The First Stable 1-Silaallene

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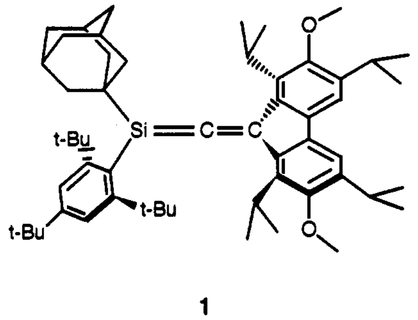
A growing variety of compounds containing stable double bonds to silicon have been reported in recent years.[1] Disilenes ($R_2Si{=}SiR_2$),[2] silenes ($R_2Si{=}CR_2$),[3] silanimines ($R_2Si{=}NR$),[4] phosphasilenes ($R_2Si{=}PR$),[5] arasilenes ($R_2Si{=}AsR$),[6] silanethiones ($R_2Si{=}S$),[7] and base-free transition-metal silylene complexes ($R_2Si{=}ML_n$)[8] have all been isolated and characterized at ambient temperature under inert atmospheres. Silanediimines ($RN{=}Si{=}NR$)[9] have also been isolated at low temperature in argon or 3-methylpentane matrices.[10] 1-Silaallenes ($R_2Si{=}C{=}CR_2$) have been proposed as transient reactive intermediates,[11] but have to data eluded isolation. We now report the first stable 1-silaallene (**1**), which, for both steric and electronic reasons, is also by far the least reactive multiply-bonded-silicon compound yet prepared.

The synthesis of **1** results from the dehalogenative intramolecular carbometalation–elimination[12] (DICE) reaction shown in Scheme I. Treatment of a diastereomeric mixture of 2-bromo-2′-[(fluorosilyl)ethynyl]biphenyls **2** with 2 equiv of *tert*-butyllithium in toluene at 0 °C gave, after warming to room temperature, **1** as the only silicon-containing product observable by ^{29}Si NMR. Removal of salts by filtration and solvent by evaporation gave **1** in nearly quantitative yield as an orange amorphous solid which could be dissolved in refluxing ethanol and handled in the presence of air and water under nonacidic conditions for many days without observable transformation, in striking contrast to all other known multiply-bonded-silicon compounds.[1-11]



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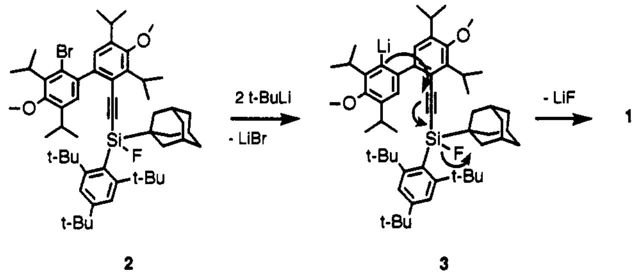
Scheme I



1 was characterized by ^{1}H, ^{13}C, and ^{29}Si NMR, IR and UV spectroscopy,[13] and X-ray crystallography.[14] A chemical shift of $\delta = +48.4$ ppm was found by ^{29}Si NMR, and a shift of $\delta = +225.7$ ppm in the ^{13}C NMR was assigned to the carbon atom involved in the double bond to silicon. The X-ray structure is shown in Figure 1. The silicon–carbon double-bond length (Si–C1) is 1.704 Å, and the sp–sp^2 carbon–carbon double-bond length (C1–C2) is 1.324 Å. The Si–C1–C2 bond angle is 173.5°. The C31–Si–C49 plane makes an angle of 178.9° with the Si–C1 double bond and an angle of 180.8° with the C1–C2 double bond (such that the C21–Si–C49 plane and the C1–C2 double bond are *trans*-bent about the Si–C1 double bond).[15] The least-squares plane containing the atoms C4, C15, C28, and C13 is canted above the Si=C double bond at an angle of 48.1°, probably in an effort to minimize steric repulsion between the proximal fluorenyl isopropyl groups and the aryl *tert*-butyl groups.

The Si=C ^{29}Si and ^{13}C chemical shifts of **1** closely match those of Brook's stable silene, $(Me_3Si)_2Si{=}C(1\text{-adamantyl})OSiMe_3$ (**4**)[3a] ($\delta = +41.4$ and $+214.2$ ppm for ^{29}Si and ^{13}C, respectively), which bears an electron-donating oxygen substituent on carbon. In comparison, the corresponding ^{29}Si and ^{13}C chemical shifts of Wiberg's stable silene $(Me)_2Si{=}C(SiMe_3)SiMe(tBu)_2$ (**5**)[3b] (+144.2 and +77.2 ppm, respectively) are strongly deshielded at silicon and shielded at carbon, suggesting a much more polar double bond which is highly electron-deficient at silicon and electron-rich at carbon. However, the Si=C double-bond lengths of **1** and **5** (1.702 Å) agree closely, while the double

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(13) The ^{13}C and ^{1}H NMR are consistent with the structure shown, but have not been fully assigned. IR shows strong absorptions at 800 (s), 1030 (br), 1090 (br), 1260 (s), 1400 (s), 1450 (br), 1600 (br), and 2960 (br) cm^{-1}. UV absorptions are observed at 267, 276 (max), 297, 318, and 334 nm, with tailing up to 540 nm.

(14) Crystals were grown by diffusion of acetonitrile into a solution of **1** in THF. The crystal structure includes one badly disordered THF molecule. X-ray data was collected on a Siemens P3f diffractometer with Cu Kα radiation. The structure was solved by use of the SHELXTL PLUS program. Crystal data for **1** + THF ($C_{60}H_{88}O_3Si$, fw 885.4): orthorhombic, space group $Pna2_1$, $a = 25.507(3)$ Å, $b = 13.794(3)$ Å, $c = 15.185(7)$ Å, $V = 142.092(0)$ Å^3, $d_{calcd} = 1.235$ g cm^{-1}, $Z = 4$, final $R = 0.0453$, $R_w = 0.0605$ for 4547 reflections.

(15) For a prediction of *trans*-bending in 1-silaallenes, see: Trinquier, G.; Malrieu, J. P. *J. Am. Chem. Soc.* **1987**, *109*, 5303.

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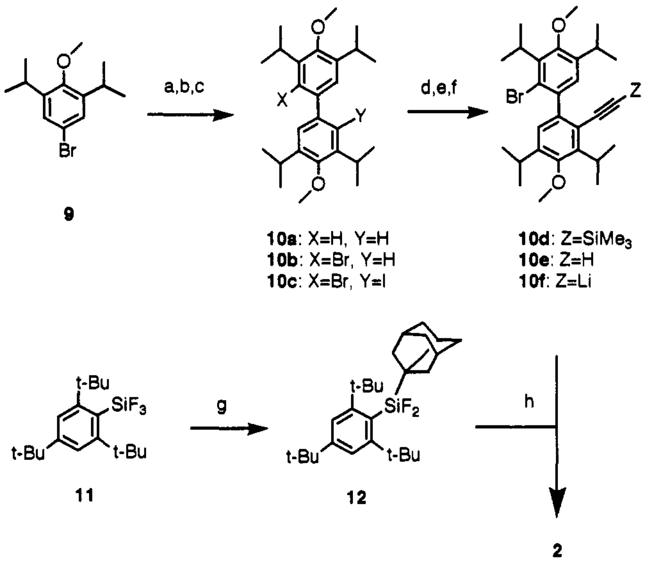
Scheme II[a]



[a] Conditions: (a) Mg, THF, then $CoCl_2$ (73%); (b) 0.9 equiv of Br_2, CH_2Cl_2, room temperature, dark, (81%); (c) I_2, $C_6H_5I(O_2CCF_3)_2$, $CHCl_3$, room temperature, dark (94%); (d) 5% $Pd(PPh_3)_2Cl_2$, 3% CuI, Et_2NH, $C_6H_5CH_3$, TMSA, 40 °C (70%); (e) KOH, EtOH, reflux (96%); (f) LDA, THF, 0 °C; (g) 1-adamantyllithium, Et_2O (42%); (h) THF, reflux (78%).

bond in **4** (1.764 Å) exhibits significant elongation. A corroboration of these trends is found in previously reported *ab initio* calculations made on the parent systems.[16] We conclude that 1-silaallenes exhibit a partial "reversed polarity" of the Si=C double bond, comparable in effect to that of an electron-donating oxygen substituent on carbon, without bond elongation. We note that a "reversed polarity" of the Si=C π-bond is believed to be "the most important single electronic factor that reduces the reactivity of silenes".[16a]

The synthesis of **2** is outlined in Scheme II. Two equivalents of aryl bromide **9** were coupled to give biphenyl **10a**. Sequential bromination and iodination[17] yielded biphenyls **10b** and **10c**, respectively. Alkynylation[18] with (trimethylsilyl)acetylene and catalytic Pd(0) occurred exclusively at the iodinated position to give **10d**. Cleavage of the trimethylsilyl group afforded **10e**, which was easily metalated with lithium diisopropylamide to give **10f**. Compound **12**, prepared by the addition of 1-adamantyllithium[19] to trifluorosilane **11**[20] in diethyl ether at −30 °C, underwent smooth nucleophilic addition of **10f** in refluxing THF to give **2**. Attempts are now under way to extend this methodology to the synthesis of new 1-silaallenes bearing a variety of different substituents on silicon and carbon.

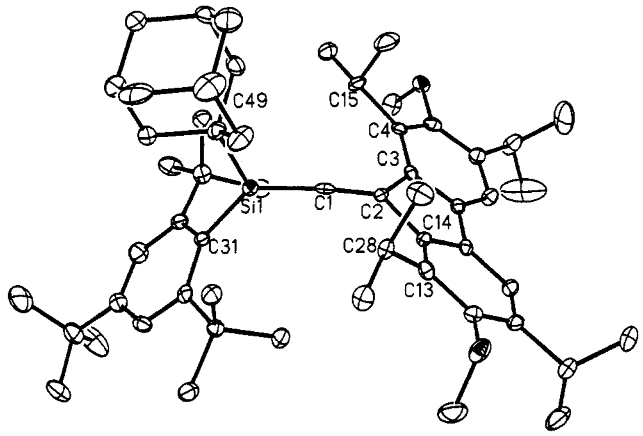


Figure 1. Thermal ellipsoid diagram of **1** with hydrogen atoms omitted for clarity. Ellipsoids are at the 50% probability level. Selected bond distances (Å): Si–C1, 1.704(4); Si–C31, 1.920(4); Si–C49, 1.903(4); C1–C2, 1.324(5). Selected bond angles (deg): Si–C1–C2, 173.5(3); C31–Si–C49, 121.6(2); C1–Si–C31, 120.9(2); C1–Si–C49, 117.5(2); C1–C2–C3, 127.2(3); C1–C2–C14, 127.0(3); C3–C2–C14, 104.0(3).

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Supplementary Material Available: Preparative procedures and spectroscopic data for **1**, **2**, and **9–12** and a structure determination summary and tables listing the atomic coordinates, bond lengths, bond angles, anisotropic displacement coefficients, and H-atom coordinates and isotropic displacement coefficients for **1** (19 pages); observed and calculated structure factors for **1** (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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