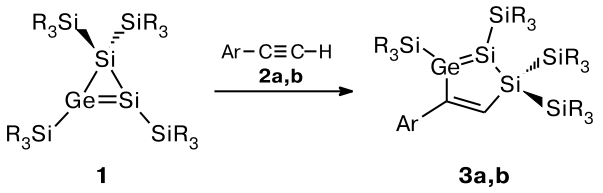
Multiple bonding between the heavier main group elements is one of the mainstream fields of contemporary organometallic chemistry.[1] To date, many room temperature stable alkene analogs of the heavier group 14 elements have been isolated and structurally characterized.[2] As for silagermenes >Si=Ge<, the first metastable tetramesitylsilagermene was prepared in 1991 (see Ref. 3), whereas the first isolable representatives were synthesized by us in 2000 (see Ref. 4). The first (and still the only) cyclic silagermene, incorporating a Si=Ge bond into the 1,3-diene fragment and representing a novel class of cyclic metalladienes, was reported by us some time ago.[4b] In the present study, we report the synthesis of novel members of the metalladiene family.

We found that the scope of the reaction of 1*H*-disilagermirene **1** (see Ref. 4a) with arylacetylenes Ar—C≡C—H **2** can be expanded by varying the aryl substituents. Thus, compound **1** readily reacts with both 1-ethynyl-4-methylbenzene (**2a**) (Ar = 4-Me—C_6H_4) and 1-ethynyl-4-trifluoromethylbenzene (**2b**) (Ar = 4-CF_3—C_6H_4) forming 1,1,2,3-tetrakis[di-*tert*-butyl(methyl)silyl]-4-(4′-Ar)-1,2-disila-3-germacyclopenta-2,4-dienes **3a**,**b**, which were isolated and characterized by spectroscopic and crystallographic (for **3a**) analyses (see Experimental, the synthesis of **3b** and its spectral data will be reported elsewhere) (Scheme 1).

Scheme 1



1 **3a,b**

R_3Si = $SiMeBu^t_2$
Ar = 4-Me—C_6H_4 (**a**), 4-CF_3—C_6H_4 (**b**)

For the reaction between **1** and **2**, one can suggest a primary π(Si=Ge)—π*(C≡C) frontier orbital interaction indicated by the contrast between the remarkable ease and high rate of the reaction in the case of **2b** (which is characterized by a strongly electron-withdrawing CF_3 group on the aryl substituent that lowers the π*(C≡C) energy level) and the case of **2a** (with its electron-releasing CH_3 group on the aryl substituent) where the reaction was several times longer.

* Dedicated to Academician of the Russian Academy of Sciences O. M. Nefedov on the occasion of his 80th birthday.

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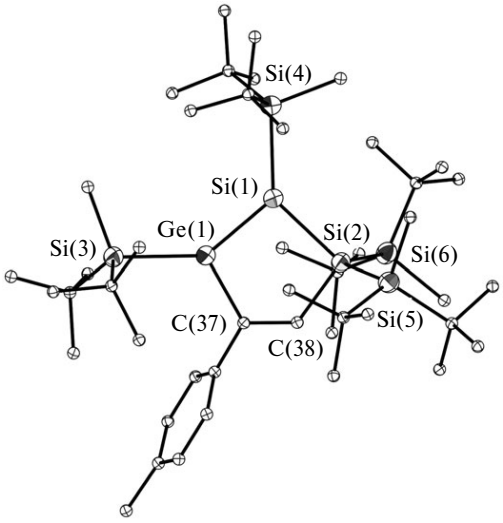

Fig. 1. Molecular structure of compound **3a** (ORTEP, hydrogen atoms are not shown).

The most peculiar NMR spectra feature of both compounds **3a** and **3b** is the low-field resonance of their sp^2-Si atoms observed at 123.6 ppm for **3a** and 127.3 ppm for **3b**. The Si_2GeC_2 five-membered ring in **3a** is nearly planar (the sum of the interior bond angles is 539.9°) with a twisted (the twist angle between the planes formed by the Si or Ge atoms and their substituents is 20.8°) Si=Ge bond, whose length of 2.2439(6) Å is between those of typical Si=Si and Ge=Ge bonds (Fig. 1). Both UV spectra (the absence of a notable bathochromic shift) and structural (the absence of shortening of the single bonds and stretching of the double bonds) features of **3a** give evidence for the lack of any observable conjugation between the Si=Ge and C=C bonds.

1*H*-Disilagermirene **1** (1.03 g, 1.36 mmol) was reacted with eightfold excess of arylacetylene **2a** (1.25 g, 10.8 mmol) in anhydrous O_2-free benzene (4 mL) in a sealed evacuated tube at room temperature. Pure **3a** was isolated by the recrystallization from anhydrous hexane as bright orange crystals (0.34 g, 29%), m.p. 166—168 °C. ^{1}H NMR (400 MHz, C_6D_6), δ: 0.38 (s, 6 H, 2 Me); 0.43 (s, 3 H, Me); 0.59 (s, 3 H, Me); 1.01 (s, 18 H, Bu^t); 1.16 (s, 18 H, Bu^t); 1.20 (s, 18 H, Bu^t); 1.32 (s, 18 H, Bu^t); 2.16 (s, 3 H, CH_3 (tolyl)); 7.06 (d, 2 H, H_{arom}, J = 8.0 Hz); 7.36 (d, 2 H, H_{arom}, J = 8.0 Hz); 7.33 (s, 1 H, C=C<u>H</u>). ^{13}C NMR (100.6 MHz, C_6D_6), δ: −3.1, −2.4 (3 C); 21.1, 22.0, 22.4, 23.0, 23.5, 29.8, 30.8, 31.0, 31.3, 127.6, 128.8, 135.4, 148.7, 149.5 (ArC=<u>C</u>H), 173.2 (Ar<u>C</u>=CH). ^{29}Si NMR (79.5 MHz, C_6D_6), δ: −46.0 (ring sp^3-Si); 19.2, 26.5, 29.9, 123.6 (ring sp^2-Si). UV, λ_{max}/nm (ε/L mol^{-1} cm^{-1}, hexane): 313 (8300), 471 (8300). Crystal data for **3a** at 120 K: $C_{48}H_{99}GeSi_6$, M = 917.40, triclinic, space group $P1^-$, a = 12.1270(8), b = 12.4810(7), c = 21.1020(11) Å, α = 96.964(3)°, β = 94.473(3)°, γ = 116.768(3)°, V = 2798.8(3) Å^3, Z = 2, d_{calc} = 1.089 g cm^{-3}, R = 0.0427 for 9751 reflections with $I_0 > 2\sigma(I_0)$ (R_w = 0.1191 for all data, 12 310 reflections), GOOF = 1.050.

Table 1. Selected bond lengths (d) and bond angles (ω) in molecule **3a**

Bond	d/Å	Angle	ω/deg
Si(1)—Ge(1)	2.2439(6)	Si(1)—Ge(1)—C(37)	101.66(6)
Si(1)—Si(2)	2.3746(8)	Ge(1)—Si(1)—Si(2)	95.29(3)
Ge(1)—C(37)	1.986(2)	Si(1)—Si(2)—C(38)	98.48(7)
Si(2)—C(38)	1.885(2)	Si(2)—C(38)—C(37)	126.18(17)
C(37)—C(38)	1.351(3)	C(38)—C(37)—Ge(1)	118.26(16)

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