Tri-*tert*-butylsilylsilylenes with Alkali Metal Substituents (*t*Bu₃Si)SiM (M = Li, K): Electronically and Sterically Accessible Triplet Ground States

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The preparation of a silylene with a triplet ground state and the exploration of its chemistry has been described as "one of the most important challenges in contemporary silicon chemistry."[1,2] A strategy employing the steric bulk and low electronegativity of trialkylsilyl substituents to reduce the one-electron promotion energy from a σ^2 to a σp configuration by increasing the p-character of the nonbonding σ orbital[3] ultimately led to success.[4] The EPR spectrum of (*t*Bu₃Si)₂Si: provided unambiguous evidence for its triplet ground state.[4] Unfortunately, steric shielding of the dicoordinate silicon of (*t*Bu₃Si)₂Si: and of (*i*Pr₃Si)(*t*Bu₃Si)Si:, to which an intramolecular reaction from a triplet state had been assigned on the basis of product studies,[5] suggests that exploration of the *chemistry* of triplet silylenes requires molecules with sterically accessible triplet ground states.

Theoretical calculations have long predicted that extremely electropositive substituents such as Li will lead to triplet ground state silylenes with no need for the expansion of the bond angle at the divalent silicon due to two bulky substituents.[6] Here, the synthesis of precursors (*t*Bu₃Si)SiC₂(Et)₂M (M = Li, Na, K) is described (Scheme 1) and the generation of triplet silylenes from two of them (M = Li, K) reported.

Formation of the lithium (**2a**)[7] and potassium (**2b**) derivatives by the reduction of 1,1-bis(tri-*tert*-butylsilyl)-2,3-diethylsilirene (**1**) was verified by trapping with triisopropylsilyltriflate (Scheme 2). **3** was isolated in yields of 36% from **2a** and 30% from **2b**.[5,8]

Lithium- and potassium-substituted silylenes **4a** and **4b**, respectively, were generated by photoextrusion, employing a low-pressure mercury lamp, from metal-substituted silirenes **2a** and **2b** (Scheme 3).[8] When a THF solution of **2a** in a quartz NMR tube was irradiated at λ = 254 nm for 6 h at room temperature, 3-hexyne was detected by NMR spectroscopy. The generation of silylenes was confirmed by EPR experiments in the temperature range from 14 to 50 K. Upon irradiation with 254 nm light (a low-pressure mercury lamp) in a frozen 2-methyl-THF glassy matrix of **2a** in a quartz EPR tube for 1 h at 14 K, the characteristic X-band EPR spectrum of randomly oriented triplet species, which has large zero-field splitting (ZFS) parameters, was observed as a broad signal at around 790 mT (Figure 1) and assigned to silylene **4a**.

In addition to the 790 mT signal of **4a**, a strong one due to a doublet state species (*g* = 2.0054) also appeared at around 340 mT.[9] The EPR signals persisted at 14 K for several hours after light irradiation.

The zero-field splitting parameters were estimated from the spectrum of **4a** as previously described[4] under the assumptions that there are no unobserved weak lines below 1400 mT, and that the free electron *g* value and *E* equal zero. The *D* value can then be evaluated as 1.507 cm⁻¹ from the resonance field of the perpendicular (*X*,*Y*) orientation.[4,10]

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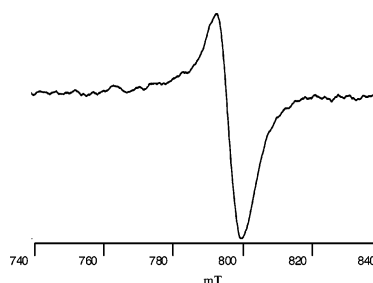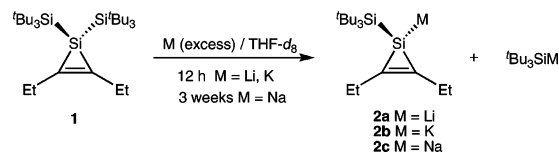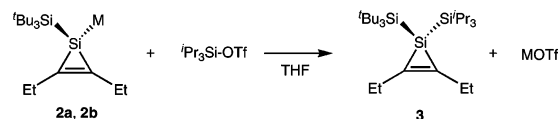§ Tohoku University.
‡ Washington University.

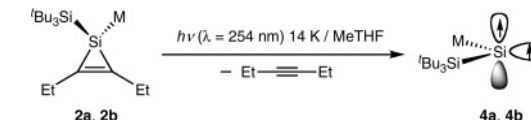**Figure 1.** The X-band EPR spectrum of **4a** generated by photolysis of **2a** in a 2-Me-THF glassy matrix at 14 K.

Scheme 1

Scheme 2

Scheme 3

To confirm that the observed EPR signal was associated with the ground electronic state of silylene **4a**, the temperature dependence of the 790 mT signal intensity was examined as shown in Figure 2. The changes were reversible between 15 and 50 K and corresponded to strict adherence to the Curie law, IT = constant, where *I* is the EPR signal intensity and *T* is absolute temperature. Thus, the ground state of **4a** is a triplet, and the singlet state is not populated to an appreciable extent at the maximum temperature examined. An alternative explanation that the ground state is a singlet with such a small S−T energy gap that thermal equilibrium with the triplet state is maintained throughout the experiment may be possible but is considered unlikely on the basis of the results from DFT calculations that follow.

Potassium-substituted silylene **4b** was generated similarly. Upon irradiation of a frozen glass containing **2b** in 2-methyl-THF at 254 nm for 1 h at 15 K, the X-band EPR spectrum of **4b** was observed as a broad signal at 780 mT (Figure 3). A *D* value of 1.510 cm⁻¹ was estimated as outlined above.
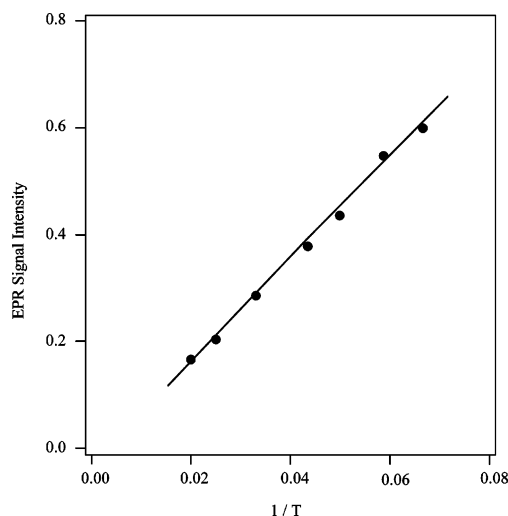
Figure 2. Temperature dependence of the intensity of the EPR signal at 790 mT attributed to silylene **4a**.
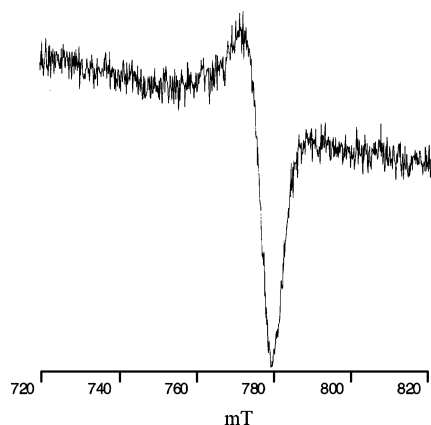

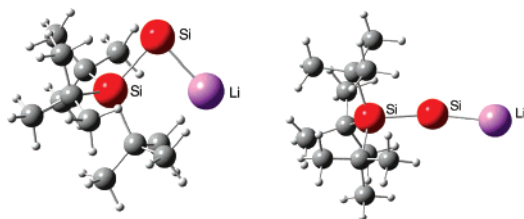**Figure 3.** The X-band EPR spectrum of **4b** generated by photolysis of **2b** in a 2-Me-THF glassy matrix at 15 K.

Figure 4. B3LYP/6-31G* optimized structures for Li(^{t}Bu₃Si)Si: **4a** (left, singlet; right, triplet).

DFT (U)B3LYP/6-31G(d) calculations were carried out to examine the nature of lithiosilylene **4a** and to predict its singlet–triplet splitting, ΔE_{S-T}. As a benchmark, E_S and E_T versus ∠Si–Si–Si or ∠Si–Si–Li were computed for (Me₃Si)₂Si: and Li(Me₃Si)Si:, respectively.[11] The potential curves for (Me₃Si)₂Si: crossed at ca. 120° with minima for the singlet (S) and triplet (T) states at ca. 100 and 130°, respectively, with S being favored by ca. 2 kcal/mol. Previously, 97.3 and 123.4° were reported from a calculation in which the singlet was treated at the TCSCF and the triplet at the RHF level with a DZ(d) basis set.[3] For Li(Me₃Si)Si:, no crossover angle was found, and the triplet was found to be the ground state at all angles.[11]

The ground state of Li(^{t}Bu₃Si)Si: was found to be a triplet with ΔE_{S-T} = 9.4 kcal/mol. The structures of S and T Li(^{t}Bu₃Si)Si:, optimized at the (U)B3LYP/6-31G* level, are shown in Figure 4. The ∠Si–Si–Li angles calculated for S and T are 81.3 and 164.9°,

Table 1. Si–Si–Li Angles (°) and Relative Energies (kcal/mol) of S and T (Me₃Si)SiLi(OMe₂)$_n$ ($n = 0 - 3$) Calculated at (U)B3LYP/6-31G(d)

	$n = 0$	1	2	3
singlet S	66.6, 0	88.6, −21.3	99.8, −35.2	109.8, −44.4
triplet T	155.8, −8.0	165.8, −32.6	169.6, −49.5	170.8, −60.8
ΔE_{S-T}	8.0	11.3	14.3	16.4

respectively, and the small bond angle of S is due to agostic interactions between Li and two H atoms leading to mean Li–H distances of 2.02 Å.

Because silylenes **4a** and **4b** were generated in ether glasses, it was suspected that coordination of the ether solvent to the metal ion would strongly influence their structures and energetics. To study this effect, calculations were carried out on a model system, (Me₃Si)SiLi(OMe₂)$_n$ ($n = 0-3$). Results are presented in Table 1.

The increase in ΔE_{S-T} with increasing degree of solvation can be explained by an increase in the effective electropositivity of the lithium. The agostic interactions in S and T disappear with solvation (see the Supporting Information). Coordination of an ether to the divalent silicon atom selectively stabilizes S,[12] but T remains the predicted ground state.[13] It is clear that coordination of ether solvent to both the metal and the silylene center strongly influences the geometry, ground state multiplicity, and singlet–triplet splitting of **4a** and **4b**.

Supporting Information Available: Experimental procedures, spectroscopic data, computational results. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) The silacyclopropenyllithium **2a** was independently prepared by the reaction of 1-bromo-2,3-diethyl-1-(tri-*tert*-butylsilyl)-1-silacycloprop-2-ene with lithium in THF. Tanaka, T.; Ichinohe, M.; Sekiguchi, A. *Chem. Lett.* **2004**, *33*, 1420.
(8) For the experimental procedure and spectral data, see Supporting Information.
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(13) The ΔE_{S-T} values for [Me₂O]$_n$Li](Me₃Si)Si: ← OMe₂ ($n = 0-3$) are calculated to be −3.2, −1.0, 6.4, and 8.9 kcal/mol, respectively.

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