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# Generation and Electron Paramagnetic Spectroscopy of the First Silenyl Radicals (R<sub>2</sub>C=Si<sup>-</sup>-R). Experiment and Theory

Daniel Pinchuk<sup>+</sup>, Yosi Kratish<sup>+</sup>, Jomon Mathew, Lieby Zborovsky, Dmitry Bravo-Zhivotovskii, Boris Tumanskii<sup>\*</sup> and Yitzhak Apeloig<sup>\*</sup>

Dedicated to Professor Josef Michl on the occasion of his 80th birthday

**Abstract:** The generation and characterization by electron paramagnetic resonance (EPR) spectroscopy of the first two persistent silenyl radicals (R<sub>2</sub>C=Si\*-R) having a half-life time ( $t_{1/2}$ ) of about 30 min is reported. The large hyperfine coupling constants (*hfccs*) ( $a(^{29}Si_{\alpha}) = 137.5-148.0$  G) indicate a substantial s-character of the unpaired electron. DFT calculations, which are in good agreement with the experimentally observed *hfccs*, predict a strongly bent structure (4C=Si-R = 134.7°-140.7°). In contrast, the analogous vinyl radical (R<sub>2</sub>C=C\*-R) ( $t_{1/2} \sim 3$  h), exhibits a small *hfcc* ( $a(^{13}C_{\alpha}) = 26.6$  G) and has a nearly linear geometry (4C=C-R = 168.7°).

Vinyl radicals, R<sub>2</sub>C=C<sup>•</sup>-R, are common intermediates widely used in organic synthesis. <sup>[1]</sup> Consequently, they were studied extensively both experimentally <sup>[2]</sup> and theoretically. <sup>[3]</sup> In contrast, very little is known about the analogous group 14 congener radicals, R<sub>2</sub>E=E<sup>•</sup>-R, (E, E<sup>•</sup>= C, Si, Ge) and they were observed only in cryogenic matrix. [4] Disilenyl radicals were proposed as intermediates in some reactions, <sup>[5]</sup> but spectroscopic evidence for their presence was not provided. Silicon is the closest congener of carbon, yet the fundamental properties of many silicon and carbon compounds, in particular multiply-bonded compounds, are very different. [6] It is therefore of fundamental interest to characterize new silicon compounds and silicon-centered reactive intermediates and to compare their properties with their carbon analogues, adding significantly to our basic understanding of molecular geometry, chemical bonding, electronic structure, etc. The recent synthesis of the first metal substituted silenes (R<sub>2</sub>C=SiRLi)<sup>[7]</sup> and disilenes (R<sub>2</sub>Si=SiRLi)<sup>[8]</sup> expand significantly the repertoire of silicon reagents leading to the isolation of novel doubly-bonded silicon compounds.<sup>[9]</sup>

Here, we report the generation and characterization by electron paramagnetic resonance spectroscopy (EPR) supported by the results of Density Functional Theory (DFT) calculations, of the first two persistent silenyl radicals  $R_2C=Si^{-}R$  (2a and 2b). The synthesis and calculated properties of the analogous persistent vinyl radical  $R_2C=C^{-}R$ , are also reported.

Recently, we reported the synthesis of two silenyl lithiums  $1a\ ^{[7a]}$  and  $1b\ ^{[7b]}$  Addition of a variety of reagents ((CO)\_5ReBr,

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CCl<sub>4</sub>, Ph<sub>3</sub>CCl, MX<sub>2</sub> (ZnCl<sub>2</sub>, HgCl<sub>2</sub>, HgF<sub>2</sub>)) to **1a** or **1b** yields the persistent silenyl radicals **2a** and **2b**, respectively (Eq. 1), which were characterized by EPR spectroscopy (Figure 1). Silenyl radicals **2a** and **2b** have a half-life time ( $t_{1/2}$ ) at 300 K of about 30 min. Interestingly, both **2a** and **2b** do not dimerize, due to steric reasons. <sup>[10]</sup> Silenyl radical **2a** decays to a complex mixture of products, among them is the corresponding H-substituted silene which is formed via hydrogen abstraction. When nBu<sub>3</sub>SnH was added to the reaction mixture (after the generation of radical **2a**) the H-substituted silene becomes the major product, but other unidentified products are also observed. For this reason, a cleaner method to generate the silenyl radicals was searched.



Silyl mercury compounds are good precursors for generating cleanly silyl radicals. <sup>[11]</sup> The mercury-substituted silene **3** was therefore prepared by addition of tBuHgCl to **1a** (Scheme 1, step a). Irradiation of a toluene solution of **3** ( $\lambda > 250$  nm, 30 min, r.t) within the EPR spectrometer cavity, produces an intensive EPR signal of silenyl radical **2a**, accompanied by precipitation of mercury (Scheme 1, step b). Upon decay of radical **2a** two products are observed: H-substituted silene **4** and cyclic 1,3-disilacyclopentane **5** (Scheme 1, step c). Interestingly, when **3** is irradiated for 2 h, cyclic **5** is the only product. <sup>[12]</sup>



Scheme 1. Synthesis and photolysis of mercury substituted silene 3.

We suggest that silenyl radical **2a** decays by hydrogen abstraction (probably from the toluene solvent), yielding silene **4** which under further irradiation undergoes intramolecular cyclization yielding **5**. Photochemical intramolecular cyclization of silenes was previously reported. <sup>[13]</sup> To support this proposal, **4** was prepared and its photochemistry was studied. Addition of tBuOH to **1a** yields silene **4** (Scheme 2, step a). The structure of **4** was confirmed by NMR and mass spectrometry. <sup>[14a]</sup> Silene **4** exhibits a characteristic <sup>29</sup>Si NMR signal at 134 ppm, assigned to a sp<sup>2</sup>-silicon atom, in excellent agreement with the calculated value of 135 ppm <sup>[14b]</sup>. In the <sup>1</sup>H NMR spectrum the silenic hydrogen (H)Si=C appears at 6.67 ppm (J<sub>(Si-H)</sub> = 173.73 Hz). Similar NMR values were previously reported for hydrogen substituted silenes. <sup>[15]</sup> Silene **4** is stable at room temperature,

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however, irradiation ( $\lambda > 250$  nm, 2 h, r.t) of 4 produces quantitatively cyclic 5 (Scheme 2, step b), supporting the suggestion that 5 is not formed directly from radical 2a, but is obtained from silene 4 which is the initial decay product of radical 2a.

	(a)	(b)	Me tBu			
2THF · Li	BuOH H SimetBu <sub>2</sub>	hv 🗩	Hand Jan			
tBu <sub>2</sub> MeSi R	tBu <sub>2</sub> MeSi <sup>2</sup> SiMe <sub>2</sub> tBu	2 h T tBu	2MeSi Si SiMe2tBu			
1a	4		quantitative			
Schame 2. Synthesis and photolysis of hydrogen-substituted silene 4						

Silenyl radical 2a was studied by EPR spectroscopy (Figure 1). Its spectrum is characterized by an unusually large hyperfine coupling constants (hfccs) of the unpaired electron with the <sup>29</sup>Si<sub>a</sub>, <sup>29</sup>Si<sub> $\beta$ </sub> and <sup>29</sup>Si<sub> $\gamma$ </sub> nuclei; <sup>[16a]</sup> [ $a(^{29}Si_{\alpha}) = 137.5 \text{ G}^{[16b]}$ ,  $a(^{29}Si_{\beta}) = 32.3 \text{ G}$ ;  $a(^{29}Si_{\gamma(trans)}) = 17.5 \text{ G}$  ( $^{29}Si$ ,  $I = \frac{1}{2}$ , natural abundance 4.7%). These hfccs are much larger than in analogous tri-coordinated silyl radicals. <sup>[17]</sup> For example, the hfccs in [(tBu<sub>2</sub>MeSi)<sub>2</sub>HSi]-(tBu2MeSi)2Si\* and (tBu2MeSi)3Si\*, having similar silyl substituents to **2a**, are:  $[a(^{29}Si_{\alpha}) = 59.3 \text{ G}, a(^{29}Si_{\beta}) = 7.3 \text{ G}, a(^{29}Si_{\gamma}) = 10.4 \text{ G}],$ <sup>[18]</sup> and  $[a(^{29}Si_{\alpha}) = 58.0 \text{ G}, a(^{29}Si_{\beta}) = 7.9 \text{ G}]$ , respectively <sup>[19]</sup> The very large a(29Sig) points to a substantial s character of the unpaired electron orbital in silenyl radical 2a and therefore a strongly bent structure at the radical center. <sup>[17]</sup> The large  $\beta$ -hfcc in 2a (a(<sup>29</sup>Si<sub>B</sub>) = 32.3 G), relative to (tBu<sub>2</sub>MeSi)<sub>3</sub>Si<sup>•</sup> (7.9 G) <sup>[19]</sup> is attributed to increased contribution of the direct coupling mechanism in 2a relative to (tBu2MeSi)3Si. [20] The hfcc of <sup>29</sup>Si<sup>4</sup><sub>y(trans)</sub> (atom numbering is given in Figure 1) is 17.5 G; in contrast, coupling with <sup>29</sup>Si<sup>3</sup><sub>γ(cis)</sub> is not observed experimentally <sup>[21]</sup> and according to calculations is 4.4 G (Table 1). The larger hfcc of  $^{29}\text{Si}^4_{\gamma(\text{trans})}$  than that of  $^{29}\text{Si}^3_{\gamma(\text{cis})}$  supports the bent structure of 2aand is a manifestation of the larger hyperconjugation interactions with a substituent anti to the singly occupied orbital than that with a syn-substituent. <sup>[2d, 17]</sup> The hyperfine coupling with the  $\delta$ -H atoms of the methyl group on Si<sup>2</sup> [a(3H<sub> $\delta$ </sub>) = 2.0 G] are much larger compared to that in  $(R_3Si)_3Si^{\bullet}$  radicals  $[a(3H_{\delta}) \sim 0.1-0.3 \text{ G}]$ . <sup>[17]</sup> Also noticeable is the marked upfield shifted g-factor (g = 2.001) relative to (R<sub>3</sub>Si)<sub>3</sub>Si<sup>•</sup> radicals (g = 2.004-2.005). <sup>[17]</sup> Silenyl radical 2b (Eq. 1) has a similar EPR spectrum to 2a. [22] Substitution of the silyl group on C in 2a by a 1-adamantyl group in 2b results in a small increase in  $a(^{29}Si_{\alpha})$  to 148.0 G, similarly to the effect observed in (R<sub>3</sub>Si)<sub>3</sub>Si<sup>•</sup> radicals. <sup>[17]</sup>



**Figure 1**. (a) EPR spectrum of silenyl radical **2a** (300 K, toluene) [g = 2.001;  $a(^{29}Si_{\alpha}) = 137.5 \text{ G}; a(^{29}Si_{\beta}) = 32.3 \text{ G}; a(^{29}Si_{\gamma}(trans)) = 17.5 \text{ G}];$  (b) Simulated EPR spectrum of **2a** <sup>[23]</sup>; (c) Expanded central quartet at g=2.001, [a(3H) = 2.0 \text{ G}]; (d) Simulation of the central quartet. <sup>[23]</sup>

Support for the interpretation of the EPR spectrum and additional insight is provided by quantum-mechanical calculations. The geometries and EPR parameters of **2a** and **2b** were calculated using Density Functional Theory (DFT) <sup>[24]</sup> at the UPBE0 <sup>[25]</sup>/def2-TZVPP//UB97D <sup>[26]</sup>/6-311+G(d,p) level of theory. <sup>[22]</sup> The calculated EPR *hfccs* for **2a** are in good agreement with the experimental *hfccs* (Table 1). The calculated spin density (Figure 2a) indicates a significant hyperconjugative interaction between the singly occupied orbital of Si<sup>1</sup><sub>α</sub> with the *trans*  $\sigma^*(C^1-Si^4)$  orbital, resulting in the larger  $a({}^{29}Si^4_{\gamma(trans)})$  compared with  $a({}^{29}Si^3_{\gamma(cis)})$ .

**2a** is calculated to have a strongly bent structure at the radical center with a  $\pm$ Si<sup>2</sup>Si<sup>1</sup>C<sup>1</sup> bond angle of 140.7° (Figure 2), by 16.6° larger than in silenyl lithium **1a** (124.1°) <sup>[7a]</sup>. The C<sup>1</sup>=Si<sup>1</sup> bond length in **2a** is 1.744 Å, by 0.018 Å shorter than in **1a** (1.762 Å) <sup>[7a]</sup>. The Si<sup>1</sup>=C<sup>1</sup> bond in **2a** is planar ( $\pm$ Si<sup>4</sup>C<sup>1</sup>Si<sup>1</sup>Si<sup>2</sup> = 0.0°) compared with 5.0° in **1a** <sup>[7a]</sup>. The Si<sup>1</sup>-Si<sup>2</sup> distance of 2.396 Å is by 0.09 Å shorter than in **1a** (2.486 Å) <sup>[7a]</sup>. Natural Bond Orbital (NBO) <sup>[27]</sup> analysis indicates that Si<sub>α</sub> in **2a** has a s<sup>(58%)</sup>p<sup>(42%)</sup> hybridization with electron occupancy of (0.9 el.), consistent with the large a(<sup>29</sup>Si<sup>1</sup><sub>α</sub>) of 137.5 G. The data for radical **2b** is similar to that for **2a** (Table 1).



Figure 2. Calculated spin density (hydrogen atoms are omitted for clarity). (a) of radical 2a. (b) of radical 6.

Table 1. Experimental and calculated a hfcos, geometries and the s/p character
of the singly occupied orbital in radicals 2a, 2b and 6.

Radical	Method	∡SiEE' (°)	E=E' bond distance (Å)	s/p- character (in %)	<sup>29</sup> Siα or <sup>13</sup> Cα	<sup>29</sup> Si <sub>β</sub>	$^{13}C_{\beta}$	<sup>29</sup> Siγ <sub>(trans)</sub>	<sup>29</sup> Siγ <sub>(cis)</sub>	C(3⊦ ;
2a	Experimental Calculated	- 140.7	- 1.744	- 58/42	137.5 122.2	32.3 30.7	- 8.2	17.5 15.6	- 4.4	2.0 2.2
2b	Experimental Calculated	- 134.7	- 1.761	- 56/44	148.0 148.7	31.0 29.4	- 8.8	-	- 4.1	1.8 2.2
6	Experimental Calculated	- 168 7	- 1 312	- 3/97	26.6 21.1	9.4 9.6	15.4 14.6	46.5 43 1	46.5 39.4	0.11

<sup>a</sup> UPBE0/def2-TZVPP//UB97D/6-311+G(d,p); <sup>b</sup> C(6H<sub>δ</sub>)

Additional support for the proposed structure of silenyl radical **2a** is provided by high resolution mass spectrometry using atmospheric pressure chemical ionization (APCI), in which ions with the exact mass of **2a** and its expected isotope distribution are observed by using both positive-ion and negative-ion methods (Figure 3). <sup>[28]</sup> Molecular ions of **2a** may also be formed by a hydrogen atom loss from **4** or **5**. To exclude this possibility, **4** and **5** were measured under the same conditions (positive-ion APCI), and only the molecular ions of [**4**+H]<sup>+</sup> and [**5**+H]<sup>+</sup> are observed with no traces of **2a** ions, supporting the conclusion that the observed **2a** mass, results from the presence of radical **2a**.

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Figure 3. (a) Negative-ion APCI high resolution mass spectrum of 2a; (b) Simulated mass spectrum of 2a.

Comparison of silenyl radical **2a** with the analogous vinyl radical **6** is of interest. Vinyl radical (tBuMe<sub>2</sub>Si)<sub>2</sub>C=C<sup>•</sup>-(SiMe<sub>2</sub>tBu) (**6**), was generated by irradiation of (tBuMe<sub>2</sub>Si)<sub>2</sub>Hg <sup>[29]</sup> in the presence of tBuMe<sub>2</sub>SiC≡CSiMe<sub>2</sub>tBu. <sup>[30]</sup> **6** is persistent at 300 K; ( $t_{1/2}$  is ~3 h), significantly longer than that of (Me<sub>3</sub>Si)<sub>2</sub>C=C<sup>•</sup>-(SiMe<sub>3</sub>);  $t_{1/2}$  ~1 min at 273 K. <sup>[2c, 2d]</sup>The higher kinetic stability of **6** results from the larger tBuMe<sub>2</sub>Si substituents which slow down decay reactions.

The EPR spectrum of vinyl radical **6** (Figure 4), is characterized by g = 2.0021 and the following  $hfccs: a({}^{13}C{}^{1}_{\alpha}) = 26.6 \text{ G}$ ,  $a({}^{13}C{}^{2}_{\beta}) = 15.4 \text{ G}$ ,  $a({}^{29}\text{Si}{}^{1}_{\beta}) = 9.4 \text{ G}$ ,  $a({}^{229}\text{Si}{}^{2.3}_{\gamma}) = 46.5 \text{ G}$ , a(9H) = 0.056 G, a(6H) = 0.11 G, a(18H) = 0.22 G, a(12H) = 0.45 G (Table 1). The relatively small *hfcc* with  ${}^{13}C_{\alpha}$  of 26.6 G, indicates a small s-character of the orbital in which the unpaired electron resides in agreement with the calculated C=C-Si of 168.7°. Furthermore, the identical *hfccs* value with the two  $\gamma$ -silicon atoms, indicates a nearly linear structure or fast inversion around the radical center. Similar *hfccs* were previously obtained for the short-lived vinyl radical (Me<sub>3</sub>Si)<sub>2</sub>C=C<sup>•</sup>-(SiMe<sub>3</sub>). [<sup>2c, 2d]</sup> In contrast, the strongly bent vinyl radical H<sub>2</sub>C=C<sup>•</sup>-H has a much larger *hfcc* of  ${}^{13}C_{\alpha} = 107.5 \text{ G}$ . [<sup>2c]</sup> Thus, silyl substitution induces linearization at the radical center, similar to its planarization effect in tricoordinate silyl radicals.



**Figure 4**. (a) EPR spectrum of vinyl radical **6** (300 K, hexane); (b) EPR spectrum of **6** at high gain; (c) Expanded EPR spectrum of **6** at high resolution [g = 2.0021; a(9H)=0.056 G, a(6H)=0.11 G, a(18H)=0.22 G, a(12H)=0.45 G]; (d) Simulated EPR spectrum (the experimental *hfccs* were used for the simulation). <sup>[23]</sup>

i ne ca	alculate	ea FF	'R niccs values	or <b>6</b> (1a)	ole 1) are	e in ge	pod
agreement	with	the	experimental	values	(Table	1).	[19]

Interestingly, the calculated  $a({}^{29}Si^{2,3})$  values, for the trans-Si<sup>3</sup> (43.1 G) and cis-Si<sup>2</sup> (39.4 G) are different, indicating a slightly bent structure while experimentally they are the same at 46.5 G. The experimental equivalence of the a(29Si2,3) results from fast inversion around the radical center in line with the calculated inversion barrier for H<sub>2</sub>C=C\*-SiMe<sub>3</sub> of only ~1 kcal·mol<sup>-1</sup>. <sup>[3f]</sup> The calculated spin density distribution (Figure 2b) indicates significant hyperconjugative interactions between the singly occupied orbital on C<sup>1</sup> with  $\sigma^*$  (C<sup>2</sup>-Si<sup>2</sup>) and  $\sigma^*$  (C<sup>2</sup>-Si<sup>3</sup>), resulting in relatively large a(<sup>29</sup>Si<sub>y</sub>) values (Table 1). According to calculations, **6** has a slightly bent structure,  $\angle C^2 = C^1 - Si^1 = 168.7^\circ$ ,  $r(C^1 = C^2) =$ 1.312 Å and it is slightly twisted with a Si<sup>1</sup>C<sup>1</sup>C<sup>2</sup>Si<sup>3</sup> torsion angle of 16.8°. NBO analysis indicates that the unpaired electron resides (0.8 el. occupancy) in an almost pure 2p orbital (s<sup>(3%)</sup>p<sup>(97%)</sup>), consistent with the observed small hfcc a(13C1 a) of 26.6 G. The significant difference in the bending angle at the radical center between silenyl radical 2a and vinyl radical 6 is mainly attributed to the extension mismatch between the radii of the 3s and the 3p orbitals of Si, reducing the degree of s-p hybridization in 2a [31]

In conclusion, we report the generation of a new class of persistent ( $t_{1/2}(300 \text{ K}) \sim 30 \text{ min}$ ) silenyl radicals, **2a** and **2b**. The large EPR *hfccs*,  $a(^{29}\text{Si}_{\alpha}) = 137.5$  and 148.0 G, for **2a** and **2b**, respectively, point to a significant s-character of the singly-occupied orbital, in agreement with the radicals strongly bent structures ( $\measuredangle C=\text{Si-R} = 134.7^{\circ}-140.7^{\circ}$ ). In contrast, the analogous vinyl radical **6** has a small *hfcc* ( $a(^{13}C_{\alpha}) = 26.6 \text{ G}$ ) and a nearly linear geometry ( $\measuredangle C=\text{C-Si} = 168.7^{\circ}$ ). The comparison of **2a** vs **6** provides one more example for the different structural rules for silicon compounds, resulting from the 3s-3p orbitals mismatch, compared with analogous carbon compounds. <sup>[6]</sup>

#### **Supporting Information**

Experimental procedures, EPR spectrum of **2b**, synthesis and NMR data of **3**, **4**, **5**, DFT optimized geometries and energies of **2a**, **2b**, **3**, **4**, **5** and **6**, calculated NMR values of **3**, **4** and **5**, and dimerization energies for silenyl radicals are presented in the Supporting Information.

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**Keywords:** Silenyl radicals • Vinyl radicals • Silyl radicals • EPR • Metal substituted silenes

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The first two persistent ( $t_{1/2} \sim 30$  min) silenyl radicals ( $R_2C=Si^{\bullet}-R$ ) were generated from lithium and mercury substituted silenes and are characterized by EPR spectroscopy and density functional theory (DFT) calculations. According to the hyperfine coupling constants (*hfccs*) and the calculations, silenyl radicals have a strongly bent structure (<SiSi=C = 140.7°), in contrast to the nearly linear  $R_2C=C^{\bullet}-R$ . The spin is mostly located in a Si(sp) orbital. Daniel Pinchuk, Yosi Kratish, Jomon Mathew, Lieby Zborovsky, Dmitry Bravo-Zhivotovskii, Boris Tumanskii and Yitzhak Apeloig.

#### Generation and Electron Paramagnetic Spectroscopy of the First Silenyl Radicals (R<sub>2</sub>C=Si<sup>•</sup>-R). Experiment and Theory