Bis-silenes

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The Synthesis and Isolation of a Metal-Substituted Bis-silene**

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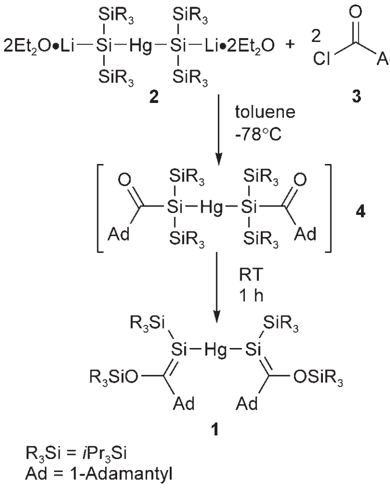
Dedicated to Professor Robert West

Since the isolation of the first stable silene ($R_2Si=CR_2$)[1] and disilene ($R_2Si=SiR_2$)[2], the field of multiply bonded silicon compounds has developed rapidly and led to the isolation of many novel compounds.[3] Yet this field of chemistry is still in its infancy. In contrast to metal-substituted olefins, which are common reagents,[4] only few metal-substituted unsaturated silicon compounds have been isolated and characterized,[5] and found to have interesting reactivity.[6] Few silene–metal complexes, in which the transition metal is coordinated to a $Si=C$ bond have been reported.[7] Metal-substituted silenes are still unknown.[8]

In this paper we report the synthesis, isolation, and X-ray molecular structure of the first metal-substituted silene **1**, which was obtained by a Brook-type thermal rearrangement (Scheme 1). Compound **1** is also the first isolated and fully characterized bis-silene, a compound with two $Si=C$ bonds.

Bis-silene **1** was synthesized in a single-pot reaction by mixing bis(lithiosilyl)mercury **2**[9] with two equivalents of 1-adamantoyl chloride (**3**) in toluene at −78 °C. After the reaction mixture was warmed to room temperature and stirred for 1 h, **1** was obtained as the only silicon-containing product. The reaction probably proceeds by means of a spontaneous Brook rearrangement of short-lived bis-acylsilane **4** (Scheme 1). Although **4** was not directly observed, we believe that **4** is an intermediate in the reaction, based on the isolation of an analogous compound, **7** (see below). Bis-silene **1** was isolated (80 % yield) by crystallization from hexane at room temperature, and its molecular structure was determined by X-ray crystallography (Figure 1).[10]



Scheme 1. Synthesis of **1**.

The average $Si=C$ (1.764(15) Å) and $Si-Si$ (2.369(6) Å) bond lengths in **1** are similar to the analogous bond lengths in Brook's silene ($[(Me_3Si)_2Si=C(OSiMe_3)Ad]$ (**5**) ($Si=C$ 1.76 Å, $Si-Si$ 2.34 Å).[1] This shows that replacement of a R_3Si group by mercury has a small effect on the $C=Si$ bond length. The Si1−Hg1 and Si4−Hg1 bond lengths in **1** (2.417(4) Å and 2.477(4) Å, respectively) are similar to that in $[(Me_3Si)_3Si]_2Hg$ (2.47 Å).[11] The double-bonded Si1 and Si4 atoms in **1** are essentially planar (sum of bond angles around Si is 359.9°), suggesting sp^2 hybridization. The Si-Hg-Si bond angle is 177.4(1)°. The two $C=Si$ bonds are nearly *gauche* to each other ($\measuredangle$ C1-Si1-Si4-Si30 = −67.9°) to minimize steric repulsions between the large substituents. Overall **1** has the structure expected for a bis-silene in which two essentially noninteracting $C=Si$ bonds are linked through a mercury atom.

The ^{13}C NMR chemical shift of the $C=Si$ units (C1 and C30) appears at 225 ppm, slightly downfield from the corresponding signal of **5** (214 ppm[1]). On the other hand, the ^{29}Si chemical shift of the double-bonded Si1 and Si4 atoms appears at 107.6 ppm and is strongly deshielded compared with the analogous signal of **5** (41.4 ppm[1]). The difference (Δ) between $\delta(^{29}Si)$ in **5** and in **1**, of −66.3 ppm, is similar in magnitude to the $\Delta\delta(^{29}Si)$ value of $(Me_3Si)_4Si$ and $[(Me_3Si)_3Si]_2Hg$,[12] (−80 ppm), indicating that Hg substitution has a similar effect on $\delta(^{29}Si)$ regardless of whether the Si atom is single or double bonded.

Bis-silene **1** exhibits surprising high stability towards water, methanol, and acetone. Thus, **1** can be kept in these

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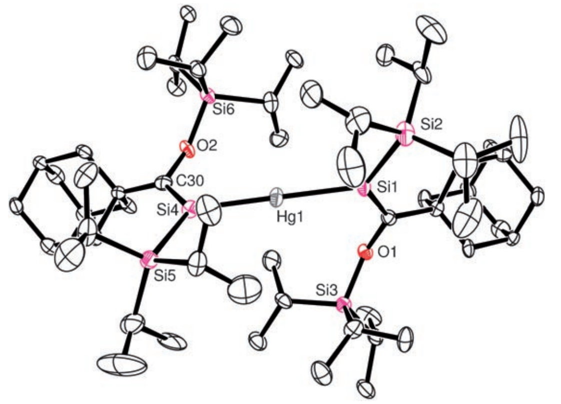
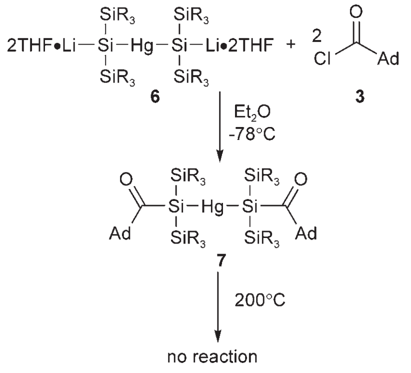


Figure 1. Molecular structure of **1** in the crystal (ORTEP drawing). The hydrogen atoms have been omitted for clarity, and the thermal ellipsoids are set at the 20% probability level. Selected bond lengths [Å], bond angles [°], and bond dihedral angles [°]: Si1–C1 1.770(15), Si4–C30 1.758(15), Si1–Hg1 2.477(4), Si4–Hg1 2.417(4), Si1–Si2 2.337(6), Si4–Si5 2.401(6), C1–O1 1.384(16), C1–C2 1.553(19), C30–O2 1.390(17), C30–C31 1.521(2); Si4-Hg1-Si1 177.39(14), C1-Si1-Si2 127.3(5), C1-Si1-Hg1 113.0(5), Si2-Si1-Hg1 119.5(5), C30-Si4-Si5 124.5(6), C30-Si4-Hg1 116.6(5), Si5-Si4-Hg1 118.5(2), O1-C1-C2 110.3(11), O1-C1-Si1 121.5(10), C2-C1-Si1 128.0(10), O2-C30-C31 109.5(12), O2-C30-Si4 118.6(11), C31-C30-Si4 131.7(11); C1-Si1-Hg-Si4 −29.2(4), O2-C30-Si4-Hg1 −15.5(6), Si5-Si4-C30-O2 166.2(7), Si6-O2-C30-Si4 −65.4(9), O1-C1-Si1-Hg1 −17.3(8), Si2-Si1-C1-O1 165.9(6), Si3-O1-C1-Si1 −65.0(13), C1-Si1-Si4-C30 −67.9(4).

solvents for weeks without any noticeable transformation! However, when exposed to air, **1** reacts instantaneously yielding a complex mixture of products. The low reactivity of **1** probably results from effective steric protection of the Si=C bonds by the surrounding large iPr$_3$Si and adamantyl groups, although electronic effect from the mercury substituent may also contribute. The low reactivity of sterically protected Si=C bond was reported previously, e.g., for (RR′)Si=C=CR″$_2$ (R = 1-adamantyl, R′ = 2,4,6-tri-*tert*-butylphenyl, CR″$_2$ = 1,3,6,8-tetraisopropyl-2,7-dimethoxy-9*H*-fluorenyl).[13]

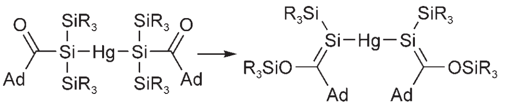
In an attempt to prepare more-reactive analogues of **1**, we synthesized bis(lithiosilyl)mercury **6**, an analogue of **2** carrying smaller tBuMe$_2$Si substituents. The coupling reaction of **6** with 1-adamantoyl chloride (**3**) yields the corresponding mercury bis-acylsilane **7** (Scheme 2), which was isolated (87% yield) by crystallization from hexane at room temperature, and its structure was determined by X-ray crystallography.[14]



$R_3Si = t$BuMe$_2$Si

Scheme 2. Synthesis of **7**.

Disappointingly, heating **7** to 200 °C does not lead to rearrangement to the desired bis-silene, in contrast to **4** which rearranges spontaneously at room temperature. A possible explanation for the dramatic difference in the reactivity of **4** and **7** is the higher steric congestion in **4** ($R_3Si = i$Pr$_3$Si) relative to that in **7** ($R_3Si = t$BuMe$_2$Si). Consequently rearrangement of **4** to the corresponding silene is favored, but the less crowded **7** does not rearrange. DFT calculations at the B3LYP/6-31G* + ZPVE level of theory[15] support this explanation. Thus, the rearrangement of **4** ($R_3Si = i$Pr$_3$Si) to the bis-silene **1** is endothermic by 1.5 kcal mol^{-1}. On the other hand, the rearrangement of **7** to **7a** is endothermic by 11.3 kcal mol^{-1}. With the smaller Me$_3$Si substituent the rearrangement **8** to **8a** is even more endothermic (15.8 kcal mol^{-1}) [Eq. (1)].

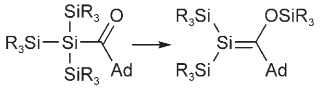


(1)

4: $R_3Si = i$Pr$_3$Si
7: $R_3Si = t$BuMe$_2$Si
8: R_3Si = Me$_3$Si

1: $R_3Si = i$Pr$_3$Si
7a: $R_3Si = t$BuMe$_2$Si
8a: R_3Si = Me$_3$Si

A similar steric enhancing effect is calculated also for the classic Brook rearrangement. The rearrangement of acylsilane **9** (R_3Si = Me$_3$Si) to silene **9a** is endothermic by 10.8 kcal mol^{-1}, decreasing to 5.2 kcal mol^{-1} for $R_3Si = t$BuMe$_2$Si substituents (**10**→**10a**) [Eq. (2)]. This insight is important for the synthesis of new silenes by means of the Brook rearrangement.



(2)

9: R_3Si = Me$_3$Si
10: $R_3Si = t$BuMe$_2$Si

9a: R_3Si = Me$_3$Si
10a: $R_3Si = t$BuMe$_2$Si

In conclusion, we have synthesized and characterized by X-ray crystallography the first bis-silene, a compound with two Si=C bonds, as well as the first metal-substituted silene, and have demonstrated that the size of the substituents in the precursor acylsilane controls the occurrence of its thermal rearrangement to a silene. We continue to explore the chemistry of **1** including its photochemistry (silyl mercurials are photosensitive yielding silyl radicals[16]) which may lead to novel silicon compounds and reactive intermediates.

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[10] Crystallographic data for **1**: $C_{58}H_{116}HgO_2Si_6$, $M_r = 1214.64$, monoclinic, space group $C2/c$, $a = 39.649(8)$, $b = 12.719(2)$, $c = 27.119(5)$ Å, $\beta = 109.37(3)°$, $V = 12\,902(4)$ Å^3, $Z = 8$, Nonius Kappa CCD, $\mathrm{Mo}_{K\alpha}$ radiation (0.71073 Å), 220 K, $2\Theta_{max} = 25°$, $R = 0.0994$ ($I > 2\sigma I$), $wR2 = 0.2585$ ($I > 2\sigma I$), $Rw = 0.1709$ (all data), GOF = 0.847. CCDC 645497 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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