Relative Reactivity

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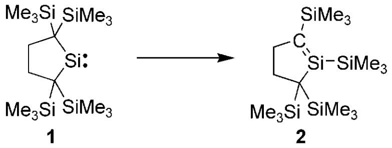
Probing the Reactivity of a Stable Silene Using Muonium[**]

Brett M. McCollum, Takashi Abe, Jean-Claude Brodovitch, Jason A. C. Clyburne, Takeaki Iwamoto, Mitsuo Kira, Paul W. Percival, and Robert West*

Since the discovery of stable multiply bonded silicon compounds in 1981, the synthesis and reactivity of silenes ($R_2Si{=}CR_2$) has been a major focus of research and many review articles have been published on this matter.[1] However, despite the level of activity in this field, there is little understanding of the radical chemistry of silenes.

The silylene 2,2,5,5-tetrakis(trimethylsilyl)silacyclopentane-1,1-diyl, **1**, rearranges to the silene 1,2,5,5-tetrakis(trimethylsilyl) silacyclopentene, **2**, at room temperature by 1,2-migration of a trimethylsilyl group (Scheme 1).[2] Herein, we report the use of an analogue of the hydrogen atom as a probe of the relative reactivity of the silenic carbon and silicon atoms of **2** toward radical addition.



Scheme 1. Rearrangement of silylene 2,2,5,5-tetrakis(trimethylsilyl) silacyclopentane-1,1-diyl into silene 1,2,5,5-tetrakis(trimethylsilyl) silacyclopentene.

The hydrogen atom is an exceptional probe of reactivity because its small size minimizes steric obstruction and its simple structure avoids additional electronic effects; we consider the hydrogen atom to be an unbiased radical probe, since it is monoatomic and, therefore, not polar. However, the hydrogen atom is not a common reagent for solution studies, largely because of complications inherent in its generation. Hydrogen atoms are usually produced by photolysis or radiolysis of water or other protic solvents, inevitably resulting in additional radical species.

Rather than make use of H atoms to generate radicals and electron spin resonance to detect them, we have employed muonium ($Mu = [\mu^+e^-]$), and detected radicals by techniques collectively known as muon spin rotation and resonance (μSR).[3–6] Muonium is a single-electron atom whose nucleus is the positive muon. It is chemically equivalent to H, but has only one-ninth the mass. The utility of muonium as a probe of hydrogen atom chemistry is well documented.[7–9] A brief description of the μSR techniques used in this work is given in the Supporting Information.

A 1.5 M solution of **2** in tetrahydrofuran was placed in a beam of positive muons and investigated by transverse-field muon spin rotation spectroscopy (TF-μSR). When positive muons stop in matter, a fraction (30–40 % in typical organic compounds) bind electrons and form muonium, which can then react with unsaturated molecules, as H does. The TF-μSR spectrum collected at 298 K in a magnetic field of 14.5 kG is shown in Figure 1. At high magnetic fields, muoniated radicals can be identified by a characteristic pair of precession frequencies, equally spaced about the diamagnetic signal (196 MHz in this case). The difference between the radical precession frequencies is equal to the muon hyperfine coupling constant (hfc), A_μ. It is clear from the TF-μSR spectrum (Figure 1) that two distinct radicals are formed. One, labeled A, has $A_\mu = 186.66(\pm 0.13)$ MHz, and the other,

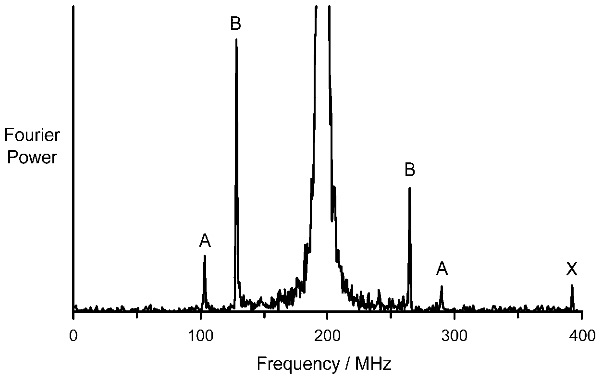


Figure 1. TF-μSR spectrum from a 1.5 M solution of **2** in THF at 298 K and 14.5 kG. The signal near 400 MHz (labeled X) is an overtone of the 196 MHz diamagnetic signal.

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[*] B. M. McCollum, Dr. J.-C. Brodovitch, Dr. P. W. Percival
Department of Chemistry, Simon Fraser University
8888 University Drive, Burnaby, BC, V5A 1S6 (Canada)
Fax: (+1) 778-782-3765
E-mail: percival@sfu.ca

Dr. J. A. C. Clyburne
Department of Chemistry, Saint Mary's University, Halifax (Canada)

Dr. T. Abe, Dr. T. Iwamoto, Dr. M. Kira
Department of Chemistry and Research and Analytical Center for Giant Molecules
Graduate School of Science, Tohoku University (Japan)

Dr. R. West
Organosilicon Research Center, University of Wisconsin (USA)

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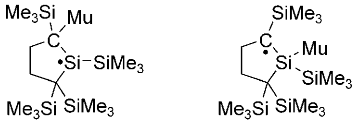
labeled B, has $A_\mu = 136.99(\pm 0.05)$ MHz. Their signal intensities indicate that they are formed in different yields. Radical B is favored over radical A by a factor of 2.2 (determined by fitting the μSR spectra in time-space).

The two radicals expected from Mu addition to **2** are **2-CMu** and **2-SiMu** (Scheme 2). Since there is no precedent in the literature for the hyperfine constants of these radicals or their H analogues, it was not immediately apparent which radical corresponds to which signal.



2-CMu **2-SiMu**

Scheme 2. Radical products formed by Mu addition to silene **2**.

To assist in the assignment, another sample of **2** was investigated by muon avoided level-crossing resonance (μLCR) spectroscopy. The spectrum obtained from a 1 M solution of **2** in THF at 312 K is shown in Figure 2. The shape of the signal is typical of two overlapping resonances.[10] Since protons are the only spin-active nuclei with large enough abundance to generate the spectrum, the resonances can be assigned to the two inequivalent protons which are β to the radical center in **2-SiMu**. In **2-CMu** the closest protons are γ to the unpaired electron and would not be detected by μLCR. In principle the proton hfcs (A_p) can be found from the two resonance-field positions (B_{LCR}). However, until structures have been assigned to radicals A and B there is ambiguity in determination of A_p, because B_{LCR} also depends on A_μ. Table 1 lists the two possible interpretations of the μLCR data, taking into account the values of A_μ determined at 312 K.

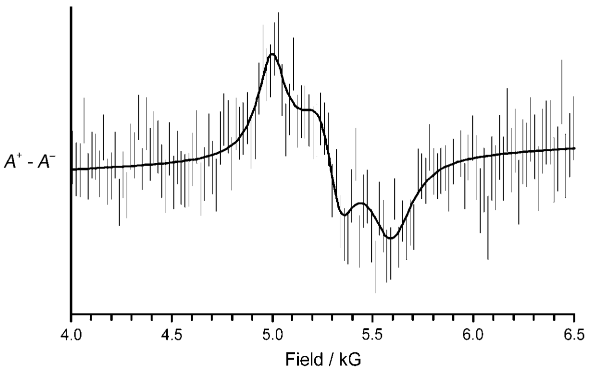


Figure 2. μLCR spectrum of a 1 M solution of **2** in THF at 312 K.

To resolve the ambiguity, hyperfine constants were computed for the two H-adduct radicals of silene **2**. Geometry optimization was performed at the UB3LYP/6-31G(d) level (see the Supporting Information for atom coordinates), and hyperfine coupling constants predicted at the UB3LYP/cc-pVDZ level. Muon hfcs were then obtained by multiplying the corresponding proton hfc by 3.18, the ratio of the muon and proton magnetic moments. The predicted muon hfcs are listed in Table 2, together with the β-proton hfcs for **2-SiMu**. No attempt was made to calculate the effect of vibrational averaging, so the hfcs listed correspond to minimum energy conformations. Furthermore, the light mass of muonium leads to higher zero-point energies than H, resulting in significant isotope effects from conformational averaging, such as a 30–40 % increase in the muon hfc for alkyl radicals.[11] Since there is no precedent, either experimental or computational, for the radicals considered here, the predictions of Table 2 must be considered a guide only.

Table 1: Potential proton hyperfine coupling constants based on a μLCR spectrum from a 1 M solution of **2** in THF at 312 K.[a]

B_{LCR} [G]	A_p [MHz] if $A_\mu \approx 190$ MHz (Radical A)	A_p [MHz] if $A_\mu \approx 137$ MHz (Radical B)
5166(7)	92.61(30)	40.30(14)
5424(10)	87.83(33)	35.52(19)

[a] Statistical errors are shown in parentheses.

Table 2: Computed muon (A_μ) and β-proton (A_p) hyperfine coupling constants for the radicals from muonium addition to **2**.

	A_μ [MHz]	A_p [MHz]
2-CMu	101	
2-SiMu	226	113, 40

The average proton hfc predicted for **2-SiMu** is 76.5 MHz, which is a closer match for radical A than radical B (Table 1). In addition, the muon hfc predicted for **2-SiMu** is closer to that of radical A. Therefore we assign the structure **2-SiMu** to radical A (larger muon hfc), and **2-CMu** to radical B (smaller muon hfc). Finally, we note that the predicted heat of reaction for formation of **2-CMu** (-340.2 kJ mol^{-1}) is lower than that for **2-SiMu** (-322.3 kJ mol^{-1}). Assuming that the activation energies for the two reaction channels follow the same order, we predict a preference for addition to the carbon atom, in agreement with the assignment of **2-CMu** to the stronger signal (radical B).

In summary, the addition of a hydrogen atom analogue to silene **2** was studied by μSR methods. The detected radicals are attributed to the species formed by muon addition to the silenic carbon or silicon atoms. The carbon atom was found to be more reactive toward radical attack than the silicon atom by a factor of 2.2. This report concerns the first case of detection and identification of a muoniated silicon-centered radical.

Experimental Section

Purified samples of **2** (1.1 g and 1.2 g) were dissolved in degassed tetrahydrofuran (THF) (3 mL and 2 mL, respectively) under a nitrogen atmosphere, and sealed oxygen-free in a stainless steel cell equipped with a thin stainless steel window. μSR experiments were performed at the M20 beam line at TRIUMF in Vancouver, Canada, using standard equipment and techniques.[12]

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[1] a) L. E. Gusel'nikov, N. S. Nametkin, *Chem. Rev.* **1979**, *79*, 529; b) G. Raabe, J. Michl, *Chem. Rev.* **1985**, *85*, 419; c) A. G. Brook, M. A. Brook, *Adv. Organomet. Chem.* **1996**, *39*, 71; d) R. West, *Polyhedron* **2002**, *21*, 467; e) "Modern Aspects of Main Group Chemistry": R. West, *ACS Symp. Ser.* **2006**, *917*, 166–178; f) H. Ottosson, A. M. Eklöf, *Coord. Chem. Rev.* **2008**, *252*, 1287.

[2] M. Kira, S. Ishida, T. Iwamoto, C. Kabuto, *J. Am. Chem. Soc.* **1999**, *121*, 9722.

[3] S. F. J. Cox, *J. Phys. C* **1987**, *20*, 3187.

[4] J. H. Brewer, *Encyclopedia of Applied Physics*, *Vol. 11*, VCH Publishers, New York, **1994**, pp. 23–53.

[5] E. Roduner, *Appl. Magn. Reson.* **1997**, *13*, 1.

[6] S. J. Blundell, *Contemp. Phys.* **1999**, *40*, 175.

[7] E. Roduner, *The Positive Muon as a Probe in Free Radical Chemistry (Lecture Notes in Chemistry 49)*, Springer, Berlin, **1988** .

[8] D. C. Walker, *J. Chem. Soc. Faraday Trans.* **1998**, *94*, 1.

[9] C. J. Rhodes, *J. Chem. Soc. Perkin Trans. 2* **2002**, 1379.

[10] P. W. Percival, J.-C. Brodovitch, K. Ghandi, B. M. McCollum, I. McKenzie, *J. Am. Chem. Soc.* **2005**, *127*, 13714.

[11] E. Roduner, W. Strub, P. Burkhard, J. Hochmann, P. W. Percival, H. Fischer, M. Ramos, B. C. Webster, *Chem. Phys.* **1982**, *67*, 275.

[12] P. W. Percival, B. Addison-Jones, J.-C. Brodovitch, K. Ghandi, J. Schüth, *Can. J. Chem.* **1999**, *77*, 326.