

Preliminary communication

Synthesis, solid-state structure, and reduction
of 1,1-dichloro-2,3,4,5-tetramethylsilole [☆]

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Abstract

The previously unknown 1,1-dichloro-2,3,4,5-tetramethyl-1-silacyclopenta-2,4-diene (**3**) was prepared in a three-step synthesis starting from zirconocene dichloride, 2-butyne, and n-butyllithium via bis(cyclopentadienyl)-2,3,4,5-tetramethyl-1-zirconacyclopenta-2,4-diene (**1**) and 1,4-diiodo-1,2,3,4-tetramethylbuta-1,3-diene (**2**).

3 was characterized by NMR spectroscopy and single-crystal X-ray diffraction. Reaction of the new silole **3** with 4 equivalents of lithium in THF gives the corresponding dianion **4**. ¹H-, ¹³C-, and ²⁹Si-NMR chemical shifts of **4** compared with **3** indicate some aromatic character for the ionic species. Trapping of **4** with Me₃SiCl gives 1,1-bis(trimethylsilyl)-2,3,4,5-tetramethylsilole (**5**) in quantitative yield.

Keywords: Silicon; Zirconium; Lithium; Silole; Crystal structure; Dianion

We are studying the reactions of mono- and dichlorosiloles with alkali metals with the objective of determining the structures of the potentially aromatic silole anions and their NMR spectroscopic properties in solution and in the solid state. Only two 1,1-dihalogenosiloles have been reported so far ¹: 1,1-dichloro-2,3,4,5-tetraphenyl-1-silacyclopentadiene [3–5] and 1,1-dibromo-2,3,4,5-tetramethyl-1-silacyclopentadiene [6]. The former is readily available from 1,4-dilithio-1,2,3,4-tetraphenylbuta-1,3-diene and SiCl₄, since the lithium compound can be easily made directly from diphenylacetylene and lithium. The 1,1-dibromo-2,3,4,5-tetramethylsilole was synthesized by Fagan et al. [6] from 1,1-bis(η⁵-cyclopentadienyl)-2,3,4,5-tetramethyl-1-zirconacyclopenta-2,4-diene (**1**) and SiBr₄, but the yield was very low and the product could not be isolated pure. Fagan and coworkers also tried to obtain the 1,1-dichloro-2,3,4,5-tetramethylsilole (**3**) by a similar transmetallation reaction using silicon tetrachloride instead of the tetrabromide, but SiCl₄ displayed no reactivity towards **1** [6].

We were successful in preparing **3** (Scheme 1) by converting the zirconacycle **1** first into (1Z,3Z)-1,4-diiodo-1,2,3,4-tetramethylbuta-1,3-diene (**2**) as recently described by Ashe et al. [7]. Further reaction of **2** with n-butyllithium gave the corresponding dilithio compound as solution in ether/hexane. The silole **3** was obtained by either cooling the solution of the dilithio compound with a dry ice/acetone bath and dropping it into a cooled solution of SiCl₄ in ether, or better, by freezing the solution with liquid nitrogen and adding an excess of SiCl₄ ².

² Procedure. **1** and **2** were prepared as described in the literature [6,7]. To a solution of **2** (6.4 g, 17.7 mmol) in 130 ml of diethylether was added, with stirring, 22.5 ml 1.57 M n-butyllithium (35.3 mmol) in hexane at –78 °C over a period of 1 h. After the addition was completed the solution was stirred at –78 °C for 2 h. Then the mixture was allowed to come to room temperature and stirred at 25 °C for 15 min, after which time it was frozen with a bath of liquid nitrogen. 10 ml SiCl₄ (14.8 g, 87.1 mmol) was added via a syringe at one time. The mixture was kept at –196 °C for 5 min before the cooling bath was removed. The solution was slowly warmed up to room temperature and stirred for 15 h. Then the volatiles were removed under reduced pressure. The residue was extracted with small portions of hexane (a total of 50 ml) and filtered. The solution was concentrated to a volume of approximately 10 ml and cooled to –78 °C for 12 h, after which time colorless crystals of **3** (2.6 g, 71%) were obtained. M.p. 35 °C. NMR data, see Table 1.

[☆] Dedicated to Professor Hideki Sakurai, a pioneer of organosilicon chemistry.

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¹ Several chlorosubstituted silafluorenes were prepared by certain gas-phase reactions of dichlorosilylene [1] or other methods [2] and considered as substituted siloles.

The crystal structure of **3** was determined by X-ray diffraction and is depicted in Fig. 1³. The molecule is highly symmetric with an almost planar five-membered ring. The Si–C bond lengths are shorter than the same bond distances in the two known structures of uncomplexed siloles (1,1-dimethyl-2,5-diphenylsilole [10], 1,1-dimethyl-2,3,4,5-tetraphenylsilole [11]). Previously it was mentioned that the significantly increased C–C (single) bond length in the silole ring of 1,1-dimethyl-2,3,4,5-tetraphenylsilole compared with 1,1-dimethyl-2,5-diphenylsilole might be due to steric interactions of the bulky phenyl rings on the β carbons [12]. But we found a value of 1.516(6) Å for this distance in **3**. Since this is similar to that found for the tetraphenyl compound, it appears that the bond lengthening may result from electronic as well as steric effects.

Stirring or sonication of **3** with 4 equivalents of lithium in THF produced a red solution. Treatment of this solution with an excess of Me₃SiCl gave 1,1-bis(tri-

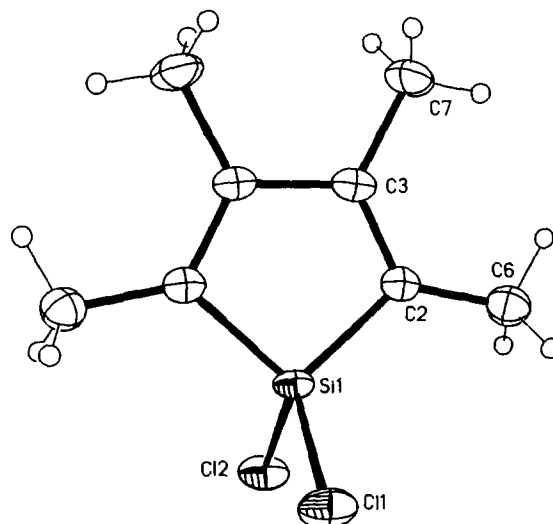
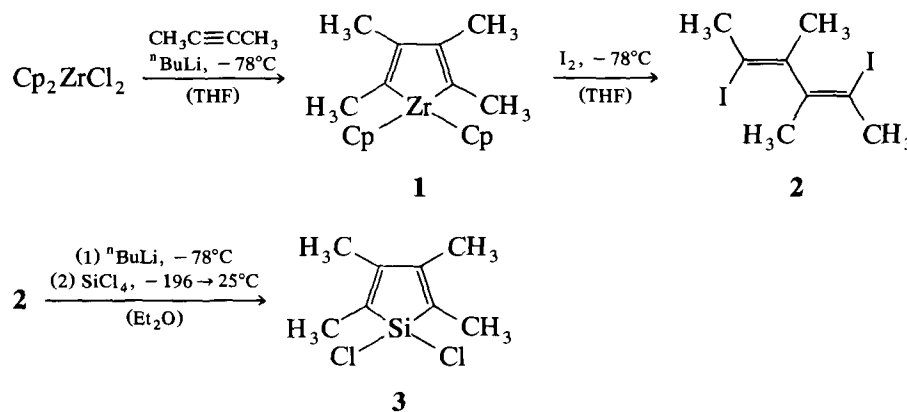
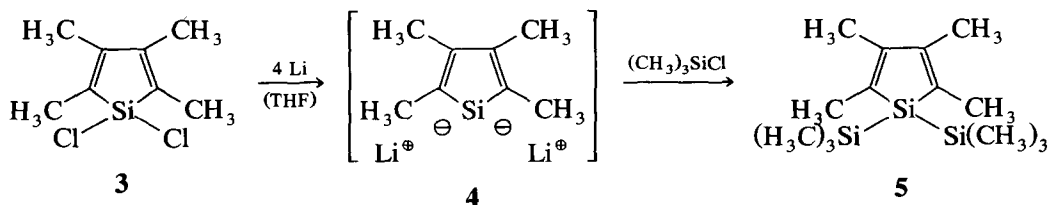


Fig. 1. The molecular structure of Me₄C₄SiCl₂ (**3**). Selected bond distances (Å) and angles (deg.): Cl(1)–Si(1) 2.0518(13), Cl(2)–Si(1) 2.0520(13), Si(1)–C(2) 1.834(3), Si(1)–C(2)#1 1.834(3), C(2)–C(3) 1.356(4), C(2)–C(6) 1.483(5), C(3)–C(7) 1.501(4), C(3)–C(3)#1 1.515(6), C(2)–Si(1)–C(2)#1 96.9(2), C(2)–Si(1)–Cl(2) 113.85(8), C(2)#1–Si(1)–Cl(2) 113.86(8), C(2)–Si(1)–Cl(1) 113.97(9), C(2)#1–Si(1)–Cl(1) 113.97(9), Cl(2)–Si(1)–Cl(1) 104.61(6), C(3)–C(2)–C(6) 127.7(3), C(3)–C(2)–Si(1) 104.6(3), C(6)–C(2)–Si(1) 127.7(2), C(2)–C(3)–C(7) 124.3(3), C(2)–C(3)–C(3)#1 117.0(2), C(7)–C(3)–C(3)#1 118.7(2). Selected torsion angles (deg.): C(2)#1–Si(1)–C(2)–C(3) 0.50(0.22), Cl(2)–Si(1)–C(2)–C(3) 120.46(0.15), Cl(1)–Si(1)–C(2)–C(3) –119.64(0.15), C(2)#1–Si(1)–C(2)–C(6) 179.91(0.18), Cl(2)–Si(1)–C(2)–C(6) –60.13(0.26), Cl(1)–Si(1)–C(2)–C(6) 59.77(0.25), C(6)–C(2)–C(3)–C(7) 0.25(0.41), Si(1)–C(2)–C(3)–C(7) 179.66(0.20), C(6)–C(2)–C(3)–C(3)#1 –179.78(0.21), Si(1)–C(2)–C(3)–C(3)#1 –0.38(0.17). Symmetry transformations used to generate equivalent atoms: #1 $x, -y + (1/2), z$.

³ Crystal data for **3**: C₈H₁₂Cl₂Si, $M = 207.17$, orthorhombic, space group $Pnma$, $a = 9.4866(9)$ Å, $b = 9.4367(8)$ Å, $c = 11.7544(12)$ Å, $V = 1052.3(2)$ Å³, $Z = 4$, $D_c = 1.308$ g cm⁻³, $m = 6.149$ mm⁻¹, $F(000) = 432$, crystal size $0.50 \times 0.35 \times 0.30$ mm³. The X-ray diffraction experiment was carried out with a Siemens P4 diffractometer ($T = 113(2)$ K, graphite-monochromated Cu K α radiation, $\lambda = 1.54178$ Å, ω scan technique, $\theta \leq 57.00^\circ$, 769 independent reflections, $R_{int} = 0.0686$). The structure was solved using the SHELXS-86 program [8] and refined using the SHELXL-93 program which refines on F^2 values [9] ($R(F) = 0.0406$, $\omega R(F^2) = 0.1041$). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.



Scheme 1.



Scheme 2.

Table 1
NMR data (δ , ppm) for **3** and **4**

NMR		3	4
^{29}Si		8.14	29.77
^{13}C	ring C	152.25	138.97
	ring C	124.10	119.97
	CH_3	14.06	18.91
	CH_3	11.12	14.27
^1H	CH_3	1.90	2.34
	CH_3	1.81	2.22

(^1H : 300.13 MHz, ^{13}C (H): 125.76 MHz, ^{29}Si (inversed gated decoupling): 99.36 MHz; **3** in THF- d_8 with TMS as internal standard; **4** in THF- d_8 with TMS as external standard).

methylsilyl)-2,3,4,5-tetramethyl-1-silacyclopenta-2,4-diene (**5**) in quantitative yield ⁴ (Scheme 2).

NMR studies of the red solution show the presence of only one compound to which we assign the structure **4**. The ^{29}Si resonance in **4** is shifted downfield compared with **3** (Table 1), consistent with delocalization of the negative charges into the silole ring [13], since usually a conversion of organochlorosilanes to silyl anions leads to upfield shifts. Additionally, we observed upfield shifts for the ring carbons in the ^{13}C spectrum and downfield shifts for the methyl carbons and hydro-

⁴ Procedure. Stirring a solution of **3** (1.00 g, 4.83 mmol) in 25 ml of THF with Li (135.2 mg, 19.32 mmol) for 24 h gave a dark red-brown solution. The solution was filtered and added to a solution of Me_3SiCl (2.15 g, 19.82 mmol) in 5 ml of THF. This mixture was stirred at room temperature for 4 h. After removing the volatiles under reduced pressure, the residue was extracted with small portions of hexane (a total of 30 ml), and each portion was filtered and combined. Removal of the solvent left **5** (1.36 g, 100%) as a colorless oil. Selected data for **5**: ^1H NMR (250.13 MHz, C_6D_6 /external TMS): δ 2.00 (s, 6H, CH_3), 1.84 (s, 6H, CH_3), 0.19 (s, 18H, SiCH_3). ^{13}C (H)NMR (125.76 MHz, C_6D_6 /external TMS): δ 149.79 (ring C), 130.98 (ring C), 15.44 (CH_3), 14.71 (CH_3), 0.25 (SiCH_3). ^{29}Si NMR (inversed gated decoupling, 99.36 MHz, C_6D_6 /external TMS): δ -14.81 (SiCH_3), -34.22 (ring Si). MS(EI): m/z 282 (51, M^+), 209 (100, $\text{M}^+ - \text{SiMe}_3$). MS exact mass: calcd. for $\text{C}_{14}\text{H}_{30}\text{Si}_3$ 282.1655, found 282.1644.

gens in the ^{13}C and the ^1H spectrum, respectively (Table 1). All these findings suggest that **4** is a species with some aromatic character.

We are currently expanding the method used for the synthesis of **3** to the preparation of other new siloles and characterizing **4** and several other silole anions in the solid state.

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