The Solution Structure of $(Me_3Si)_3CSiBr$—An Ab Initio/NMR Study

Michaela Flock* and Alk Dransfeld[a]

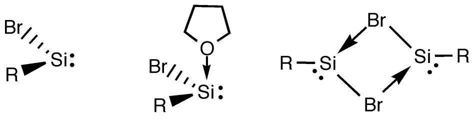
Abstract: The first halosilylene stable in solution was investigated by ab initio/NMR calculations (IGLO SOS-DFPT PW91/B2//B3LYP/6-31 + G(d)). The $\delta\,^{29}Si_{calc}$ of $(Me_3Si)_3CSiBr$ (446 ppm) does not agree with the measured NMR signal at 106 ppm assigned to the free halosilylene. From the possible silylene complexes in the reaction solution, two structures agree with the observed NMR signal: the $(Me_3Si)_3CSiBr_2$ anion ($\delta\,^{29}Si_{calc} = 124$ ppm) and the unsolvated and solvated complex of the anion with two Li^+ ($\delta\,^{29}Si_{calc} = 117$ and estimated 134 ppm). Additionally the $\delta\,^{29}Si_{calc}$ of alkylsilylenes, R-Si-X, ranging from 200 to 900 ppm are presented to guide NMR identification in future silylene synthesis.

Keywords: density functional calculations · NMR spectroscopy · silicon · silylene

Introduction

Recently, Lee et al.[1] reported the first halosilylene stable in a solution of tetrahydrofuran. The formation and reaction of the intermediate, expected to be bromo-[tris(trimethylsilyl)]-methylsilylene, were monitored by gas chromatography and NMR analysis. The ^{29}Si NMR spectrum shows a resonance signal at $\delta = 106$ ppm, assigned to the intermediate. Identification of the compound as silylene was based on the products of trapping reactions and its chemical shift being in the range of previously characterized diaminosilylenes (78,[2] 97,[3] 117 ppm[4]). The huge difference between the 106 ppm and the $\delta\,^{29}Si$ of the stable dialkylsilylene[5] (567 ppm) was ignored. But is the ^{29}Si chemical shift range of R-Si-Br really similar to that of aminosilylenes including the known diaminosilylenes?

Early computations on silylenes show that their adducts with donor molecules are kinetically stable (e.g. $SiH_2{-}OH_2$ has an association energy of 13.3 kcal mol^{-1} and a rearrangement barrier of 38.3 kcal mol^{-1}).[6] Experimental evidence was provided by Takeda et al.,[7] who reported a silylene–isocyanide complex stable in solution and undergoing the characteristic trapping reactions. Accordingly, Lee et al. suggested additional structures for their intermediate: a silylene–THF adduct and a head-to-head silylene dimer (Scheme 1).

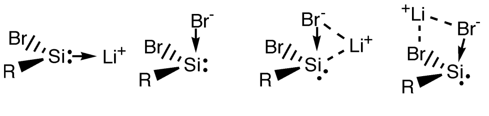


1 2 3

Scheme 1. Proposed intermediate structures **1**, **2**, and **3** with R = H (**a**), CH_3 (**b**), $C(SiH_3)_3$ (**c**), and $C(SiMe_3)_3$ (**d**).

However, it is well known that silylenes can react both as electrophiles and nucleophiles.[8–10] Therefore silylene–Li^+ complexes also have to be considered to be stable. Thus another question arises: is the halosilylene in the reaction solution with THF, Li^+, and Br^- a free silylene or is it part of some kind of complex?

This paper addresses the open questions by presenting results of ab initio NMR calculations for the R-Si-Br silylene **1** with R = H (**a**), H_3C (**b**), $(H_3Si)_3C$ (**c**), and $(Me_3Si)_3C$ (**d**). The largest substituent **d** is also used in Lee's[1] synthetic work. Furthermore, complexes of **1** with Li^+ and/or Br^- (structures **2** to **6** in Schemes 1 and 2) were investigated in this context.



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Scheme 2. Possible intermediate structures **4**, **5**, and **6**.

Additionally, NMR chemical shift ranges for a comprehensive set of alkylsilylenes are reported to provide practical estimates and to assist the identification of silylenes by ^{29}Si NMR analyses.

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Computational Methods

Geometry optimizations were carried out at the hybrid density functional B3LYP/6-31 + G(d) level of theory[11] without symmetry constraint. Magnetic shieldings were computed by using the IGLO SOS-DFPT[12] Perdew–Wang91 (PW91)/B2 approach.[13] The reported chemical shifts, $\delta\,^{29}Si_{calc}$, were calculated from these shieldings with the reference molecule TMS (Me_4Si, $\delta\,^{29}Si_{exp} \equiv 0$) with the magnetic shielding $\sigma = 366.1$ ppm at the same theoretical level. The quality of the NMR calculations was evaluated by comparison with ^{29}Si chemical shifts measured for a set of silylenes, bromosilanes, and dibromosilanes (see Figure 1 and Supporting Information). For this set, the deviation between observed and calculated $\delta\,^{29}Si$, characterized by the root-mean-square error (rmse), is 32 ppm. A downfield deviation of up to + 40 ppm occurs for the dibromosilanes H_2SiBr_2 and Me_2SiBr_2.

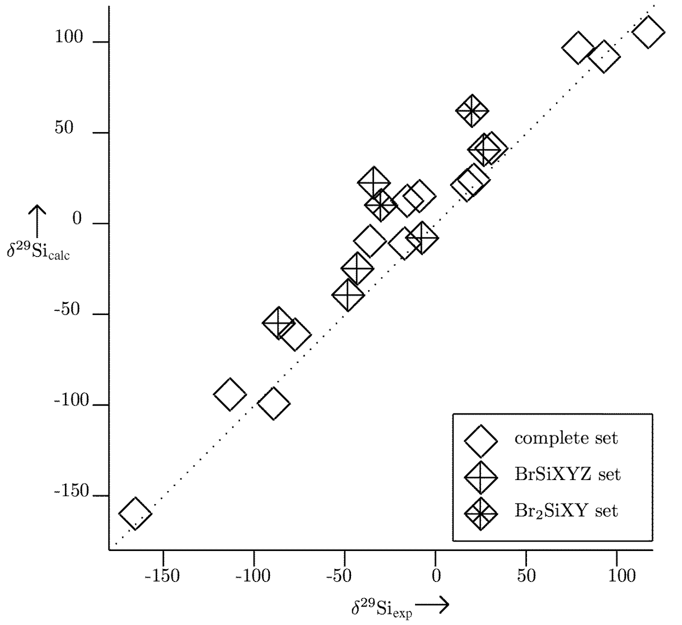

Figure 1. Plot of the measured versus the IGLO-PW91/B2//B3LYP/6–31 + G(d) calculated ^{29}Si chemical shifts of silylenes, bromosilanes, and dibromosilanes. The values of $\delta\,^{29}Si_{exp} = 567.4$ and $\delta\,^{29}Si_{calc} = 578.6$, related to a dialkylsilylene,[5] are not displayed but are included in the statistics (rmse = 32 ppm).

One of the reasons for this large error is the neglect of relativistic effects.[14] Including one-electron spin–orbit-coupling effects diminishes the chemical shift of HSiBr by 4 ppm ($\delta\,^{29}Si_{corr} = 530$), of $HSiBr_2^-$ by 16 ppm ($\delta\,^{29}Si_{corr} = 83$), of H_2SiBr_2 by 57 ppm ($\delta\,^{29}Si_{corr} = -45.3$ vs. $\delta\,^{29}Si_{exp} = -30.36$[15]), and Me_2SiBr_2 by 55 ppm ($\delta\,^{29}Si_{corr} = 8.0$ vs. $\delta\,^{29}Si_{exp} = 19.9$[16]).[17] The two-electron spin–orbit-coupling effects are expected to reduce these corrections by 10 to 20 %.

Results and Discussion

Already the calculated shifts for the small silylenes H-Si-F ($\delta\,^{29}Si = 375.0$), H-Si-Cl ($\delta\,^{29}Si = 483.6$), H-Si-Br ($\delta\,^{29}Si = 525.5$), and H-Si-H ($\delta\,^{29}Si = 638.1$) point to much higher shift values. Generally, the $\delta\,^{29}Si$ values of free silylenes X-Si-R (X being H, CH_3, NH_2, OH, F, SiH_3, PH_2, SH, Cl, Br and R = H (**a**), CH_3 (**b**), $(H_3Si)_3C$ (**c**), and $(Me_3Si)_3C$ (**d**)) are calculated to be between 200 and 900 ppm (see Figure 2 and Supporting Information). The chemical shift ranges of F-Si-R, Cl-Si-R, and Br-Si-R follow the expected trend[18] of increasing chemical shifts with decreasing electronegativity of X. In most R-Si-X sets the substituents R have a similar effect on $\delta\,^{29}Si_{calc}$ (**a** and **b** at the low field end). Substituent **c**, $(H_3Si)_3C$, shows the strongest magnetic shielding effect (upfield shift) on the silylene Si. The depicted ranges partially overlap with the exception of the H_3Si-Si-R range, which shows the highest NMR chemical shifts (742 to 881 ppm). With the exception of the H_2N-Si-R and the HS-Si-R molecules, the sets in Figure 2 have 100 to 200 ppm wide ranges. An unusual substituent effect on $\delta\,^{29}Si_{calc}$ is observed in the H_2P-Si-R set: 438 ppm in H-Si-PH_2, 597 in Me-Si-PH_2, 515 in $(H_3Si)_3C$-Si-PH_2, and 597 in $(Me_3Si)_3C$-Si-PH_2. The cause is a considerable π conjugation between phosphorus and silicon (the Wiberg bond index of Si–P is 1.26) occurring only in the H-Si-PH_2 molecule. In symmetrically substituted silylenes, X-Si-X, the effects of the X groups add up, so that $\delta\,^{29}Si_{calc}$ is smaller in $Si(NH_2)_2$ (86 ppm) than in $(H_3Si)_3C$-Si-NH_2 and $\delta\,^{29}Si_{calc}$ is larger in $Si(SiH_3)_2$ (1125 ppm) than in H_3C-Si-SiH_3.

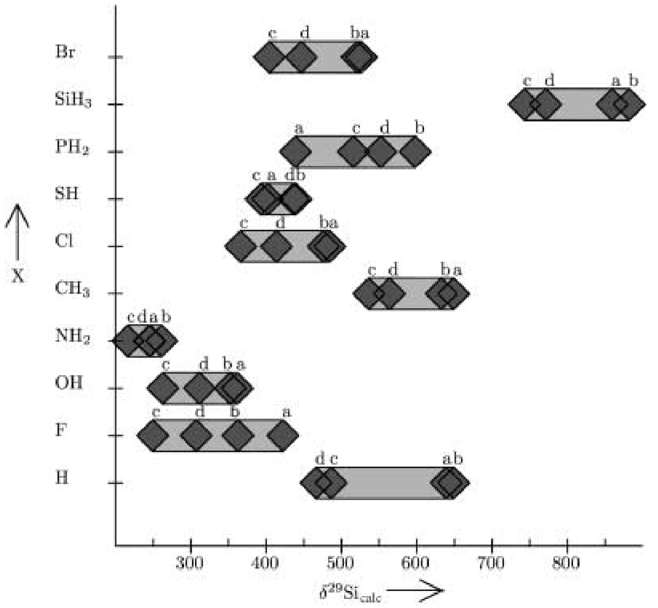

Figure 2. Calculated ^{29}Si chemical-shift ranges of the silylenes X-Si-R, with R = H (a), CH_3 (b), $(H_3Si)_3C$ (c), $(Me_3Si)_3C$ (d).

The ^{29}Si chemical shift of **1d** corresponding to the postulated free silylene is calculated to be 445 ppm. Therefore it cannot be associated with the intermediate ($\delta\,^{29}Si = 106$ ppm). Table 1 shows the substituent effects of R in R-Si-Br molecules on bond lengths, angles, and $\delta\,^{29}Si$. Remarkably, the shifts of **1b** and **1c** differ by 116 ppm; this shows that including the silyl groups as β substituents is crucial to

Table 1. Geometry parameters of the R-Si-Br molecules optimized at the B3LYP/6–31 + G(d) level and the IGLO PW91/B2 calculated $\delta\,^{29}Si$ for these geometries.

	Si-C	Si-Br	C-Si-Br	$\delta\,^{29}Si$[a]
1a	–	2.268	–	526
1b	1.913	2.286	98.5	520
1c	1.908	2.301	102.3	403
1d	1.907	2.328	105.6	446
Exp.				106

[a] Reference TMS, PW91/B2//B3LYP/6–31 + G(d), $\sigma\,^{29}Si = 366.1$ ppm.

obtaining reasonable predictions. Even the γ-substituent effect on δ^{29}Si is larger than the error of the method ($\delta^{29}Si_{calc}(\mathbf{1d}) - \delta^{29}Si_{calc}(\mathbf{1c}) = 42$ ppm).

Since the free silylene can be excluded, the question arises as to whether the observed $^{29}Si_{exp}$ stems from other structures, such as the silylene–solvent complex **2** or the cyclic dimer **3**.

Silylene–solvent interactions were tested for **1** with water, dimethyloxide, and the experimentally applied THF. Table 2 shows that the geometry of the silylene backbone is not substantially affected by the choice of solvent.

Table 2. Influence of the solvent molecule ROR (ROR = H_2O, Me_2O, THF) on structure[a] and ^{29}Si chemical shift of the silylene $(H_3Si)_3CSiBr$ (**1c**).

ROR	Si···O	Si–Br	Si–C	C–Si–Br	δ^{29}Si
H_2O	2.141	2.369	1.950	100.4	172
Me_2O	2.161	2.350	1.949	102.3	194
THF	2.078	2.363	1.953	102.0	159

[a] The chemical shift of **1c** increases with increasing Br-Si-C angle by about 3 ppm per degree.

The association energies E_{ass} of **1c**(ROR) complexes do not change significantly on going from ROR = H_2O to Me_2O to THF ($E_{ass} = -11.6$, -10.9, and -14.5 kcal mol^{-1}, respectively). Note, the solvent causes an upfield shift of 244 ppm (**1c** to **2c**). The bulkiness of the attached solvent molecules does not systematically influence the chemical shifts: $\Delta\delta^{29}$Si(**1c**–**1c**(ROR)) is 232 ppm for H_2O, 193 ppm for Me_2O, and 244 ppm for THF (**2c**). A second THF molecule on **2c** causes a further upfield shift of only 7 ppm. For the larger complex **1d**(ROR) (= **2d**), δ^{29}Si is 245 ppm. Despite the dramatic lowering of the chemical shift due to complexation with a solvent (201 ppm for **1d** to **2d**) the difference to the measured signal is too large to claim a match.

Structure **3**, suggested by Lee et al., is a Br-bridged dimer. Two structures, one with a *trans* and the other with a *cis* arrangement of the substituents R, are minima (E_{rel}(*cis*-**3c**) = 0.5 kcal mol^{-1}). The *trans* preference can be expected to be larger in **3d** than in **3c** due to steric effects. *trans*-**3c** resonates at 199 ppm, while *cis*-**3c** has a δ^{29}Si of 180 ppm. According to the substituent effects observed for structures **1a**–**d** and **2a**–**d**, we can expect the chemical shifts of **3d** to be at least 40 ppm higher than the ones of **3c**. Therefore, comparison of the observed with the calculated chemical-shift values also rules out both of Lee's alternative structures for the intermediate.

But what other structure could evoke the measured NMR signal of 106 ppm? Acyclic dimers of **1**, the 1,2-dibromodisilenes, have chemical shifts in the appropriate range. However, these molecules should not undergo the observed silylene trapping reactions. Other potential candidates to form loose interactions with the silylene backbone are naphthalene from the reducing agent, Br$^-$, and Li$^+$ ions. Since none of our attempts to optimize a silylene–naphthalene adduct was successful, these complexes are not further discussed. Scheme 2 sketches the complexes of the silylene with Li$^+$ (**4**), with Br$^-$ (**5**), and with a LiBr ion pair (**6**). According to orbital considerations, Li$^+$ coordinates in plane to the Si lone pair, while Br$^-$ adds perpendicularly to the Br-Si-C plane (donating a lone pair into the empty p atomic orbital of Si).

The chemical shift of the cation adduct **4c** differs by only 6 ppm from the free silylene (δ^{29}Si(**4c**) = 409 ppm). Consequently δ^{29}Si of **4d** is expected at about 440 ppm.

In contrast, the addition of bromide yields a silyl anion, **5d**, with a calculated chemical shift that is 321 ppm upfield from **1d**. δ^{29}Si(**5d**) is 124 ppm and fits the measured value considering the error of the method. The Si–Br bond lengths in **5d** are approximately equal (Si–Br 2.441 Å). The bond angle sum of 301° indicates distinct pyramidality. Note, the effect of the substituent R on δ^{29}Si is much smaller in the anion structures **5** (δ^{29}Si(**5c**) = 114 ppm, δ^{29}Si(**5d**) = 124 ppm) than in the corresponding silylene structures.

Anion **5** can be expected to attract Li$^+$ cations. The discussion of possible geometries and NMR signals of **6** is complicated by the occurrence of two alternative minima. As for the silylenoid $H_2SiClNa$,[10] the optimized structure **6c** has a lithium interacting both with silicon and one of the bromines. In the alternative structure **6c′** the Li cation interacts with both Br atoms (Figure 3). **6c′** is 11.9 kcal mol^{-1} more stable than **6c**. The chemical shift of **6c** is 153 ppm, while **6c′** (δ^{29}Si = 122 ppm) has a shift similar to that of the anion **5c** (114 ppm).

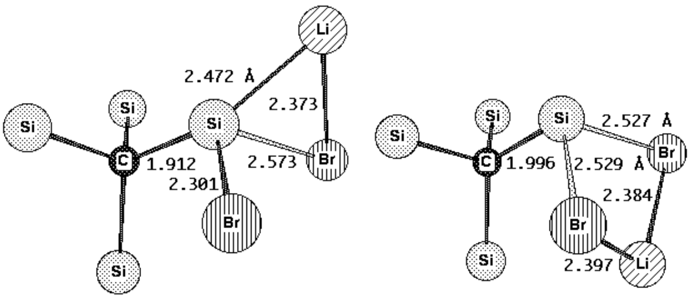

Figure 3. Gas-phase geometries of minima **6c** and **6c′**.

To model the solvation of Li$^+$ dimethyloxide, Me_2O, was used in place of THF. Adding three Me_2O molecules produces two isomers with very similar energy (ΔE = 1.8 kcal mol^{-1}) and geometry. In both structures, Li$^+$ interacts with only one of the bromines, causing one elongated Si–Br bond (2.534 Å vs. 2.445 Å). The chemical shifts of **6c**$(Me_2O)_3$ and **6c′**$(Me_2O)_3$ (144 and 147 ppm) do not differ considerably.

Structures **6** can be regarded as neutral complexes of LiBr with **1** and serve probably as precursors for the reacting silylene. The dissociation of **6** is likely to occur readily enough for further reactions with the trapping agents. A similar observation has been described by Takeda et al. for an intermediate silylene–isocyanide complex that is also stable in solution.[7] Since the silylenoid **6** still has a lone pair on Si, it can interact with another Li cation forming structure **7** (Figure 4). The chemical shifts are 91 ppm for the unsolvated **7c** and 117 ppm for **7d**. Adding three Me_2O to each Li$^+$ increases δ^{29}Si(**7c**$(Me_2O)_6$) to 124 ppm. δ^{29}Si of the larger **7d**$(Me_2O)_6$ can be estimated to be approximately 140 ppm. Consequently, both structures **6** and **7** are reasonable candidates for the intermediate identified by Lee and co-workers.

Calculations for $H_2MeSiSiCl$, $H_2MeSiSiCl_2^-$, and $H_2MeSiSiCl_2Br$ indicate that one of the signals detected by Wiberg et al.[19] in a reaction solution could be assigned to the $MeR^*_2SiSiCl_2^-$ anion (δ^{29}Si(R* = H) = 104 ppm, δ^{29}Si(R* =

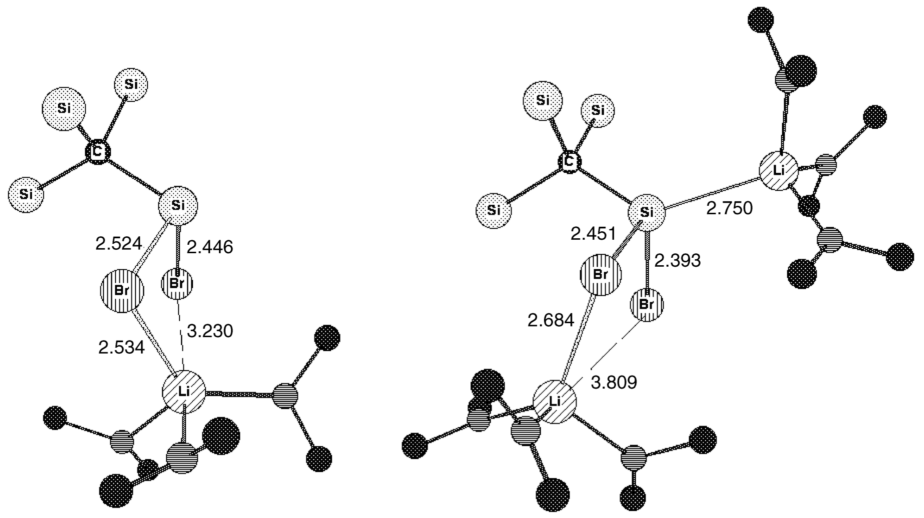

Figure 4. Geometries of silylenoid $\mathbf{6c}(Me_2O)_3$ (left) and the cationic complex **7c** (right). Bond lengths in Ångströms.

$SitBu_3) = 92$ ppm in experiment). As in Lee's experiment, the free silylene shows a NMR signal at much lower field ($\delta^{29}Si_{calc}(Me(Me_3Si)_2SiSiCl) = 872$ ppm) than the observed precursor.

Conclusion

In conclusion, while trapping reactions point to the presence of a bromosilylene in solution, the observed $\delta^{29}Si$ of 106 ppm certainly does not belong to the free silylene **1** ($\delta^{29}Si_{calc} = 446$ ppm). Based on our ab initio calculations, we also rule out the other previously proposed intermediate structures, namely the solvated silylene **2** ($\delta^{29}Si_{calc} = 245$ ppm) and the dimer **3** ($\delta^{29}Si_{calc} > 199$ ppm). In contrast, the Br^- adduct, forming anion **5** with $\delta^{29}Si_{calc} = 124$ ppm, differs by less than the rmse of the method. The $\delta^{29}Si_{calc}$ of the silylenoid, **6**, composed of **5** with one unsolvated Li^+, is, at 167 ppm, slightly too high to fit the observed $\delta^{29}Si$ of the intermediate. However, $\delta^{29}Si_{calc}$ of complex **7**, formed of **5** with two Li^+, lies within the correct range. When solvation is neglected, $\delta^{29}Si_{calc}$ of complex **7** is 117 ppm. Including three solvent molecules per Li^+ has a chemical shift of 124 ppm for **7c** and estimated 140 ppm for **7d**.

To bridge the gap between some measured diaminosilylenes (78–117 ppm) and the dialkylsilylene[5] (567 ppm), the calculated ranges for a number of alkylsilylenes are presented. The ten investigated R-Si-X sets, with the $\delta^{29}Si$ of $R\text{-}Si\text{-}NH_2$ at the high-field end and $R\text{-}Si\text{-}SiH_3$ shifts at the low-field end, span an overall range from 200 to 900 ppm ($X = H$, CH_3, NH_2, OH, F, SiH_3, PH_2, SH, Cl, and Br and $R = H$, CH_3, $(H_3Si)_3C$, and $(Me_3Si)_3C$). Extreme chemical shifts are predicted for $Si(NH_2)_2$, 86 ppm, and $Si(SiH_3)_2$, 1125 ppm. These results should help in identifying transient free silylenes through reaction monitoring by ^{29}Si NMR.

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