Silacyclopentadienylidene, the first silylene incorporated in a silole ring

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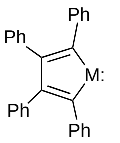
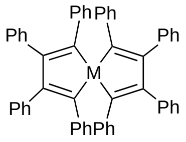
Silacyclopentadienylidene 1 was generated photochemically using 7-silanorbornadiene and norbornene precursors and observed in frozen hydrocarbon matrices at 77 K.

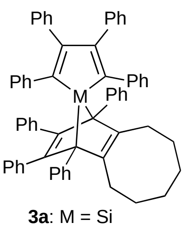
In recent years, renewed attention has been focused on the chemistry of silacyclopentadiene (silole) and germacyclopentadiene (germole).[1] Mono- and di-anions of siloles and germoles have been studied extensively by NMR spectroscopy and X-ray crystallography mainly from the viewpoints of aromaticity of π-electron systems involving the heavier group 14 elements.[2] Meanwhile, sila- and germa-cyclopentadienyl transition metal complexes have been synthesized and reported to constitute delocalized structures.[3] However, there has been no example of siloles containing a dicoordinate silicon, namely a silylene unit. Here we report the formation and some reactions of silacyclopentadienylidene **1**, providing a novel reactive species in the silole chemistry. Moreover, *ab initio* SCF/MP2 calculations on the parent silacyclopentadienylidene were carried out to gain an insight into this interesting ring system.



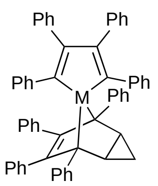
1: M = Si
7: M = Ge



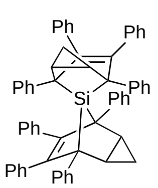
2: M = Si
8: M = Ge



3a: M = Si
9a: M = Ge



3b: M = Si
9b: M = Ge

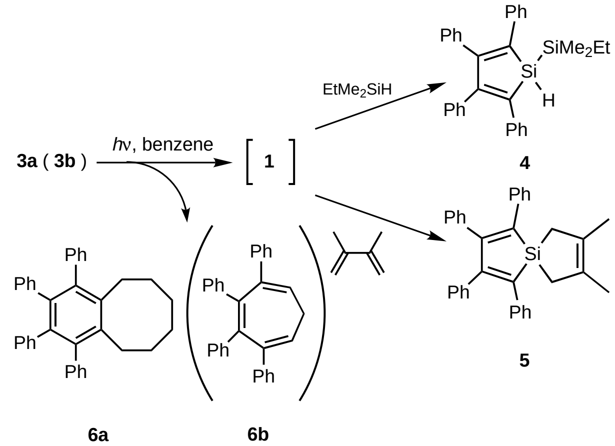


3c

Table 1 Photolyses of **3a** and **3b**

Precursor	Silylene trap	Products and yields (%)
3a	Ethyldimethylsilane	**4** (43)
3a	2,3-Dimethylbuta-1,3-diene	**5** (46)
3b	Ethyldimethylsilane	**4** (44)
3b	2,3-Dimethylbuta-1,3-diene	**5** (40)

Although trisilane functionality has been widely used to generate a central silicon atom as a free silylene both in photochemical and in thermal reactions,[4] it has been recognized that bis(trimethylsilyl)siloles undergo only intramolecular silyl migration without affording the corresponding silacyclopentadienylidenes.[5] Therefore, alternative synthetic routes were explored and we have found that cycloreversion of 7-silanorbornadiene[1] and 7-silanorbornene[6] derivatives is advantageous to generate 1-silacyclopenta-2,4-dien-1-ylidene **1**. Thus, 1,1′-spirobisilole **2**[7] was subjected to the Diels–Alder reaction with cyclooctyne in benzene at 50 °C to give the corresponding adduct **3a** as a pale yellow solid in 91% yield. On the other hand, when **2** was heated under bubbling cyclopropene, **3b** was obtained in 38% yield along with **3c** (30% yield) as a byproduct. The validity of **3a** and **3b** as silylene precursors was indicated as follows. Photolysis of **3a** in the presence of EtMe$_2$SiH or 2,3-dimethylbuta-1,3-diene, well-known efficient silylene traps,[4] using a medium pressure mercury-arc lamp led to facile formation of the corresponding siloles **4** and **5** in 46 and 43% yields, respectively, accompanied by **6a** as depicted in Scheme 1. In the absence of the silylene traps, however, no identifiable product was obtained besides **6a**. Although it has been established that silylenes with bulky substituents dimerize to produce stable disilenes,[8] none of the products resulting from dimerization of **1** were detected even after the treatment of the photolysate with methanol. Similar results were produced in the case of **3b** as shown in Table 1.

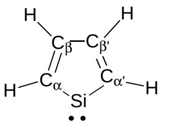


Scheme 1

When benzene solutions of 1,1′-spirobigermole **8**[9] were heated in the presence of cyclooctyne or cyclopropene at 50 °C, the expected 7-germanorbornadiene **9a** or **9b** was not detected, but **6a** or **6b** was formed as the sole product, respectively. Since 7-germanorbornadiene derivatives have been documented to undergo cycloreversion to give germylenes at a much lower temperature than the corresponding silicon analogues,[10] **9a** and **9b** should not be stable enough to be isolated, but should extrude germacyclopenta-2,4-dien-1-ylidene **7** instantly.

Table 2 Calculated bond distances (Å), angles (°) and total energy (au) for C_4H_4Si **10**

	10a (singlet)	**10b** (triplet)
$Si{-}C_\alpha$	1.930	1.857
$C_\alpha{-}C_\beta$	1.333	1.346
$C_\beta{-}C_{\beta'}$	1.503	1.478
$C_\alpha{-}Si{-}C_{\alpha'}$	87.3	94.5
$Si{-}C_\alpha{-}C_\beta$	110.5	105.2
$C_\alpha{-}C_\beta{-}C_{\beta'}$	115.8	117.6
Total energy	−442.756 270	−442.735 196



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Upon irradiation of **3a** in a 3-methylpentane (3-MP) matrix at 77 K with a medium pressure mercury-arc lamp, a weak absorption band appeared at *ca.* 500 nm, which grew more intense on continuing irradiation and disappeared completely after annealing the matrix. When $EtMe_2SiH$ or 2,3-dimethylbuta-1,3-diene was present in the matrix, the corresponding adduct **4** or **5** was detected by MS and NMR analyses respectively,† which confirmed that **1** was generated in the matrix. No absorption band attributable to disilene derived from **1** was detected from the photolysis and after annealing the matrices. It has been well documented that the presence of Lewis base in matrices causes a substantial hypsochromic shift of a silylene absorption band by forming a silylene–Lewis base complex.[11] Upon irradiating **3a** in a pure 2-MeTHF (2-methyltetrahydrofuran) matrix at 77 K, neither the absorption band at 500 nm nor the new absorption band attributable to **1**–2-MeTHF complex was observed. When a similar photolysis of **3a** was carried out in a 3-MP–2-MeTHF (95:5) matrix, the absorption band at 500 nm was also observed with less intensity than in the pure 3-MP matrix, but disappeared upon annealing without developing any additional absorption band. From these results at this moment, we tentatively assign the absorption band at 500 nm to the n–p transition of the silacyclopentadienylidene **1**. The detection of a **1**–2-MeTHF complex and a disilene derived from **1**, which would have absorptions at shorter wavelength than the parent silylene **1**, if any,[11] might be difficult because of the intense absorption due to the starting material **3a**.‡ Taking into account the results of the photolysis at room temperature, in which no dimerized product was detected, it should be also considered that the reaction of **1** may take some different mechanistic courses such as polymerization *via* intermolecular silylene addition to C−C double bonds of another silole ring.

To gain insight into the characteristics of **1**, we performed *ab initio* calculations on unsubstituted silacyclopentadienylidene **10** at the HF and the MP2 levels with the MIDI-4+ polarization function basis set.[12] The optimized structures of C_4H_4Si with C_{2v} symmetry for the lowest singlet and triplet states were obtained by the RHF and the ROHF theories, respectively. Singlet state **10a** was calculated to be more stable than triplet state **10b** by 13.2 kcal mol^{-1}.§ The geometrical parameters are shown in Table 2, which suggests that the geometry of **10a** is closely related to those of the known siloles $Me_2SiC_4H_2Ph_2$,[13] $Me_2SiC_4Ph_4$,[14] $Cl_2SiC_4Me_4$[2m] and $Cl_2SiC_4Ph_4$[2o] determined experimentally by X-ray analyses. Ordinary bond alternation in the butadiene moiety is indicated by the large differences between C−C endocyclic bond distances leading to a low Julg's parameter A[2n] of 0.252 for **10a** and 0.549 for **10b**, respectively. Assuming that sp^2-hybridized **10a** has an in-plane lone pair on silicon, **10a** can be described as an anti-aromatic 4π electron ring system.¶

Acknowledgements

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† Selected spectral data, **3a**: *m/z* (EI, 70 eV) (%) 848 (100); (C_6D_6) $\delta_H(C_6D_6)$ 7.36–6.33 (m, 40H) and 1.96–1.62 (m, 12H); $\delta_{Si}(CDCl_3)$ 40.44. **3b**: *m/z* (EI, 70 eV) (%) 781 (98), 780 (100), 416 (46) and 398 (38); $\delta_H(C_6D_6)$ 7.73 (d, 2H, $J = 7.8$ Hz), 7.58 (d, 4H, $J = 7.8$ Hz), 7.20–6.60 (m, 34H), 2.03 (dd, 2H, $J = 7.2$ and 3.6 Hz), 1.43 (td, 1H, $J = 5.4$ and 3.6 Hz) and 0.87 (td, 1H, $J = 7.2$ and 5.4 Hz); $\delta_{Si}(CDCl_3)$ 30.66. **3c**: *m/z* (EI, 70 eV) (%) 821 (23), 820 (15), 425 (100), 398 (17) and 246 (25); $\delta_H(CDCl_3)$ 7.68 (d, 4H, $J = 7.5$ Hz), 7.26 (t, 2H, $J = 7.5$ Hz), 7.15 (t, 2H, $J = 7.5$ Hz), 7.00–6.94 (m, 8H), 6.93–6.88 (m, 8H), 6.82 (d, 4H, $J = 7.5$ Hz), 6.78–6.70 (m, 8H), 6.39 (d, 8H, $J = 7.5$ Hz), 1.72 (td, 2H, $J = 7.2$ and 3.8 Hz), 1.61 (td, 2H, $J = 7.2$ and 3.8 Hz) and 0.80 (m, 4H); $\delta_{Si}(CDCl_3)$ 33.48. **4**: *m/z* (EI, 70 eV) (%) 472 (34), 443 (14), 365 (17) and 105 (100); $\delta_H(CDCl_3)$ 7.15–6.80 (m, 20H), 5.00 (s, 1H), 0.92 (t, 3H, $J = 8.0$ Hz), 0.57 (q, 2H, $J = 8.0$ Hz) and 0.04 (s, 6H). **5**: *m/z* (EI, 70 eV) (%) 466 (100), 373 (6), 307 (6), 205 (13), 178 (12) and 129 (21); $\delta_H(CDCl_3)$ 7.10–6.98 (m, 12H), 6.89 (d, 4H, $J = 7.0$ Hz), 6.82 (d, 4H, $J = 7.0$ Hz), 1.83 (s, 4H) and 1.762 (s, 6H).

‡ Lack of solubility of **3b** prevents low temperature matrix isolation of **1** using **3b** as a precursor.

§ 1 cal = 4.184 J.

¶ 1,3,2-Diazasilol-2-ylidene, a stable silylene, has been claimed to be stabilized by contribution of 6π-aromaticity (see ref. 15).

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