

Bis(tri-*tert*-butylsilyl)silylene: Triplet Ground State Silylene

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It is well known that the electronic ground state of carbenes, $R_2C:$, can be either singlet or triplet depending on the electronic and steric characteristics of the substituents on the carbene center.¹ In contrast to such well-documented chemistry of carbenes, the question of electronic ground states of the silylenes, $R_2Si:$, is still under very active investigation.^{2,3} Gaspar et al. have reported the photochemical generation of $(^iPr_3Si)(^tBu_3Si)Si:$, for which they suggested the possibility of a triplet ground state based on its reactions, in which a disilacyclobutane derivative was formed by the intramolecular insertion of the silylene center into a C–H bond of the *tert*-butyl substituents.⁴ However, it is not possible to draw any definitive conclusions for the existence of triplet silylene without direct detection of radical species by electron paramagnetic resonance (EPR) measurements. A recent density functional theory calculation on $(^iPr_3Si)(^tBu_3Si)Si:$ concluded that it has a singlet ground state, and the C–H insertion product can be explained by the existence of an equilibrium between singlet (S) and triplet (T) states.⁵ Apeloig et al. predicted by computational studies that $(^tBu_3Si)_2Si:$ (**2**) has a triplet ground state, even considering the most conservative error estimated.⁶ We have synthesized silacyclopropenes **1a** and **1b** as precursors of **2**, by the reductive condensation of $(^tBu_3Si)_2SiBr_2$ with 3-hexyne or 2-butyne (Chart 1).⁷ Here, we report the first EPR observation of a triplet ground state silylene **2**, and its chemical behavior, which also corresponds to this multiplicity.

EPR spectra were recorded on a Bruker 380E EPR spectrometer equipped with an Oxford ESR 900 liquid helium transfer system over the temperature range of 9–80 K. Upon irradiation with $\lambda = 254$ nm light at 77 K, methylcyclohexane glass matrixes of **1a** and **1b** were tinged with a rose color. A strong EPR signal was observed at 340 mT in both **1a** and **1b** cases.⁸ In addition, a weak and broad signal at 845 mT was also detected, as shown in Figure 1. The intensities of the signals were unchanged at 77 K for at least several hours after irradiation was stopped. The appearance of a broad signal at the same magnetic field (845 mT) upon the irradiation of both silacyclopropenes **1a** and **1b** indicates the generation of the same paramagnetic species. We assigned that species to the triplet state silylene produced by a photoinduced cycloelimination reaction.

The signals due to the triplet species were assigned in terms of the Hamiltonian:

$$H = g\beta B_0 S + DS_z^2 + E(S_x^2 - S_y^2)$$

The zero field splitting (ZFS) parameters were obtained from the observed spectra. In **1a** and **1b**, the existence of just one broad line below 1400 mT from the triplet species indicates a large value for D . Assignment of the ZFS parameters, D and E , which give the interaction of the unpaired electrons, requires the observation of additional resonance lines. However, if we assume that there

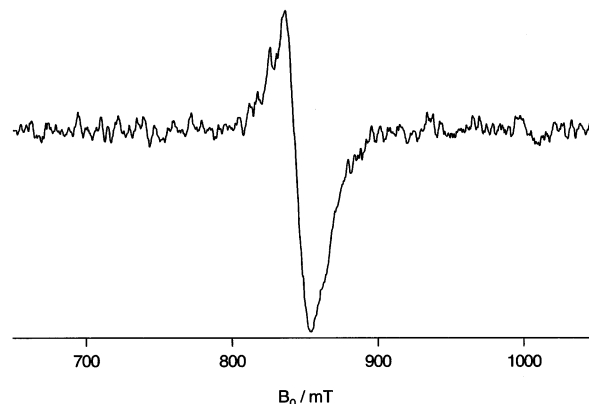
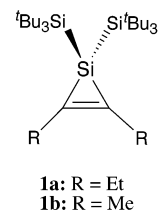


Figure 1. The EPR spectrum of **2** generated by the photolysis of **1a** or **1b** in methylcyclohexane glass matrixes at 9 K (X-band).

Chart 1



are no unobserved weak lines below 1400 mT, some approximate estimates can be made. Assuming that the free electron g value and E equal zero,⁹ the D value can be evaluated to be 1.64 cm^{-1} from the resonance field of the perpendicular (X , Y) orientation.

It should be noted that the D value for silylene is much larger than those for di-*tert*-butylmethylene¹⁰ and phenylmethylene.¹¹ Two factors could contribute to the observed large ZFS: spin dipolar interaction between the two unpaired electrons and second-order spin–orbit coupling (SOC). From theoretical considerations, the ZFS parameters strongly depend on the valence angle as well as on the S–T separation. For larger angles, where the triplet state lies below the singlet state, the spin–orbit contribution to D becomes dominant because of the SOC values increasing by a factor of 5.08 obtained from the ratio $\zeta_{SO}(Si-H)/\zeta_{SO}(C-H)$.¹² For angles in the vicinity of 120° , where the energy difference between the singlet and triplet state is only a few kcal/mol, D values in the order of $1\text{--}3 \text{ cm}^{-1}$ were expected.¹³ Assuming a negligible contribution from the substituent to D , we obtained a valence angle of ca. 125° from the experimental value.^{13,14}

When the valence angles are larger than 120° , the triplet ground state is always predicted.^{6,15} To confirm the spin multiplicity in the ground state, we examined the observed signal intensity at 845 mT as a function of temperature, as shown in Figure 2. As can be seen, the plot is linear over the entire temperature range studied (9–80 K). We interpreted the result to mean that the ground state of the silylene is a triplet and that the singlet state is not being

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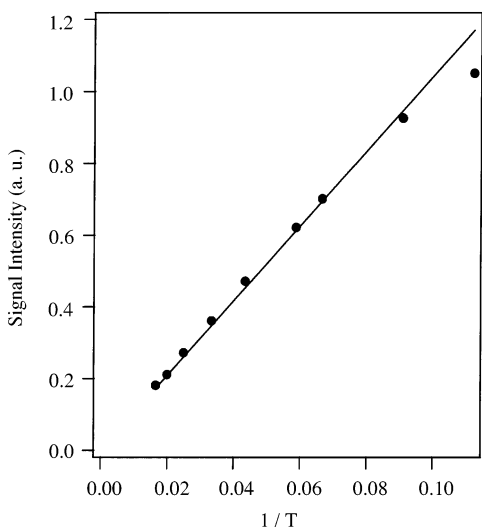
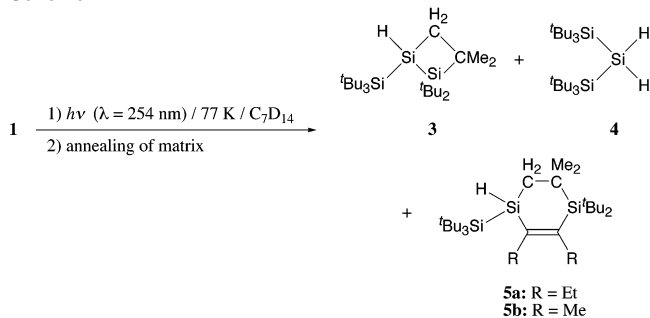


Figure 2. Temperature dependence of the intensity of the EPR signal at 845 mT.

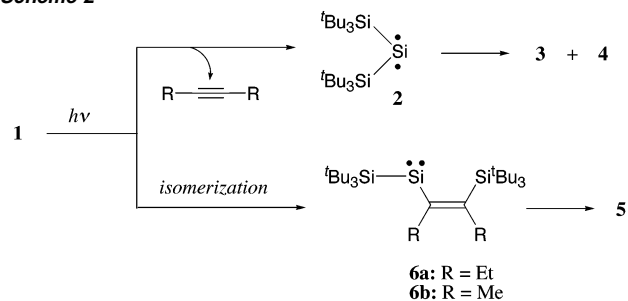
Scheme 1



populated to any discernible extent at the maximum temperature of the experiment. An alternative possibility is that the ground state of the species is a singlet with a very small S–T energy gap, which results in thermal equilibrium with the upper triplet state even at the lowest temperatures used. We consider this possibility unlikely for the present silylene in view of the moderate contribution of SOC to the *D* values.

The product analysis was examined under the conditions where EPR data were collected. Thus, photolysis of the deuterated methylcyclohexane glass matrix of **1a** at 77 K with $\lambda = 254$ nm light for 5 min followed by annealing the matrix produced three products, 1,2-disilacyclobutane **3** (35%), dihydrosilane ($(\text{Bu}_3\text{Si})_2\text{SiH}_2$) (**4**) (4%), and 1,4-disilacyclohex-2-ene **5a** (44%) (Scheme 1).^{7,16} The precursor **1b** also gave similar results, **3** (21%), **4** (3%), and **5b** (74%).⁷ It is reasonable to assume that the products **3** and **4** are derived from the triplet silylene **2** by the intramolecular insertion of the silylene center into a C–H bond of a *tert*-butyl group as reported by Gaspar et al. for $(\text{Pr}_3\text{Si})(\text{tBu}_3\text{Si})\text{Si}^{\cdot}$ ⁴ and by abstraction of the two hydrogen atoms, respectively.¹⁷ The product **5** is explained by the photochemical isomerization of **1** to a silylene **6** via tBu_3Si group migration to an olefinic carbon atom with Si–C bond breaking, followed by intramolecular insertion of the silylene center into the C–H bond of a *tert*-butyl group (Scheme 2). The silylene **6** has a singlet ground state due to electronic and steric reasons.¹⁸ The EPR signal by the photolysis of **1** is evidently due

Scheme 2



to **2**, not **6**, and we have concluded that **2** has a triplet ground state, in full agreement with previous theoretical calculations.⁶

Supporting Information Available: Experimental procedure, spectral data, tables of crystallographic data including atomic positional and thermal parameters for **1a**, **1b**, **5a** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (7) For details of the experimental procedure and spectral data of all new compounds, see the Supporting Information.
- (8) The EPR signal observed at 340 mT corresponds to a *g* value of 2.0055, which is very similar to that of typical silyl radicals, but its structure is unclear at this moment.
- (9) The *E* value is estimated to be below 0.002 cm^{-1} from the line width of the signal at 845 mT.
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- (14) Bond angles of $\text{tBu}_3\text{Si}-\text{Si}-\text{Si}^{\cdot}\text{tBu}_3$ in the silacyclopropenes are 137.9° for **1a** and 138.1° for **1b** (the values are determined by X-ray crystallography). See the Supporting Information.
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- (16) Photolysis ($\lambda > 280 \text{ nm}$) of **1a** in cyclohexane containing a 60-fold excess of *cis*-2-butene at room temperature gave **3** (18%), **4** (2%), and **5a** (30%). No silacyclopropane derivative by the [1 + 2] cycloaddition of **2** to *cis*-2-butene was found.
- (17) The silylene **2** has been postulated as a possible intermediate by the dehalogenation of $(\text{Bu}_3\text{Si})_2\text{SiX}_2$ (*X* = F, Cl, Br), see: Wiberg, N.; Niedermayer, W. *J. Organomet. Chem.* **2001**, *628*, 57. However, a silylenoid intermediate $(\text{Bu}_3\text{Si})_2\text{SiXM}$ (*X* = halogen, *M* = alkali metal) cannot be ruled out.
- (18) A DFT calculation of **6a** by the B3LYP/6-31G(d) method shows that the singlet state lies below the triplet state ($\Delta E_{S-T} = -13.4 \text{ kcal/mol}$), whereas the triplet state **2** lies below the singlet state ($\Delta E_{S-T} = 5.6 \text{ kcal/mol}$).

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