DOI: 10.1002/ange.201000166

Organosilicon Radicals

A Silyl Radical formed by Muonium Addition to a Silylene**

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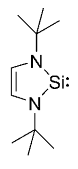
Recently, we published transverse field muon spin rotation (μSR) spectra for the stable N-heterocyclic silylenes **1** and **2**, after exposure to a positive muon beam at the TRIUMF cyclotron.[1–4] These were the first μSR spectra of silicon-centered radicals to be reported. The spectrum of **1** is shown in Figure 1 a. The muon hyperfine coupling constant (hfc) for a muoniated radical can be estimated from the calculated proton hfc of an isotopomeric radical in which the muonium atom has been replaced by a hydrogen atom. Corrections must be made for the larger muon gyromagnetic ratio (a factor of 3.18), and for the effects of increased zero-point vibrational energy in the muoniated radical (typically 20 %). This procedure affords values that are in reasonable agreement with the measured hfcs for muonium adducts of stable carbenes.[5] However, for the silylenes, the muon hfcs measured for **1** and **2** (235 and 155 MHz, respectively) are far lower than the values predicted for these species by DFT calculations (700–1000 MHz, depending on the magnitude of the zero-point energy correction). To explain this discrepancy we proposed that the initially formed silylene–muonium adducts react with other silylene molecules to produce the muoniated disilanyl radicals **1a** and **2a**, as shown for **1** in Scheme 1.[3,4]



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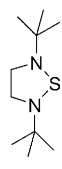

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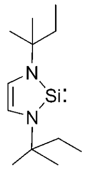

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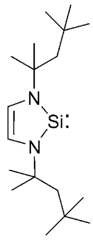

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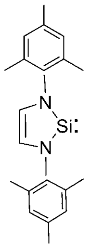

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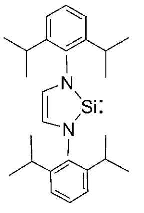

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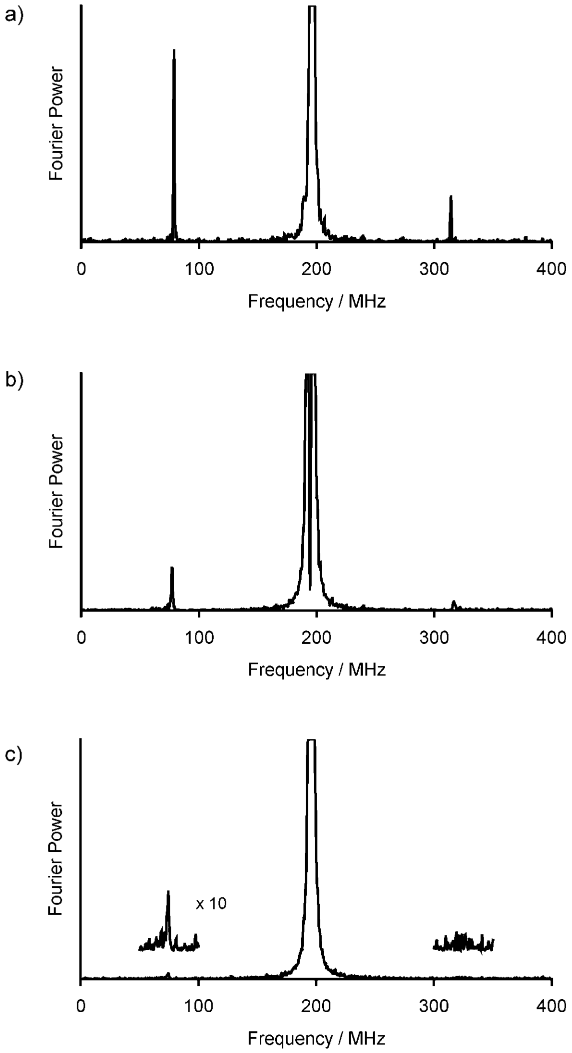

Figure 1. Transverse field μSR spectra at 14.5 kG that were obtained from solutions of various silylenes: a) **1** (1.55 M in tetrahydrofuran, 26 °C), b) **3** (1.16 M in *n*-hexane, 25 °C), and c) **4** (1.27 M in *n*-hexane, 25 °C). The truncated peak at 196 MHz is due to muons that are in diamagnetic environments, which precess at the muon Larmor frequency. In each spectrum, the two peaks that are equidistant from, and either side of, the diamagnetic signal are characteristic of a muoniated radical. The vertical scale is the same in each spectra (except where indicated); however, as these are Fourier power plots, the relative peak heights correspond to the squares of signal amplitudes.

μSR detection of disilanyl radical products requires special kinetic conditions, in particular, a fast reaction

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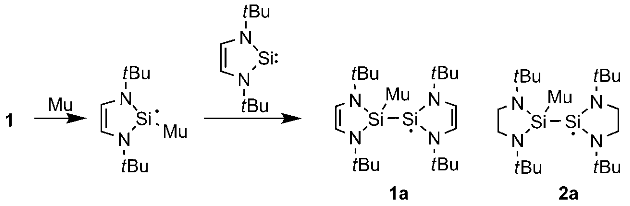
[**] We thank the staff of the Centre for Molecular and Materials Science at TRIUMF for technical support. This research was supported by the Natural Sciences and Engineering Research Council of Canada, and by the Organosilicon Research Center at the University of Wisconsin-Madison.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201000166.



Scheme 1. Coupling of a muoniated radical with silylene.

between the initially formed muoniated radical and the native silylene.[3] Nevertheless the calculated hfcs for the proposed disilanyl radicals are in satisfactory agreement with the measured values. Furthermore, the µSR spectrum obtained from a 1:1 mixture of **1** and **2** exhibited four radical signals whose hfc values (235, 155, 212, and 177 MHz) correspond to dimers **1a** and **2a** and the two possible cross-coupled products, respectively.[4]

Although these observations are consistent with the dimerization hypothesis, we lacked a genuine example of a silylene–muonium adduct. To generate such a species, we increased the steric bulk of the substituents on the nitrogen atoms. Upon muon irradiation, silylenes **3** and **4**, which contain *tert*-amyl and *tert*-octyl substituents, respectively,[6,7] yielded spectra similar to those for **1** and **2**; as such, we assigned these products as similar disilane radicals. However, the spectra became progressively weaker as the size of the alkyl groups increased (Figure 1 b,c), and there was a clear trend toward larger values in the muon hfcs as the steric hindrance increased (Table 1).

Table 1: Muon hyperfine coupling constants.[a]

Parent silylene	Muon hfc [MHz]
1	235.4 ± 0.1
3	239.6 ± 0.1
4	244.3 ± 0.3
6	931.3 ± 0.2

[a] Coupling constants were determined from the µSR spectra of radicals that were derived from a series of silylenes.

Silylene **5**, in which the *tert*-butyl groups were replaced with mesityl substituents,[6] yielded no observable µSR spectrum. However, when the alkyl groups on the nitrogen atoms were replaced by 2,6-diisopropylphenyl (dipp) groups (**6**),[6,7] an entirely different spectrum was obtained (Figure 2) that corresponded to a radical with a muon hfc of 931.3 MHz (Table 1). This value exceeds the largest muon hfc value reported for an organic radical by over 25 %.[8] It is only evident at a negative precession frequency (defining the muon Larmor precession as positive). Details of how the hfc is extracted from the spectrum are given in the Supporting Information.

The validity of the high muon hfc was tested by comparison of the muon level crossing resonance (µLCR) spectra obtained from samples of **3** and **6**. The expected resonances from ^{14}N nuclei occur at very different fields (Figure 3) because the resonance field is proportional to the difference in hfcs of the muon and the interacting spin nucleus. Quantitative analysis (for details, see the Supporting Information) gave ^{14}N nuclei hfcs of 12.0 MHz for the radical derived from **3**, and 16.3 MHz, or 15.4 MHz and 16.9 MHz, for the radical derived from **6**. The latter uncertainty arises because the signal-to-noise ratio in spectrum 3 b is insufficient to distinguish between a single resonance or two overlapping signals. These values are close to the ^{14}N nuclei hfcs that were reported for muoniated radicals that were derived from other N-heterocyclic carbenes and silylenes,[4,5] but can not be used to distinguish between the primary muonium adducts and potential coupling products. Nevertheless, the detection of a high-field µLCR signal from **6** is additional evidence for an unprecedented high muon hfc.

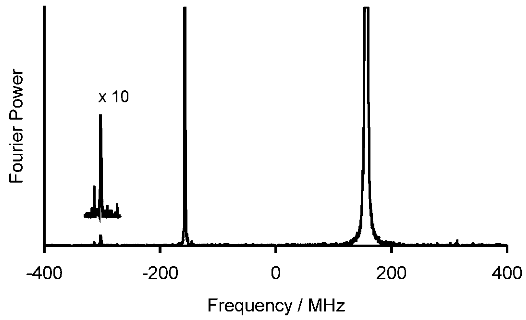


Figure 2. Transverse field µSR spectrum at 11.6 kG obtained from silylene **6** (1.15 M in tetrahydrofuran, 23 °C). The diamagnetic signal is at +157 MHz. Only one of the radical precession frequencies is evident (at −302 MHz), the other being too high (+619 MHz) for detection. The peak at −157 MHz is a "ghost" of the diamagnetic signal and is due to the imperfect quadrature setting of the positron detectors.

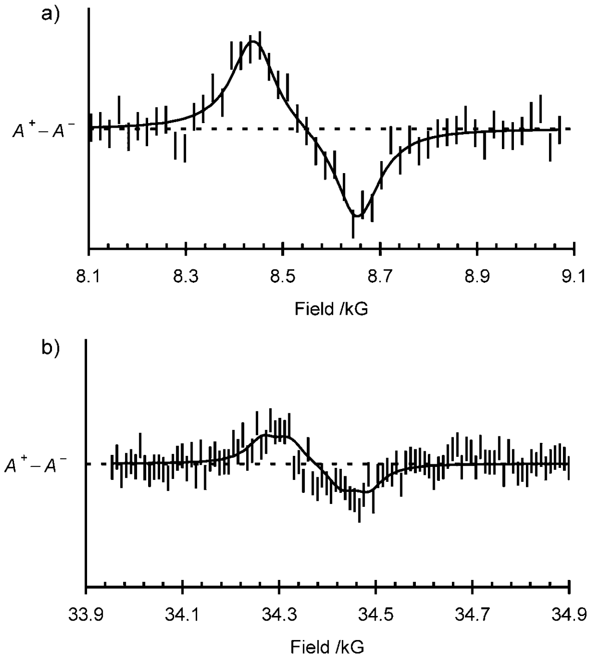
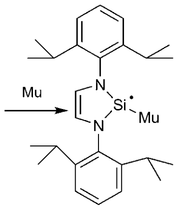


Figure 3. µLCR spectra that show radical ^{14}N nuclei resonances formed from: a) **3** (1.16 M in *n*-hexane, 25 °C), and b) **6** (1.15 M in tetrahydrofuran, 23 °C). The vertical scale of (b) is twice that of (a). $A^+ - A^-$ = field-modulated muon asymmetry.

The large hfc that was obtained from **6** is in the range expected for a simple muonium adduct of the silylene, and therefore, we assign it to radical **6a**.

6



6a

The hydrogen atom analogue of **6a** was investigated using DFT calculations. Geometry optimization was performed at the UB3LYP/6-31G(d) level (for atom coordinates, see the Supporting Information) and hyperfine coupling constants predicted at the UB3LYP/cc-pVDZ level. The proton hfc of the hydrogen atom attached to the silicon center is predicted to be 210.7 MHz, compared with 671 MHz for the muonium equivalent. Comparing this with the muon hfc of 931 MHz obtained experimentally, we infer a zero-point vibrational correction of almost 40%. This is high but not unprecedented.[9] The unusually large hfc arises from a structure in which the Si–Mu(H) bond is almost perpendicular to the ring plane (Figure 4), so that the Mu(H) atom overlaps the silaimidazole π system.[10] In contrast, the muonium adduct of a carbene has a near-planar radical center with the muonium in a sigma-type orbital, which leads to much weaker muon–electron coupling.[5]

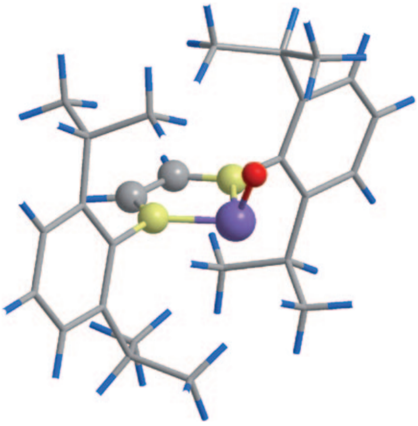


Figure 4. Optimized molecular geometry of silyl 6a showing the location of the Mu atom (red) with respect to the silaimidazole ring (Si violet, N yellow, C gray, H blue).

We now offer an explanation for the decreasing signal intensity upon going from **1** to **3**, **4**, and **5**. The amplitude of the muoniated disilanyl radical μSR signals depends on the amount of coherent muon spin precession. Spin dephasing (i.e. incoherence) occurs when the rate of transformation from the silyl species into the disilanyl product is slower than the difference in precession frequencies of the two radicals.[3] The larger substituent groups led to slower coupling reactions and hence to weaker μSR signals. In the case of the mesityl-substituted compound, the coupling rate evidently falls into a "window of invisibility"—too fast for the initially formed silyl radical to be detected, but too slow for the disilanyl product to be observed. This region comprises a first-order rate of transformation of a primary radical into a secondary radical of approximately $10^{7}\,s^{-1} > \lambda > 2\times10^{8}\,s^{-1}$.

In conclusion, we have detected a primary radical adduct between a silylene and muonium for the first time. This was possible by preventing the conversion of the primary radical into a secondary disilanyl radical by introducing bulky substituents close to the silicon atom. The effects of various substituents at different positions on the silaimidazole ring on the nature of the silylene–muonium adduct and their corresponding reaction rates are currently under investigation.

Recent years have seen a blossoming of the chemistry of stable silylenes, with a variety of novel structures being reported.[10] We anticipate that many of these new silylenes will also display useful and interesting muonium chemistry.

Received: January 11, 2010

Keywords: disilanes · muonium · radicals · silylenes

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[1] TRIUMF in Vancouver, Canada, is one of only four accelerators in the world that has intense beams of spin-polarized muons that are necessary for μSR spectroscopy. For a full explanation of μSR, see: a) I. McKenzie, E. Roduner, *Naturwissenschaften* **2009**, *96*, 873–887; b) S. J. Blundell, *Chem. Rev.* **2004**, *104*, 5717–5735.

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[10] Upon muon irradiation, N-heterocyclic germylenes also produce radicals with large coupling constants, probably for similar reasons. For example, the germanium analogue of **1** has a muon hfc of 650 MHz.[4]

[11] For examples, see: M. Driess, S. Yao, M. Brym, C. van Wullen, D. Lentz, *J. Am. Chem. Soc.* **2006**, *128*, 9628–9629; C.-W. So, H. W. Roesky, P. M. Gurubasavaraj, R. B. Oswald, M. T. Gamer, P. G. Jones, S. Blaurock, *J. Am. Chem. Soc.* **2007**, *129*, 12049–12054; H. Cui, Y. Shao, X. Li, L. Kong, C. Cui, *Organometallics* **2009**, *28*, 5191–5195; A. Mitra, J. P. Wojcik, D. Lecoanet, T. Mueller, R. West, *Angew. Chem.* **2009**, *121*, 4130–4133; *Angew. Chem. Int. Ed.* **2009**, *48*, 4069–4072; S. S. Sen, A. Jana, H. W. Roesky, C. Schulzke, *Angew. Chem.* **2009**, *121*, 8688–8690; *Angew. Chem. Int. Ed.* **2009**, *48*, 8536–8538; S. Yao, M. Brym, C. van Wullen, M. Driess, *Angew. Chem.* **2007**, *119*, 4237–4240; *Angew. Chem. Int. Ed.* **2007**, *46*, 4159–4162; L. Kong, J. Zhang, H. Song, C. Cui, *Dalton Trans.* **2009**, 5444–5446; S. Sen, H. W. Roesky, D. Stern, J. Henn, D. Stalke, *J. Am. Chem. Soc.* **2010**, *132*, 1123–1126.