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Halophilic Reactions of a Stable Silylene with Chloro and Bromocarbons

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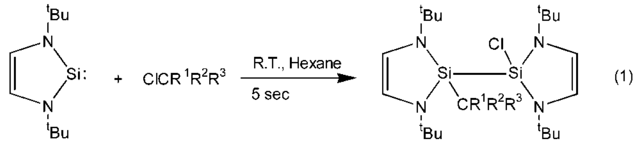
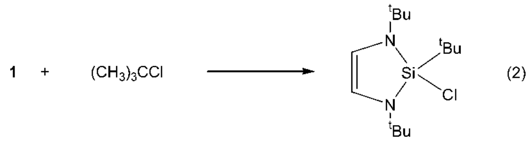
A large variety of reactions have been described for stable silylenes in the seven years since they were first isolated.[1−3] Until recently, however, reactions of stable silylenes with halocarbons had not been attempted. We report here some surprising reactions of the stable silylene, *N*,*N*′-di-*tert*-butyl-1,3-diaza-2-silacyclopent-4-en-2-ylidene, **1**, with chloro and bromocarbons leading to disilanes.

When trichloromethane was added to a colorless solution of **1** in hexane, the immediate formation of the yellow 2:1 adduct, **2b**, was quantitative (by NMR). *The disilane was the exclusive product even in the presence of a 100-fold excess of $CHCl_3$.*



1

2a, $R^1=R^2=R^3=Cl$
2b, $R^1=R^2=Cl$, $R^3 = H$
2c, $R^1=Cl$, $R^2=R^3=Cl$
2d, $R^1=Ph$, $R^2=R^3=H$

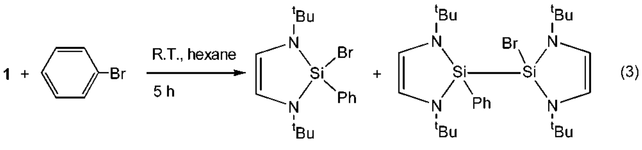


3

The crystal structure of **2b** is shown in Figure 1.[4] Viewing the molecule down the Si(1)−Si(2) bond reveals that the chlorine atom on Si(1) and the dichloromethyl group on Si(2) are in a perfect gauche conformation. Also, the planes of both rings are tilted approximately 39° from the Si(1)−Si(2) vector.

Similar 2:1 adducts, **2a**, **2c**, and **2d**, were formed quantitatively when **1** was treated with CCl_4, CH_2Cl_2, or benzyl chloride (eq 1).[5,6] However, when **1** was allowed to react with *tert*-butyl chloride, the exclusive product is that of silylene insertion into the C−Cl bond (eq 2).

Some insight into a possible mechanistic pathway for these reactions was gained from the reaction of **1** with bromobenzene. In this case, the reaction proceeded much more slowly, over 5 h, and was monitored by NMR to completion. Both products, the 1:1(**4**) and 2:1(**5**) adducts, were obtained (eq 3).



4 **5**

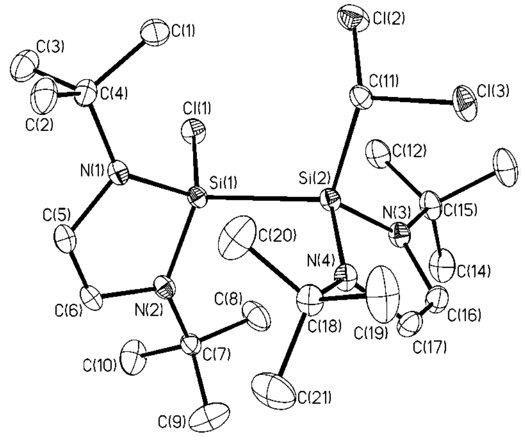


Figure 1. Molecular Structure of **2b**. Thermal ellipsoids are shown at the 30% probability level. Selected bond distances (Å) and angles (deg): Si(1)−Si(2), 2.4228(11); Si(1)−N(1), 1.731(2); Si(1)−N(2), 1.725(2); Si(2)−N(3), 1.737(3); Si(2)−N(4), 1.742(2); Si(1)−Cl(1), 2.1032(11); Si(2)−C(11), 1.937(3); N(1)−Si(1)−N(2), 93.64(12); Cl(1)−Si(1)−Si(2), 110.12(4); N(1)−Si(1)−Si(2), 119.83; N(2)−Si(1)−Si(2), 111.27(9).

The proportion of products, **4** and **5**, depended on the ratio of the reactants. Increasing the amount of bromobenzene in the reaction increased the amount of the 1:1 adduct. Eventually, adding 4 equiv of bromobenzene to **1** led to exclusive formation of **4**. However, when **4** was treated with excess silylene **1**, no reaction took place to form disilane **5**, even upon extended heating at 70 °C for 24 h. Thus, in this case and probably in others, the disilane product does not arise from reaction of the 1:1 adduct with additional silylene.

We suggest that the results shown arise from a halophilic attack of the silylene nucleophile on the halogen atom of the reactants. This could lead the formation of a weak acid−base complex, **6**, containing a hypervalent halogen atom (Scheme 1). The silylene silicon atom in **6** becomes somewhat electron-deficient, and might accept coordination of a lone pair from a second silylene molecule into its vacant p-orbital leading to **7**. A simple 1,3-shift in **7** would result in disilane formation.

In the case of the formation of the 1:1 adduct with *tert*-butyl chloride, we deduce that the intermediate 1:1 complex is too hindered to permit the approach of a second silylene, so that the 1,3-shift is not possible. Further indication that the products are sterically determined was obtained from the reaction of **1** with 1-bromonaphthalene and 9-bromofluorene, which both yield only a 1:1 insertion product similar to **3**. These products could arise from the 1:1 complex by a 1,2-shift, or by single-electron transfer and radical combination. Silylene **1** reacts with methyl iodide[7] and iodobenzene to give 1:1 insertion products analogous to **3**, perhaps by a radical mechanism.

While this communication was under review, Kira and coworkers reported the reaction of a marginally stable dialkysilylene

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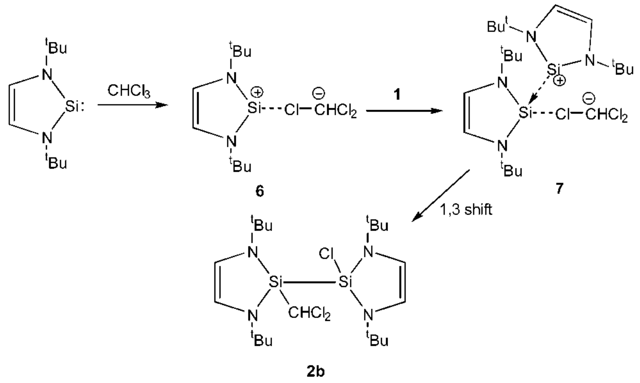
Scheme 1. Proposed Halophilic Reaction of Silylene with Trichloromethane



with two chlorocarbons.[8] These reactions take a completely different course from those described here and were rationalized in terms of a more conventional Lewis acid−base complex intermediate, with chlorine donating an electron pair to silicon. This is reasonable, since their dialkysilylene should be a much stronger Lewis acid than **3**. Similarly, the reactions of transient alkyl- and arylsilylenes with halocarbons are thought to proceed through conventional acid−base complexation.[9,10]

Halophilic reactions, to our knowledge, have not been reported for silylenes, either stable or transient. However, they are well established for phosphines,[11] which are isolobal with silylenes. Examples of halophilic pathways have also been reported for arsenic,[12] sulfur,[13] oxygen,[14] and nitrogen[15] nucleophiles. Reactions of silylenes with other halocarbons are under investigation.

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Supporting Information Available: Tables of crystallographic data, atomic coordinates, thermal parameters, and bond lengths and angles for **2b** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(4) Crystal data for **2b**: orthorhombic, space group: $P2_12_12_1$, color: yellow, a = 10.1224(11) Å, b = 15.9526(18) Å, c = 16.8701(18) Å, V = 2724.2(5) Å^3, Z = 4, T = 173(2) K, R value of 0.038 for 4754 unique reflections, Goodness of Fit: 1.05.
(5) Accurate elemental analyses and consistent NMR spectra (^{1}H, ^{13}C, ^{29}Si) were obtained for all the compounds reported here and will be published elsewhere.
(6) In a typical experiment, a solution of **1** (0.200 g, 1.02 mmol) in 10 mL of hexane was added to $CHCl_3$ (0.122 g, 1.02 mmol) at room temperature. The mixture immediately turned bright yellow. The solvent was removed in vacuo, and the resulting saturated solution was refrigerated to grow crystals. Large rectangular yellow crystals were isolated. Yield: 0.248 g (95%). ^{1}H NMR (300 MHz, 298 K, C_6D_6) δ 5.79 (s, 2H, CH), 5.78 (s, 2H, CH), 5.38 (s, 1H, $CHCl_2$), 1.36 (s, 18H, $C(CH_3)_3$), 1.30, (s, 18H, $C(CH_3)_3$); ^{13}C NMR (75 MHz, 298 K, C_6D_6) δ 115.3 (s, **C**H), 114.5 (s, **C**H), 63.9 (s, **C**HCl$_2$), 52.9 (s, **C**(CH$_3$)$_3$), 52.3 (s, **C**(CH$_3$)$_3$), 31.5 (s, C(**C**H$_3$)$_3$), 31.0 (s, C(**C**H$_3$)$_3$); ^{29}Si NMR (99 MHz, 298 K, C_6D_6) δ −24.2, −33.9. Anal. (Chemisar Laboratories Inc., Guelph, ON) Calcd (found) for $C_{21}H_{41}Cl_3N_4Si_2$: C, 49.25 (48.75); H, 8.41 (8.07); N, 10.94 (10.86).
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