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Synthesis and structural characterization of a silacycloheptadiene

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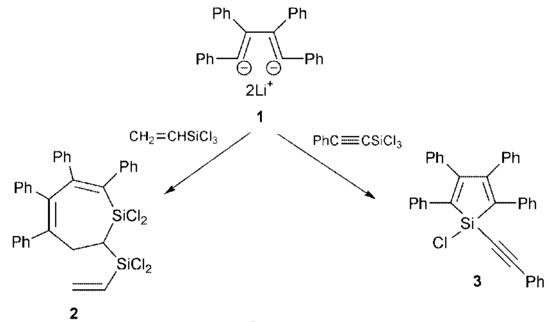
The dilithium salt of tetraphenylbutadiene (1) reacts normally with phenylethynyltrichlorosilane to give 1-chloro-1-phenylethynyl-2,3,4,5-tetraphenylsilole (3), but with vinyltrichlorosilane the unexpected product is the silacycloheptadiene 2, and X-ray crystal structures were obtained for 2 and 3; the seven-membered ring in 2 adopts a boat conformation, and a possible mechanism for the formation of 2 is suggested.

The reaction of vinylchlorosilanes with a bulky organolithium compound such as *tert*-butyllithium has been reported by Jones and Lim[1] and later extensively studied by Auner[2] for almost 20 years. However only one report, by Balasubramanian and George,[3] for the reaction of 1,2,3,4-tetraphenylbuta-1,3-diene dianion **1** with an alkenylchlorosilane, $Me(CH_2{=}CH)SiCl_2$, to give 1-methyl-1-vinyltetraphenylsilole has been published.[3]

Here, we report the reactions of **1** with phenylethynyltrichlorosilane and vinyltrichlorosilane. Although many synthetic routes for siloles have been reported,[4] siloles can often be synthesized in high yield by using our previously reported method[5] in which a solution of the dilithio compound **1** is frozen with liquid nitrogen, an excess of a chlorosilane is added *via* a syringe in one portion and the mixture is slowly warmed. However, the reaction of **1** with vinyltrichlorosilane using the method described above gave, surprisingly, a reaction involving two molecules of the chlorosilane yielding silacycloheptadiene **2** (Scheme 1).† No evidence for the formation of the expected silole $C_4Ph_4SiCl(CH{=}CH_2)$ was observed. Even preparative scale reactions of **1** with just 1 equiv, rather than an excess of vinyltrichlorosilane, gave only **2** in 50% yield, leaving 50% of **1** unreacted**.** The reaction produced two enantiomers which could result from the chiral carbon C(6).

The X-ray crystal structure of **2** was determined and is shown in Fig. 1.‡ The molecule has two localized double bonds, and the vinyldichlorosilyl substituent group is attached to carbon atom C(6), as shown. The conformation of the seven-membered ring is boat like. The silicon atom Si(1) and carbon atoms C(1), C(2), C(3) are nearly coplanar, as are carbon atoms C(2), C(3), C(4), C(5), but there is a twist (51.3°) between C(2) and C(3), and a strong bend at the C(4)–C(5) junction (−89.8°). The result is that the silyl substituent group is moved away from the hindering phenyl groups on the ring.



Scheme 1

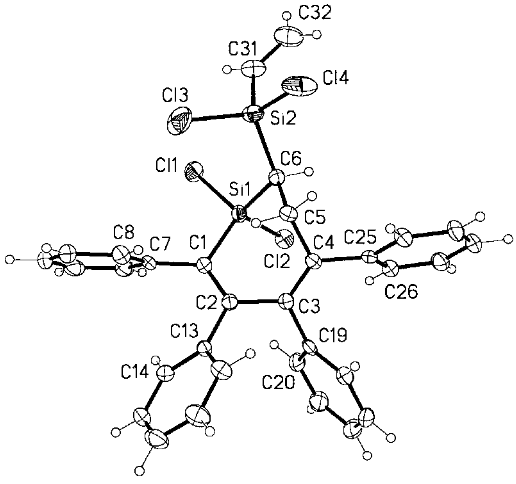
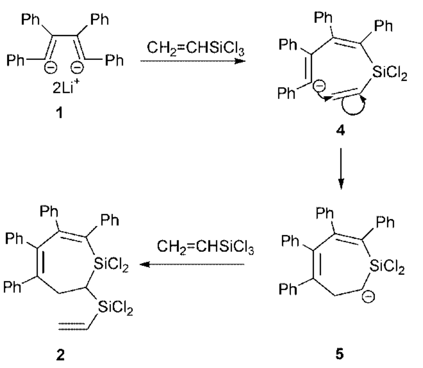


Fig. 1 Thermal ellipsoid diagram of structure of **2**. Selected bond lengths, (pm): Si1–C1 187.2(4), Si1–C6 186.8(4), Si1–Cl1 205.23(13), Si1–Cl2 207.01(13), Si2–C6 186.7(4), Si2–C31 183.5(4), C1–C2 136.1(5), C2–C3 150.7(5), C3–C4 135.3(5), C4–C5 152.0(5), C5–C6 156.2(5), C31–C32 131.5(6), Intramolecular angles, (°): C1–Si1–C6 111.8(2), Si1–C1–C2 118.8(3), Si1–C6–C5 105.9(2), C1–C2–C3 121.5(3), C2–C3–C4 122.7(3), C3–C4–C5 122.2(3), C4–C5–C6 110.4(3), Si1–C6–Si2 118.4(2), C6–Si2–C31 115.0(2), Si2–C31–C32 123.4(4), Cl1–Si1–Cl2 103.83(6), Cl3-Si2–Cl4 107.32(8). Selected torsion angles, (°): C1–C2–C3–C4 51.3(5), Si1–C1–C2–C3 −0.7(5), C2-C3–C4–C5 3.9(5), C3–C4–C5–C6 −89.8(4), C4–C5–C6–Si1 55.5(4), C4–C5-C6-Si2 −172.9(2), C7–C1–C2–C13 7.5(5), C13–C2–C3–C19 51.2(4), C19–C3–C4–C25 7.8(5).

A possible mechanism for the formation of **2** is shown in Scheme 2. Nucleophilic reaction of the butadiene anion in **4** with the β-carbon atom of the vinyldichlorosilane moiety could give an intermediate which could close to give the dichlorosilacycloheptadienyl anion **5**. This anion could react with another molecule of vinyltrichlorosilane to give **2**. An alternative mechanism would involve loss of LiCl from the anion of **5** to give a Si=C bond. This would then be followed by Si–Cl addition across the Si–C double bond to give the product **2**. However, the reaction of **1** with 1 equiv. of vinyltrichlorosilane



Scheme 2

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in the presence of a trapping reagent such as a 2,3-dimethylbutadiene gave only **2** without any addition product of buta-1,3-diene across the Si=C bond. This result argues against the alternative mechanism.

In contrast to the reaction described above, the reaction of **1** with phenylethynyltrichlorosilane proceeded normally to give the silole **3**,§ with no indication of formation of a seven-membered ring, even when an excess of $PhC{\equiv}CSiCl_3$ was present. The crystal structure of **3**, shown in Fig. 2,‡ is very similar to that for previously known siloles.[6] The ring is nearly planar, with a torsion angle C(1)–C(2)–C(3)–C(4) for the butadiene moiety of 5.3°. The Si(1)–C(29) bond distance of 181.6 pm for **3** is shorter by *ca.* 3.6–4.6 pm than intra ring bond distances of Si(1)–C(1) and Si(1)–C(4). The angle Si(1)–C(29)–C(30) of 174.3° and the torsion angle Si(1)–C(29)–C(30)–C(31) of 25.0° show that the Si–C≡C–C moiety is non-linear; this distortion may result from crystal packing forces.

Tetraphenylsilole and its polymers have been reported to exhibit interesting photophysical properties.[7] Surprisingly, silacyclohepta-2,4-diene **2** is also photoluminescent. Compound **2** and **3** exhibit two broad bands at *ca.* 300 and 380 nm in their electronic absorption spectra, assignable to the butadiene moiety. As shown in Fig. 3, both **2** and **3** have a broad emission band at *ca.* 380 nm in the fluorescence spectra.

Although several silacyclohepta-2,4,6-trienes[8] and silacycloheptenes[9] are known, as are some dihydrobenzosilepins,[10] **2** appears to be the first example of a silacycloheptadiene. We plan to extend the method used for the synthesis of **2** to prepare other new silacycloheptadiene compounds and their polymers.

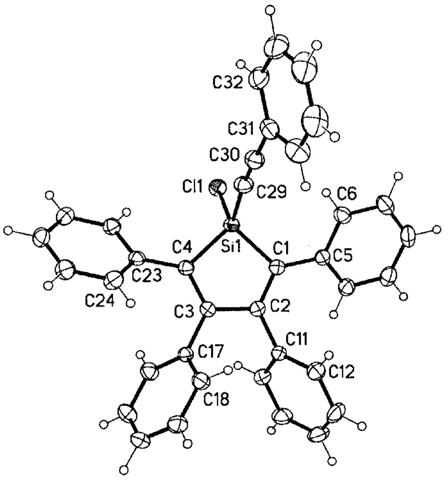

Fig. 2 Thermal ellipsoid diagram of structure of **3**. Selected bond lengths, (pm): Si1–C1 186.2(2), Si1–C4 185.2(2), Si1–Cl1 205.89(5), Si1–C29 181.6(2), C1–C2 136.1(2), C2–C3 151.4(2), C3–C4 135.9(2), C29–C30 120.5(2), C30–C31 144.1(2). Intramolecular angles (°): C1-Si1–C4 95.35(7), Si1–C29–C30 174.3(2), Si1–C1–C2 105.19(11), Si1–C4–C3 105.34(11), C1–C2–C3 116.80(13), C2–C3–C4 116.95(13), C1–Si1–C29 115.11(7), C29–C30–C31 177.5(2).

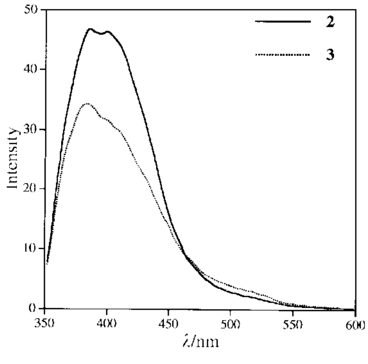

Fig. 3 Fluorescence spectra of **2** and **3** at 10^{-5} M in THF. Excitation was at 340 nm.

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Notes and references

† *Synthesis* of **2**: diphenylacetylene (4.5 g, 25 mmol) and lithium (0.35 g, 50 mmol) were stirred in diethyl ether (50 mL) at room temperature for 3.5 h. The solution was cannulated to remove the residual lithium metal and frozen with a bath of liquid nitrogen. Vinyltrichlorosilane (3.2 mL, 25 mmol) was added by a syringe in one portion. The mixture was kept at −196 °C for 5 min before the cooling bath was removed, then the solution was allowed to warm up slowly to room temperature and stirred for 4 h to give a yellow solution. The solution was cannulated, concentrated, and crystallized at −20 °C to give product as yellowish-green crystals (19.2 g, 63%); mp 178–-180 °C. Selected data ^{1}H NMR (300.133 MHz, $CDCl_3$), δ 6.70–7.55 (br m, 20H, Ph), 6.05–6.35 (br m, 3H, vinyl H), 3.77 (dd, 1H, J 14.0, 12.5 Hz), 3.28 (dd, 1H, J 15.4, 3.3 Hz), 2.17 (dd, 1H, J 14.0, 3.7 Hz); ^{13}C{H} NMR (75.403 MHz, $CDCl_3$), δ = 158.61, 140.70, 139.94, 138.89, 138.68, 138.51, 138.21, 131.60, 131.47, 130.62, 129.89, 129.51, 128.33, 128.00, 127.79, 127.68, 127.32, 127.23, 127.05, 126.52, 35.31, 33.26; ^{29}Si NMR (71.548 MHz, $CDCl_3$), δ = 10.58, 8.53; MS(EI): *m/z* (%): 608 (100) [M$^+$], 481 (5) [M$^+$ −Si(CH=CH$_2$)Cl$_2$]. High-resolution MS: calc. for $C_{32}H_{26}Si_2Cl_4$, 608.0303; found, 608.0313.

‡ *Crystal data*: for **2**: $C_{32}H_{26}Si_2Cl_4$, M_r = 608.51, monoclinic, $P2_1/n$, a = 6.8402(3), b = 20.6247(9), c = 21.2353(10) Å, β= 92.484(2)°, V = 2993.0(2) Å^3, Z = 4, D_c = 1.350 Mg m^{-3}, F(000) = 1256, λ = 0.71073 Å, T = 133(2) K, crystal size 0.35 × 0.25 × 0.03 mm. Intensity data were collected by the ϕ-scan method (1.38 < θ < 26.01°) on a Siemens P4 diffractometer equipped with a CCD area detector. From a total of 11579 measured data, 4952 were independent (R_{int} = 0.0377). The structure was solved by direct methods and refined by the full-matrix least-squares method on F^2 using the SHELXTL+ program. $R(F_o)$ = 0.0516, $wR(F^2$, all) = 0.1215, S = 1.204 for 4949 data and 343 variables.

For **3**: $C_{36}H_{25}SiCl$, M_r = 521.10, monoclinic, $P2_1/n$, a = 9.1677(3), b = 16.5631(4), c = 18.6634(6) Å, β= 101.333(2)°, V = 2778.70(14) Å^3, Z = 4, D_c = 1.246 Mg m^{-3}, F(000) = 1088, λ = 0.71073 Å, T = 133(2) K, crystal size 0.20 × 0.20 × 0.20 mm. Data were collected by the ϕ-scan method (2.54 < θ < 29.17°) on a Siemens P4 diffractometer equipped with a CCD area detector. From a total of 13288 measured data, 6555 were independent (R_{int} = 0.0204). The structure was solved by direct methods and refined by the full-matrix least-squares method on F^2 using the SHELXTL+ program. $R(F_o)$ = 0.0394, $wR(F^2$, all) = 0.1059, S = 1.022 for 6555 data and 343 variables.

CCDC 182/1574. See http://www.rsc.org/suppdata/cc/b0/b000585l/for crystallographic files in .cif format.

§ *Synthesis* of **3**: the method described for **2** was followed, using $PhC{\equiv}CSiCl_3$ (5.1 g, 25 mmol). **3** was crystallized from diethyl ether as yellow crystals (4.9 g, 76%) at −20 °C, mp187–188 °C. Selected data; ^{1}H NMR (300.133 MHz, $CDCl_3$), δ = 6.82–6.89 and 7.00–7.54 (br m, 25H, Ph); ^{13}C{H} NMR [75.403 MHz, $CDCl_3$ (δ = 77.00)], δ 155.84, 137.56, 136.57, 133.90, 132.48, 129.83, 129.54, 129.39, 128.32, 128.06, 127.71, 127.02, 126.66, 121.37, 109.63, 85.42; ^{29}Si NMR (71.548 MHz, $CDCl_3$), δ −17.15; Anal. Calc. for $C_{36}H_{25}SiCl$: C, 82.97; H, 4.84. Found: C, 82.28; H, 4.99%. MS(EI): *m/z* (%): 520 (6) [M$^+$]. High-resolution MS: calc. for $C_{36}H_{25}SiCl$, 520.1414; found, 520.1390.

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