Synthesis and X-ray Molecular Structure of the First Stable Organic Radical Lacking Resonance Stabilization

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Carbon-centered radicals constitute an important and extensively studied group of reactive intermediates.[1] However, despite extensive research the experimental structures of only four types of stable organic radicals have been reported: (1) triarylmethyl radicals **1**, with X = NO$_2$,[2] halogen;[3] (2) a per-pyridinium-substituted allyl radical, **2**;[4] (3) the cyclopentadienyl radical, **3**;[5] (4) the dodecamethylcarba-*closo*-dodecaboranyl radical (CB$_{11}$-Me$_{12}$•).[6] All of these radicals are strongly stabilized thermodynamically by effective delocalization of the unpaired electron and kinetically by the bulky substituents.[2−6] Bulky alkyl and silyl substituents can reduce the reactivity of simple localized carbon-centered radicals to the extend that they become "persistent".[1a,b] However, there are no examples of such radicals being a pure crystal.

1

2, P$^+$ = 4-Me$_2$N-pyridine

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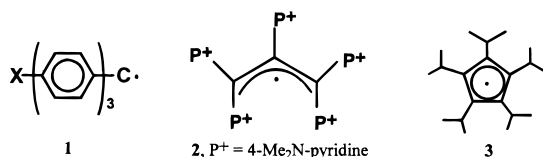
In this paper we report the preparation, the isolation, and the first X-ray characterization of an alkyl radical, which is not stabilized thermodynamically by conjugation with adjacent unsaturated bonds.

We reported that the reaction of acylsilane **4** with a 2-fold excess of Et$_3$GeLi in THF yields after hydrolysis the trisilacyclobutane **5** (Scheme 1).[7] However, recently we found that, if hydrolysis is avoided, the same reaction yields 15% of air-

Scheme 1

5 (55%) + **6 (15%)** + unidentified products (30%)
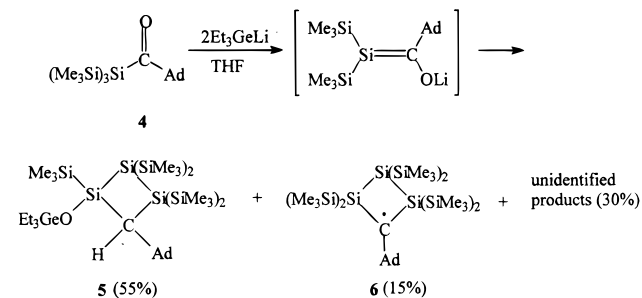
sensitive red crystals,[8] which were identified by X-ray analysis[9] to be the trisilacyclobutyl radical **6**. Both crystalline **6** and its hexane solution reveal unusual stability, retaining their paramagnetic properties for more than one year under vacuum at 0 °C.

An ORTEP drawing of the molecular structure of **6** and its most important geometrical parameters are given in Figure 1. The full crystallographic data are reported in the Supporting Information.

Radical **6** has a planar symmetric four-membered Si$_3$C ring. Comparison of the molecular structure of **6** with that of the closely related silane **5**[7] reveals that the main structural changes resulting from radical formation occur around the radical center; thus, r(C(10)−Si(3)) and α(Si(3)−C(10)-Si(3*)) in **6** (of 1.877(5) Å and 106.0(4)°, respectively) are by ~0.07 Å shorter and by 5° wider, respectively, than in **5**.

Crystalline **6** reveals an intense ESR spectrum showing a symmetrical singlet absorption with a *g* factor (2.00297) close to that of a free electron, having a line width of 0.182 mT an a concentration of paramagnetic centers of 0.9 ×10^{21} spin/g, (corresponding to one unpaired spin per molecule). The ESR spectrum[10] of an hexane solution of **6** (Figure 2) shows a strong central peak and four doublets with additional hyperfine coupling constants (hfc). The following assignments (Figure 2) can be made on the basis of ENDOR and simulated ESR data:[10] $a_{1-1'}$ = 3.800 mT corresponds to ^{13}C(10); $a_{2-2'}$ = 2.889 mT corresponds to ^{13}C-(11); $a_{4-4'}$ = 0.970 mT corresponds to the adamantyl's β-^{13}C nuclei of C(11a)*, C(11b), and C(11c); $a_{3-3'}$ = 1.902 mT corresponds to the ^{29}Si(1), ^{29}Si(1)*, ^{29}Si(2), and ^{29}Si(2)* nuclei. The satellites from ^{29}Si(3) and ^{29}Si(3)* are not observed, but they appear in the ENDOR spectra with a constant of 1.683 mT.[10] The best agreement between the experimental ESR spectrum and computer simulations[10,11] is obtained for the following hfc between C(10) and the adamantyl hydrogens: a = 0.0646 mT for the six α-H nuclei; a = 0.0371 mT for the three β-H nuclei; a = 0.0202 mT for the six γ-H and for the 36 H of methyl groups attached to Si(1), Si(1)*, Si(2), and Si(2)*.

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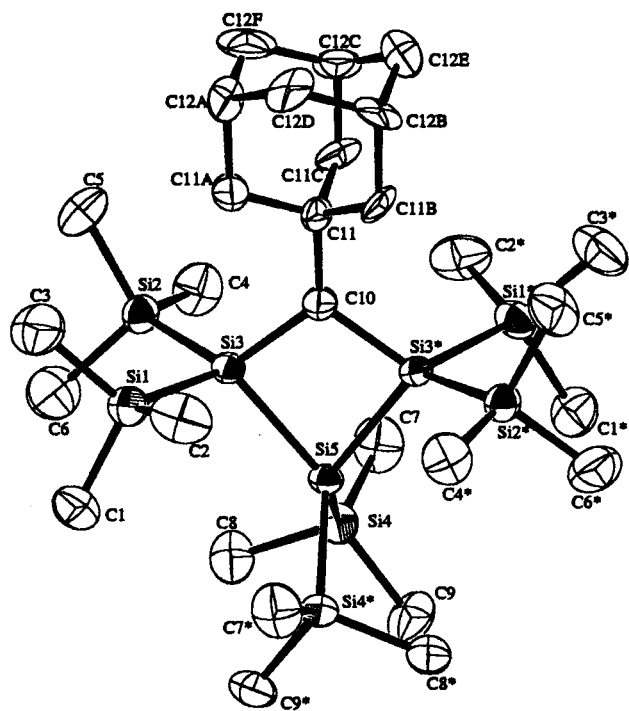(3) Armet, O.; Veciana, J.; Rovira, C.; Riera, S.; Castauer, S.; Molius, E.; Rins, J.; Niravitlles, C.; Olivella, S.; Brichfeus, S. *J. Phys. Chem.* **1987**, *91*, 5608.
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(8) All operations were carried out under vacuum using Schlenk techniques; 1.10 g (6.9 mmol) of Et$_3$GeLi in 5 mL of THF was added at 20 °C to a solution of **4** (1.35 g, 3.3 mmol) in 10 mL of THF. The reaction mixture becomes dark red. After being stirred for 45 min, the solvent and the volatile products were removed in vacuum and the red solid material was dissolved in hexane. After 24 h at 20 °C a white precipitate (0.19 g, 34%) of Ad(LiO)C= C(OLi)Ad[7] was formed. The pink filtrate was slowly evaporated at −5 °C, and red crystals of **6** (0.16 g, 15%) suitable for X-ray analysis were isolated.
(9) Crystal data for **6** (C$_{29}$H$_{69}$Si$_9$): orthorhombic, *Pbnc*, red prism (0.35 × 0.30 × 0.27 mm), *a* = 12.744(7), *b* = 20.051(7), *c* = 16.462(3) Å, *V* = 4207(3) Å^3, *Z* = 4, d_{calc} = 1.01 g/cm^3, μ = 3.65 cm^{-1}, *T* = 150 K, Mo Kα radiation. Intensities of 3042 (1538) reflections (unique) were measured with a Syntex *P*2$_1$ diffractometer (Mo Kα, 16° < 2Θ < 56°), R_{int} = 0.0039, 373 parameters refined, GOF = 1.027, ω/2Θ method, *R* = 0.0536, R_w = 0.1320. The structure was solved by direct methods and refined anisotropically for nonhydrogen atoms. The adamantyl group is disordered because of the presence of a 2-fold axis. Two possible positions of the adamantyl group were included, and the positions of all carbon atoms were refined with constrained bonds and half occupancy.
(10) The full description of the ENDOR and ESR spectra and of the ESR simulated spectrum are given in the Supporting Information.
(11) The WINEPR SimFonia 1.25 program was used. Bruker, Inc. 1996.

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Figure 1. An ORTEP drawing of radical **6**. Selected bond lengths (Å) and bond angles (deg): C(10)−C(11), 1.519(10); C(10)−Si(3), 1.877(5); Si(3)−Si(5), 2.393(2); Si(2)−Si(3), 2.369(3); Si(4)−Si(5), 2.374(2); Si-(3)−C(10)−Si(3)*, 106.0(4); C(10)−Si(3)−C(1), 88.2(2); Si(3)−Si(5)−Si(3)*, 77.56(10); Si(1)−Si(3)−Si(2), 102.61(10); Si(4)−Si(5)−Si(4)*, 101.46(11).
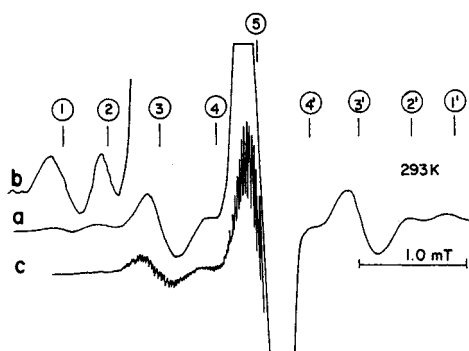
Figure 2. ESR spectrum (hexane) of **6**: (a) survey ESR spectra (ampl. mode 0.1 mT, receiver gain 0.5×10^4); (b) side components of ^{13}C and ^{29}Si (ampl. mod. 0.1 mT receiver gain 4×10^4); (c) low field part at high-resolution conditions (ampl. mod. 0.01 mT, receiver gain 4×10^4).
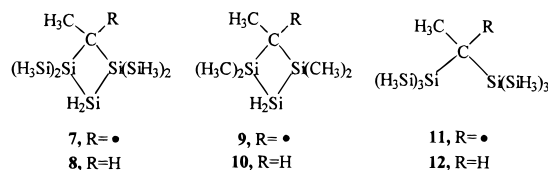
Further insights into the electronic nature of radical **6** and its surprising high kinetic stability are provided by molecular orbital and density functional calculations for model systems.[12−14] The calculated spin densities show that most of the α-spin in **7** resides on the radical center (0.84 el.). However, there is significant spin

delocalization to the β-silyl groups ($0.058 \times 2 + 0.062 \times 2 = 0.24$ el.), as well as significant spin polarization to the α-C and Si atoms. For comparison, the spin at C_α of Me$_3$C• and Ph$_3$C• is 0.96 and 0.65 el. respectively.

7, R= •
8, R=H

9, R= •
10, R=H

11, R= •
12, R=H

Is **6** stabilized by electronic effects? This might be suggested by the well-documented ability of polysilyl substituents to stabilize aromatic cation radicals and anion radicals.[15] The calculated energies[16] of the isodesmic eqs 1 and 2 show, however, that **6** does *not* possess a special thermodynamic stability and that the energetic consequences of β-silyl hyperconjugation (HC) are small. Thus, **7** (with 4 β-silyl groups) is more stable than **9** (with 4 β-methyl groups) by only 2.6 kcal/mol (eq 1, by 3.3 kcal/mol if the Me groups in **9** are substituted by H). Ring closure has little effect on the stability of **7** (eq 2). Furthermore, **7** is only 6.9 kcal/mol more stable than the highly reactive *tert*-butyl radical (**7** + t-BuH → **8** + t-Bu•)[17] and is by 12.6 kcal/mol *less stable* than Ph$_3$C• (**7** + Ph$_3$CH → **8** + Ph$_3$C•).[16] We conclude that HC between the unpaired electron and the β-(Si−Si) bonds is of minor energetic consequences.

$$\mathbf{7} + \mathbf{10} \rightarrow \mathbf{9} + \mathbf{8} \quad \Delta E = 2.6 \text{ kcal/mol} \quad (1)$$

$$\mathbf{7} + \mathbf{12} \rightarrow \mathbf{11} + \mathbf{8} \quad \Delta E = 0.9 \text{ kcal/mol} \quad (2)$$

As **6** does not possess special thermodynamic stability and its unpaired spin is not strongly delocalized, we attribute its successful isolation to its high kinetic stability, resulting from the presence of the bulky adamantyl and branched polysilyl groups, which shield the radical center from further reactions (e.g., dimerization).[18] Further studies on this interesting radical as well as on the intriguing mechanism leading to its formation are in progress.

Supporting Information Available: Crystallographic data for **6**, simulated ESR spectrum of **6**, and ENDOR spectra of **6** recorded at 3 different field settings and different temperature. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Calculations were performed using density functional methods[13] implemented in the GAUSSIAN 94 program.[14] The geometries of all molecules were fully optimized, including frequency calculations, at the B3LYP/6-31G* level of theory;[14] energy comparisons include zero-point vibrational energies (ZPVE).
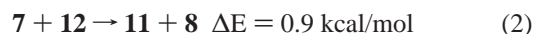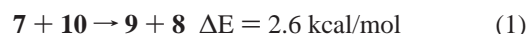
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(16) The high reliability of B3LYP/6-31G* calculations for radicals is demonstrated by the good agreement between the calculated (19.5 kcal/mol) and the experimental (20 ± 1.7 kcal/mol) energies (see: Beckhaus, H. D.; Dogan, B.; Schaetzer, J.; Rüchardt, C. *Chem. Ber.* **1990**, *123*, 137) for the isodesmic equation: Ph$_3$C• + Me$_3$CH → Me$_3$C• + Ph$_3$CH.

(17) Me(H$_3$Si)$_2$C• is more stable than Me$_3$C• by 5.0 kcal/mol (at B3LYP/6-31G* + ZPVE).

(18) This conclusion is supported by MM3 calculations (Macromodel 5.0, Columbia University, 1995; the missing parameter for the SiSiCSi angle was set to 0.11 kcal/mol), which shows that the hypothetical dimer of **6** spontaneously dissociates due to steric congestion, even for r(C−C) = 1.65 Å.