Highly Planar Silane $[(i\text{-Pr})_3Si]_3SiH$ and Silyl Radical $[(i\text{-Pr})_3Si]_3Si•$

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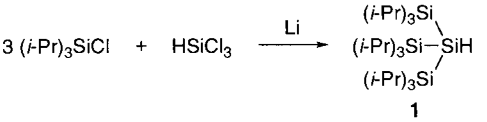
Tris(trialkylsilyl)silane $[(i\text{-Pr})_3Si]_3SiH$ (**1**) was synthesized, and the molecule was found to have a nearly planar structure of the polysilane skeleton by X-ray crystallography. Hydrogen abstraction from **1** by *tert*-butoxyl radicals gave the highly stable silyl radical $[(i\text{-Pr})_3Si]_3Si\cdot$ (**2**), which also has a planar structure.

Tris(trialkylsilyl)silanes have attracted attention as precursors of tris(trialkylsilyl)silyl radicals[1] and reducing agents for various organic compounds.[2] Recently, Guerra has reported the calculated structure of $(Me_3Si)_3SiH$, in which the geometry around the central silicon atom deviates somewhat from an ideal tetrahedral structure to a planar one.[3] Quite recently, we have reported that $(Et_nMe_{3-n}Si)_3Si\cdot$ (n = 1–3), which are generated from $(Et_nMe_{3-n}Si)_3SiH$, can be observed at room temperature.[4] As part of our research on polysilanes,[5] we have been interested in the creation of $(R_3Si)_3SiH$ bearing bulkier alkyl groups for the following reasons: (1) introduction of bulkier alkyl groups would induce more significant deformation of the silicon skeleton by the large steric repulsion; (2) bulkier silyl groups much more effectively stabilize $(R_3Si)_3Si\cdot$. We report herein a nearly planar structure of $[(i\text{-Pr})_3Si]_3SiH$ (**1**) and the formation, structure, and properties of the highly stable radical $[(i\text{-Pr})_3Si]_3Si\cdot$ (**2**).[6,7,8]

Compound **1** was synthesized by coupling of $(i\text{-Pr})_3SiCl$ and $HSiCl_3$ with Li.[9]



$$3\,(i\text{-Pr})_3SiCl + HSiCl_3 \xrightarrow{Li} [(i\text{-Pr})_3Si]_3SiH$$

1

The molecular structure of **1** is presented in Figure 1.[10] The molecule has a threefold axis along the central Si–H bond. A remarkable feature of **1** is the nearly planar structure of the polysilane skeleton. The Si–Si–Si bond angle is 118.10(3)°, and the sum of the three Si–Si–Si bond angles around the central silicon atom is 354.30°. The value is close to that of an ideal sp^2 silicon atom (360°) and considerably different from that of an ideal sp^3 silicon atom (328.5°). The Si–Si–H bond angle is significantly small (97.99(7)°). It is noted that the deformation from a tetrahedral structure to a planar one causes the crowded arrangement around the central hydrogen atom: the shortest distance between the central hydrogen atom and hydrogen atoms of isopropyl groups is 2.25 Å, which is smaller than the sum of their van der Waals radii.[11]

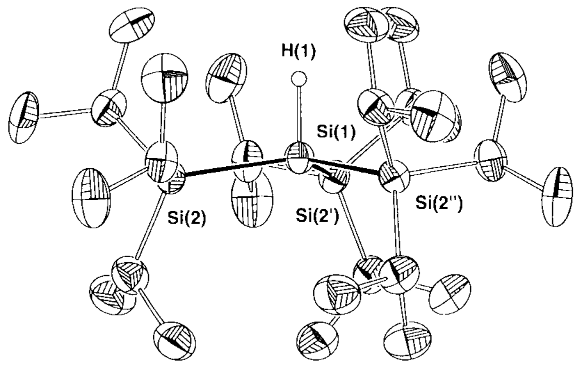


Figure 1. Molecular structure of **1**. Selected bond lengths (Å) and angles (°): Si(1)–Si(2) 2.405(1), Si(1)–H(1) 1.39(7); Si(2)–Si(1)–Si(2') 118.10(3), Si(2)–Si(1)–H(1) 97.99(7).

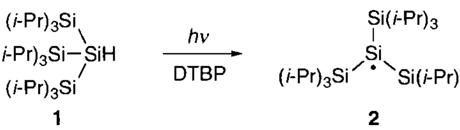
The structural change is also shown in NMR spectra. In Table 1, ^1H and ^{29}Si NMR parameters of **1** and related silanes are summarized. Coupling constants $J(^{29}Si–H)$ increase as substituents on the silicon atoms become bulkier. Because the s-character of the silicon hybrid orbital is well-known to be correlated with $J(^{29}Si–H)$,[12] the tendency of $J(^{29}Si–H)$ in Table 1 indicates that the s-character of the Si–H orbitals becomes smaller as the substituents become bulkier. Especially, $J(^{29}Si–H)$ of **1** (−137.4 Hz) is the largest among those of hydrosilanes so far reported,[13] and the result is in accord with the nearly planar structure of **1**. The trend of the chemical shifts of ^{29}Si nuclei at the α- and β-positions in Table 1 is explained by the inductive effect of the trialkylsilyl groups because the electron-donating properties of the trialkylsilyl groups increase as the alkyl groups change in the order 1° < 2° < 3°. The downfield shift of the central hydrogen atoms seems to be rationalized by the effect of steric compression.[14]

Table 1. NMR parameters for $(R_3Si)_3SiH$ in C_6D_6

$(R_3Si)_3SiH$	$\delta(H)^a$	$\delta(^{29}Si(\alpha))^a$	$\delta(^{29}Si(\beta))^a$	$J(^{29}Si–H)^b$
$(Me_3Si)_3SiH$	2.52	−115.6	−11.6	−154.4
$(EtMe_2Si)_3SiH^c$	2.53	−123.6	−7.0	−152.8
$(Et_2MeSi)_3SiH^c$	2.59	−131.9	−2.3	−149.9
$(Et_3Si)_3SiH^c$	2.63	−139.8	2.1	−146.5
1	3.10	−146.4	13.7	−137.4

^{a}ppm. ^{b}Hz. ^{c}Reference 4.

Radical **2** was generated by irradiation of a solution containing **1** and di-*tert*-butyl peroxide (DTBP, 5.5 equiv.) at room temperature.



$$[(i\text{-Pr})_3Si]_3SiH \xrightarrow[DTBP]{h\nu} [(i\text{-Pr})_3Si]_3Si\cdot$$

1 **2**

In the ESR spectrum of **2**, a sharp signal with three kinds of satellites was observed as shown in Figure 2. These satellites, which have splitting constants 5.56, 0.81, and 0.22 mT, are due to a ^{29}Si nucleus at the α-position, three ^{29}Si nuclei at the β-positions, and nine ^{13}C nuclei at the γ-positions, respectively, because the intensity of these satellites relative to the central signal

(2.6, 6.8, and 4.6%) is in good accord with calculated values (2.6, 7.7, and 5.0%). The splitting by hydrogen atoms could not be observed because the line width of the signal is too small (0.03 mT). ESR parameters of **2** and related silyl radicals are summarized in Table 2. As alkyl groups on silicon atoms become bulkier, $a(^{29}\mathrm{Si}(\alpha))$ becomes smaller, indicating that the structure around the radical center becomes more planar. $(\mathrm{Me_3Si})_3\mathrm{Si}\cdot$ was reported to have a nearly planar structure around the radical center;[1] therefore, the results show that **2** has a highly planar structure probably due to the steric repulsion among the bulky silyl substituents.

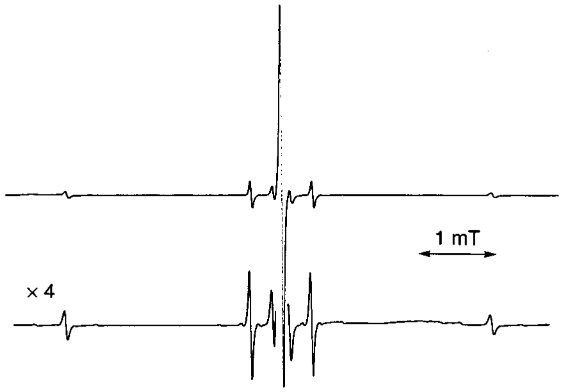


Figure 2. ESR spectrum of **2** in pentane at room temperature.

Table 2. ESR parameters for $(\mathrm{R_3Si})_3\mathrm{Si}\cdot$

$(\mathrm{R_3Si})_3\mathrm{Si}\cdot$	g	$a(^{29}\mathrm{Si}(\alpha))^{a}$	$a(^{29}\mathrm{Si}(\beta))^{a}$	$a(^{13}\mathrm{C}(\gamma))^{a}$
$(\mathrm{Me_3Si})_3\mathrm{Si}\cdot^{b}$	2.0053	6.38	0.71	
$(\mathrm{EtMe_2Si})_3\mathrm{Si}\cdot^{c}$	2.0060	6.28	0.71	
$(\mathrm{Et_2MeSi})_3\mathrm{Si}\cdot^{c}$	2.0060	6.03	0.73	0.32
$(\mathrm{Et_3Si})_3\mathrm{Si}\cdot^{c}$	2.0063	5.72	0.79	0.30
2	2.0061	5.56	0.81	0.22

[a]mT. [b]Reference 1c. [c]Reference 4.

Radical **2** has several other features. When irradiation was stopped and ESR signals almost disappeared, compound **1** was reproduced quantitatively,[15] and the dimerization product $[(i\text{-Pr})_3\mathrm{Si}]_3\mathrm{SiSi}[\mathrm{Si}(i\text{-Pr})_3]_3$ was not detected in contrast with the cases of $(\mathrm{Et}_n\mathrm{Me}_{3-n}\mathrm{Si})_3\mathrm{Si}\cdot$ (n = 1–3).[4] Moreover, when $\mathrm{CCl_4}$ was added to a solution of **2**, the silyl radical did not react with $\mathrm{CCl_4}$, and **1** was obtained quantitatively.[15] The result is remarkable because silyl radicals have been known to be readily trapped by $\mathrm{CCl_4}$ to give chlorosilanes.[16] It is thus indicated that in **2** the steric hindrance around the radical center is considerably large.

As mentioned above, radical **2** was observed by ESR at room temperature. After irradiation was stopped, the ESR signals of **2** were observed for several days (Figure 3). The half-life is 5 days at 15 °C. The half-life is much longer than those of $(\mathrm{Et}_n\mathrm{Me}_{3-n}\mathrm{Si})_3\mathrm{Si}\cdot$ (n = 1–3), the ESR signals of which disappeared immediately when these radicals were generated from $(\mathrm{Et}_n\mathrm{Me}_{3-n}\mathrm{Si})_3\mathrm{SiH}$ with DTBP.[4] From these results, **2** was found to be a highly stable and inert silyl radical.

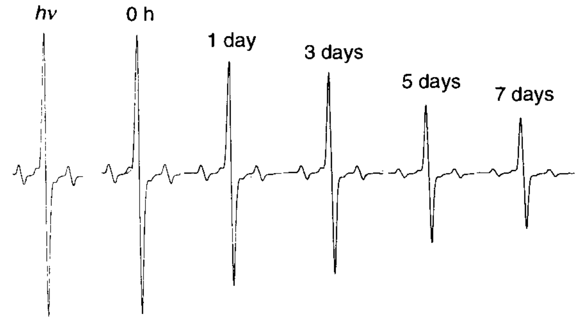


Figure 3. Decay of ESR signals of **2** at 15 °C after the light was shut off. Only the central signal is shown in each case.

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7 Also, the synthesis, planar structure, and photolysis of **1** leading to the silylene $[(i\text{-Pr})_3\mathrm{Si}]_2\mathrm{Si}$: have been reported at 30th Organosilicon Symposium, London, Canada, May, 1997 by P. P. Gaspar, A. M. Beatty, T. Chen, T. Haile, W. T. Klooster, T. F. Koetzle, D. Lei, T. S. Lin, and W. R. Winchester, Abstract A-16, and at the 29th Central Regional ACS Meeting, Midland, USA, May, 1997 by P. P. Gaspar, A. M. Beatty, T. Chen, T. Haile, D. Lei, W. T. Klooster, and T. F. Koetzle, Abstract 179.

8 The stable silyl radical $[(t\text{-Bu})\mathrm{Me_2Si}]_3\mathrm{Si}\cdot$ has been reported recently by us[6] and another group. See, I. Kon, M. Ichinohe, and M. Kira, the 72nd Annual Meeting of the Chemical Society of Japan, Tokyo, March, 1997, Abstracts I, p 414; M. Ichinohe, I. Kon, and M. Kira, 30th Organosilicon Symposium, London, Canada, May, 1997, Abstract P-45.

9 **1**: 3% yield; mp 150–153 °C; ^{1}H NMR ($\mathrm{C_6D_6}$) δ 1.29 (d, 54H, J = 7.2 Hz), 1.40 (sept, 9H, J = 7.2 Hz), 3.10 (s, 1H); ^{13}C NMR ($\mathrm{C_6D_6}$) δ 16.0, 20.9; ^{29}Si NMR ($\mathrm{C_6D_6}$) δ −146.4, 13.7; IR (KBr, cm^{-1}) 2950, 2870, 2050, 1460, 1380, 1360, 1070, 1020, 880, 690; MS m/z (%) 457 ($\mathrm{M^+}$–(i-Pr), 5), 342 (37), 300 (22), 157 (100), 115 (92), 87 (41), 73 (50), 58 (68); HRMS. Found: 457.3553. Calcd for $\mathrm{C_{24}H_{57}Si_4}$ ($\mathrm{M^+}$–(i-Pr)): 457.3537.

10 Crystal data for **1**: $\mathrm{C_{27}H_{64}Si_4}$, F_w = 501.15, cubic, space group $Pa\bar{3}$, a = 18.912(1) Å, V = 6763.7(7) Å^3, Z = 8, D_o = 0.980, D_c = 0.984 g cm^{-3}, R = 0.048, R_w = 0.039 (w = $1/\sigma^2(F_\mathrm{o})$) for 910 observed reflections.

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15 Although the hydrogen source is not clear, radical **2** has the possibility of abstracting a hydrogen atom from decomposition products of *tert*-butoxyl radicals. Considering the half-life of **2**, the hydrogen abstraction process is very slow and does not seem energetically and sterically favorable.

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