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A New Spirocyclic System: Synthesis of a Silaspirotropylidene

Honglae Sohn, Justin Merritt, Douglas R. Powell, and Robert West*

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53705

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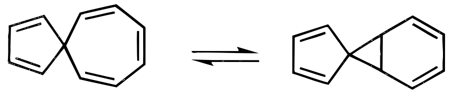
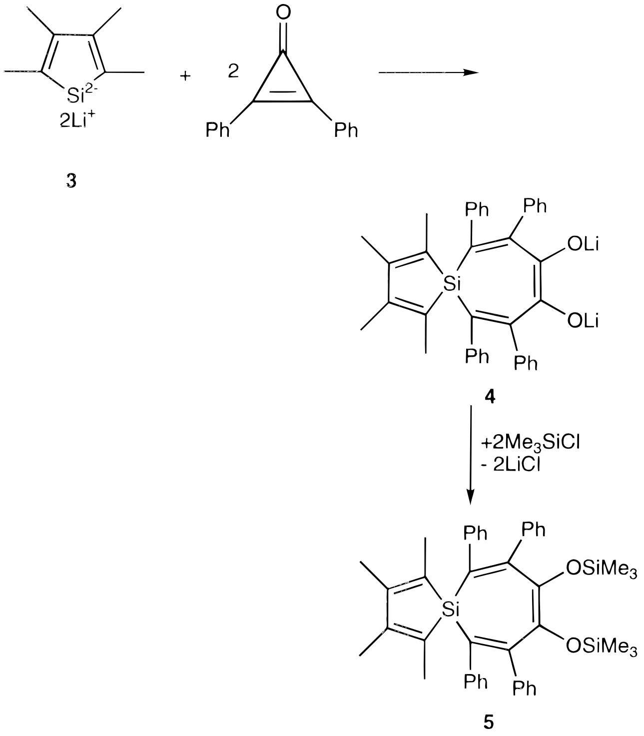
Summary: A silaspirotropylidene, ***5****, has been obtained from the reaction of the lithium salt of tetramethylsilole dianion (**3**) with 2 equiv of diphenylcyclopropenone, followed by quenching with Me_3SiCl. The X-ray crystal structure of* ***5*** *indicates that the five-membered ring is planar and the silepine ring adopts a boat conformation.*

Several spirotropylidenes having the ring structure shown as **1** were synthesized by Dürr and co-workers almost 30 years ago.[1,2] Although these compounds possess 10 π-electrons and so might be regarded as homoaromatic,[3] they are actually rather unstable. NMR studies showed that all of the compounds of type **1** were in equilibrium with their spironorcaradiene valence isomers (**2**).[2,4] To our knowledge, no heteroatom-containing rings of type **1** or **2** have appeared in the literature.

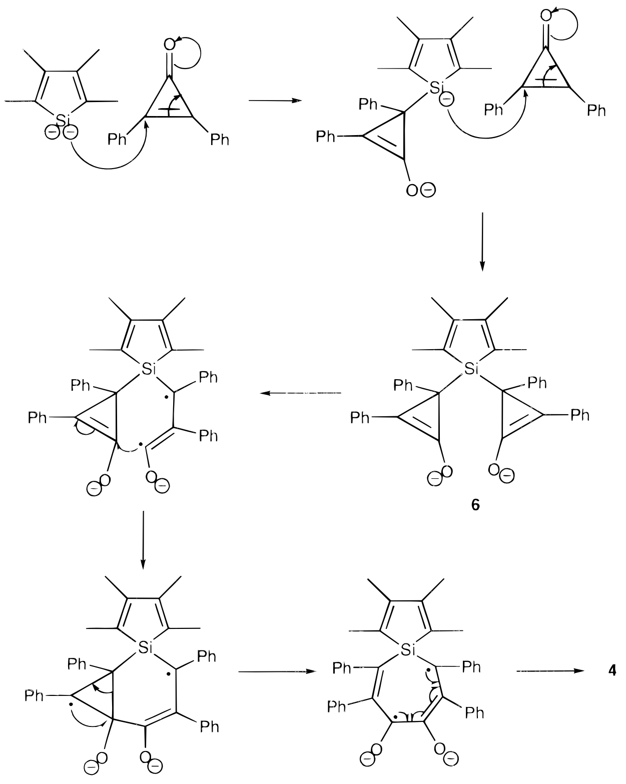


1 **2**

Scheme 1



Scheme 2



Recent studies have made anions and dianions of siloles readily available.[5,6] We report here the reaction of the tetramethylsilole dianion of **3** with 2 equiv of diphenylcyclopropenone to give the silaspirotropylidenyl dianion of **4**. Subsequent quenching with Me_3SiCl produced yellow crystals of **5** in 90% yield (Scheme 1). Even when less than 1 equiv of diphenylcyclopropenone was used, **4** was obtained as the sole product. It is difficult to rationalize the surprising formation of **4**, but one possible mechanism is suggested in Scheme 2. Two succesive nucleophilic reactions of the negatively charged silicon of the silole dianion of **3** on the ring carbon of the cyclopropenone molecules could take place to give **6**. Ring opening to a diradical followed by ring closure

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* To whom correspondence should be addressed. Fax: (608) 262-6143. E-mail: west@chem.wisc.edu.

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and rearrangement might then take place to produce the seven-membered ring.

The X-ray crystal structure of **5**,[8] shown in Figure 1, indicates that **5** has the tropylidene structure (rather than a norcaradiene structure) in the solid state, with five localized double bonds. The C_4Si ring is nearly planar and perpendicular to the CSiC plane of the C_7Si ring, which has a boat conformation. The CSiC angles in the C_4Si ring and C_7Si ring are 93.65(7) and 100.86(6)°, respectively. The nonbonding distance C10···C15 is 290.4(2) pm.

The ^1H, and ^{13}C, and ^{29}Si NMR spectra of **5** in solution are consistent with the silatropylidene structure found in the crystal structure. No evidence was seen for isomerization to a silanorcaradiene isomer. The lack of such isomerization may reflect the high strain energy of the silacyclopropane ring[9] which would be present in the silanorcaradiene. The ^1H and ^{13}C NMR spectra of **5** do show broad signals for the methyl groups of the silole moiety, perhaps due to fluxionality of the seven-membered ring. This point is under investigation.

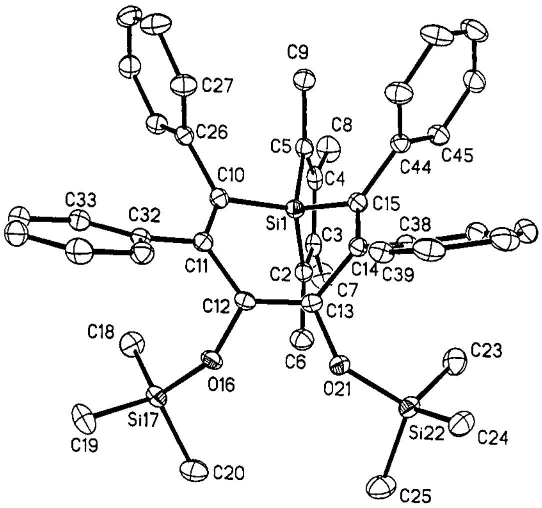

Figure 1. Thermal ellipsoid diagram of the structure of **5**. Selected bond lengths (pm): Si1−C2, 187.2(2); Si1−C5, 187.8(2); Si1−C10, 188.8(2); Si1−C15, 188.4(2); C2−C3, 136.5(2); C3−C4, 151.3(2); C4−C5, 135.0(2); C10−C11, 136.6(2); C11−C12, 148.5(2); C12−C13, 135.6(2); C13−C14, 149.4(2); C14−C15, 136.5(2). Intramolecular angles (deg): C2−Si1−C5, 93.65(7); C10−Si1−C15, 100.68(6); Si1−C2−C3, 105.84(11); Si1−C5−C4, 106.92(11); C2−C3−C4, 117.41(14); C3−C4−C5, 116.10(13); Si1−C10−C11, 119.86(11); Si1−C15−C14, 118.74(11); C10−C11−C12, 121.50(13); C11−C12−C13, 126.85(13); C12−C13−C14, 127.84(13); C13−C14−C15, 122.13(13).

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Supporting Information Available: Tables giving details of the X-ray structure determinations, atomic coordinates and isotropic thermal parameters, bond lengths and bond angles, anisotropic displacement parameters, and hydrogen atom coordinates for $\mathbf{3}\cdot C_4H_8O$ and ^1H, ^{13}C, and ^{29}Si NMR spectra for $\mathbf{3}\cdot C_4H_8O$ (14 pages). Ordering information is given on any current masthead page.

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(7) (a) Preparation of **5**: A solution of tetramethylsilole dianion, **3**, was prepared as described in the literature.[5] A solution of diphenylcyyclopropenone (1.99 g, 9.66 mmol) in 20 mL of THF was slowly added to a dark red solution of 4.8 mmol of **3** in 50 mL of THF at −78 °C and stirred for 3 h. The solution was warmed to room temperature and stirred for an additional 3 h to give a red solution of **4**. A solution of Me_3SiCl (1.22 mL, 9.6 mmol) in 5 mL of THF was added to the solution of **4** at −78 °C, and the mixture was stirred at room temperature for 4 h. After the volatiles were removed, the residue was crystallized from THF at −25 °C, yielding 3.3 g of **5** (90%). (b) Characterization of **5**: yellow transparent crystals; ^1H NMR (300.133 MHz, $CDCl_3$) δ 6.60−7.24 (br m, 20H, Ph), 1.75−2.04 (br m, 12H, Me), −0.13 (s, 18H, $SiMe_3$); $^{13}C\{^1H\}$ NMR (75.403 MHz, $CDCl_3$) δ 152.66, 149.47, 145.07, 144.10, 143.26, 142.40, 139.02, 131.35, 128.65, 128.55, 127.55, 127.50, 126.78, 125.05, 15.35, 14.69, 14.05, 12.08, 1.40; ^{29}Si NMR (99.36 MHz, C_6D_6) δ 18.27 ($-OSiMe_3$), −18.37 (ring Si); MS (EI) m/z (%) 694 (2) [M^+], 621 (2) [$M^+ - SiMe_3$], 548 (6) [$M^+ - 2SiMe_3$]; high-resolution MS m/z calcd for $C_{44}H_{50}O_2Si_3$ 694.3119, found 694.3082.

(8) X-ray structure analysis of $\mathbf{5}\cdot C_4H_8O$: $C_{44}H_{50}O_2Si_3\cdot C_4H_8O$, M_r = 767.21, triclinic, $P\bar{1}$, a = 12.5835(2) Å, b = 14.3312(2) Å, c = 14.3733(2) Å, α = 74.0972(6)°, β = 69.4803(5)°, γ = 64.6198(6)°, V = 2169.69(5) Å^3, $Z = 2$, ρ_{calcd} = 1.174 Mg m^{-3}, $F(000) = 824$, λ = 0.710 73 Å, T = 133(2) K. A yellow transparent single crystal (crystal size 0.44 × 0.36 × 0.10 mm) was mounted under a coating of Paratone-N. Intensity data were collected by the ψ-scan method (1.53° < θ < 28.32°) on a Siemens P4 diffractometer equipped with a CCD area detector. From a total of 21 503 measured data, 9367 were independent ($R_{int} = 0.0217$). The structure was solved by direct methods and refined by a full-matrix least-squares method on F^2 using the SHELXTL+ program. $R(F_o) = 0.0408$, $R_w(F^2(\text{all})) = 0.1018$, $S = 1.055$ for 9364 data and 516 variables. The thermal ellipsoids were drawn at the 50% probability level.

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