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「化学と工業」ロバート・ウェスト教授　英文論文

「化学と工業」誌 61巻11月号 p.1059-1061 話題「ミューオンスピン共鳴：有機金属化合物の新分光法」の原文。（英文）
日本語訳では詳細な数値、図、本分光法の測定できる研究機関など、一部を割愛した。

Muon Spin Resonance: A New Spectroscopy for Organometallic Compounds

Robert West

Organosilicon Research Center, University of Wisconsin, Madison WI 53706 USA

The first muon spin resonance experiments have been carried out for organosilicon and organogermanium compounds within the past year. Muon spin resonance, which will be abbreviated μSR, is distantly related to NMR and EPR spectroscopy, though unfortunately somewhat more complicated to carry out. However it provides information about organometallic compounds not obtainable in any other way. This review presents a greatly simplified explanation of muon spin resonance,[1] followed by some examples from recent μSR studies of silicon and germanium compounds

First, what are muons? They are subatomic particles of antimatter. To generate them a high-energy beam of protons is needed, from a cyclotron or similar nuclear accelerator. When the protons are allowed to strike a target of a light element (beryllium or carbon are usually used), they cause a nuclear reaction leading to the formation of pi mesons. These "pions" are unstable, with a lifetime of only 26 nanoseconds; they decay into a muon[2] and a neutrino:

$$\pi^+ \longrightarrow \mu^+ + \nu_\mu$$

The muons are also unstable, decaying into a positron and a pair of neutrinos:

$$\mu^+ \longrightarrow e^+ + \nu_e + \nu_\mu$$

The muon lifetime is 2.2 microseconds. Remarkably, this window of time is long enough to permit us to study their chemical reactions.

In their chemical behavior muons resemble protons. Table 1 compares the properties of muons and protons. Both have +1 charge and spin ½.
The muon mass is about 1/9 that of a proton, and the magnetic moment of the muon is 3.18 times that of a proton. Notice the lifetimes differ enormously!

Table 1. Muons compared to protons

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	H^+	μ^+
charge	+1	+1
spin	½	½
mass	1.008	0.113
magnetic moment	(1)	3.18
mean lifetime	10^{36} y	2.2×10^{-6} sec

In contact with matter, the muons capture electrons and become muonium atoms, which are here symbolized Mu. The muonium atom can be regarded as an ultralight isotope of hydrogen. What we observe by muon spin resonance spectroscopy are the addition products of muonium with unsaturated molecules. The positrons formed in the muon decay are then detected and counted individually, one-by-one.

There are two main types of muon resonance experiments. The most common and straightforward is transverse field muon spin resonance, TFμSR.

Figure 1 diagrams this experiment. A beam of muons, 100% polarized, passes through a muon detector which starts an electronic clock, preparing the positron detectors to receive a positron. The clock later resets to wait for the next positron.

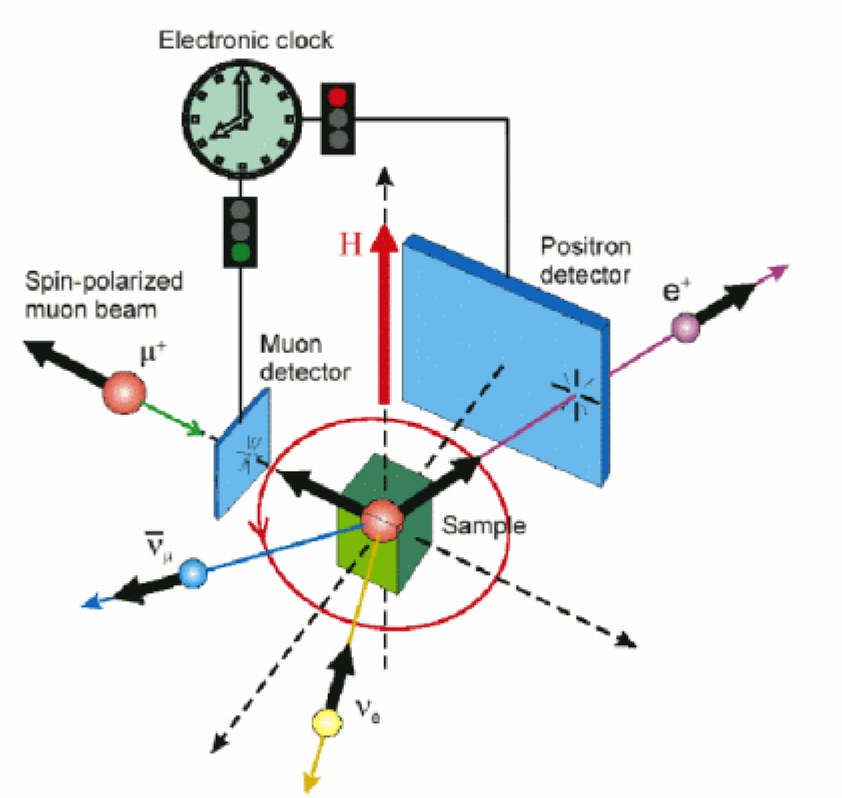


Figure 1. The transverse field μSR experiment. Drawing by Jeff Sonier, TRIUMF.

As the name indicates this experiment is carried out in a transverse magnetic field, The muon spins precess in this field, just as spins do in NMR experiments. Most of the muonium atoms do not carry out chemical reactions, and for these the muon spins precess at their natural Larmor frequency. Such muons eventually decay in a diamagnetic environment, producing a strong line in the μSR spectrum. But, if a suitable substrate molecule is present, some of the muonium atoms may react with it to form a new, muoniated, radical species. In this case the precession is modulated and the positron detectors find resonances for the muoniated radical. At a sufficiently high magnetic field, after Fourier transformation, resonances appear as a pair of lines, symmetrically placed about the line for the unreacted muons. The difference between the two radical lines is the muon hyperfine splitting constant, Aμ, a measure of the interaction between the muon and the unpaired electron. Figure 2 shows an example.

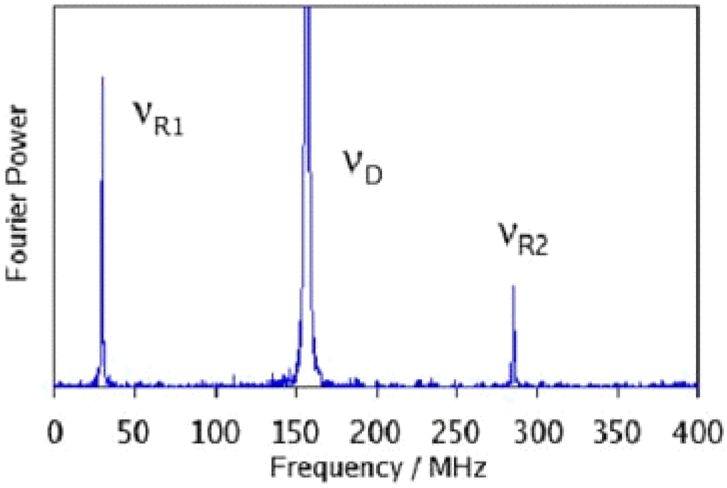
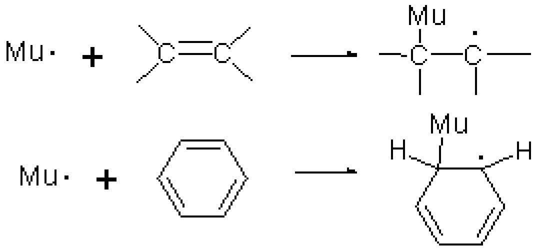


Figure 2. A typical TFμSR spectrum. nD is the resonance for the unreacted muons, which decay in a diamagnetic environment. The hyperfine splitting constant Aμ is given by $\nu_{R2} - \nu_{R1}$.

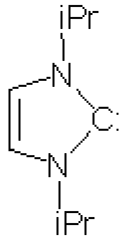
Muon spin resonance is not actually a new technique; the first TFμSR was recorded thirty years ago,[3] and many spectra have been determined for unsaturated organic compounds, including alkenes, alkynes, aromatic compounds, nitriles, and ketones.[1b] The muonium atoms add to the multiple bonds or aromatic bonds to give muon-containing radicals:



Some typical values of the hyperfine coupling constant, Aμ, in MHz are: benzene, 515 ;toluene, 169 and 183; 2-methylpropene, 292; 2,3-dimethyl-2-butene, 161; 2-methylbutadiene, 181 and 200; and acetone, 26. Ketones produce lower values for Aμ because the muon attaches to the oxygen atom, and then interacts only weakly with the unpaired electron.

These spectra can be calculated theoretically (using hydrogen in place of the muon, and adjusting for the differences between them), and while questions remain, these organic hyperfine splitting constants are now fairly well understood. However nearly all of the compounds studied have been those which yield carbon-centered radicals. The application of this method to heavier elements has been almost unknown.[4] The reason is that for muon capture to take place, a site of unsaturation is required. And although unsaturated compounds of heavier main group elements have also been known for nearly thirty years,[5] they were not generally available to physical chemists studying μSR.

Our interest in this kind of spectroscopy arose from a paper published by a group from Simon Fraser University led by P. W. Percival, displaying μSR spectra for a stable diaminocarbene, 1.[6] This interested us greatly, because for several years we had been deeply concerned with the chemistry of stable silylenes (2, 3) and germylenes (4, 5) with similar structure.[7] All of these compounds are stabilized by electron donation from the nitrogen atoms to the vacant p orbital of the divalent atom. In addition the unsaturated compounds, 1, 2 and 4, may be stabilized by aromatic cyclodelocalization in the 6-pi-electron ring (6).[8]



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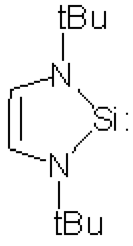

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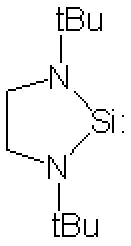

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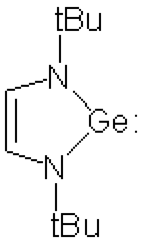

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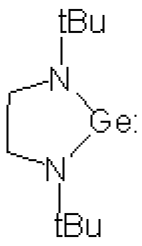

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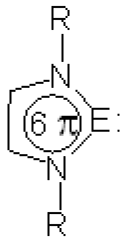

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Carbenes like 1 reacted with muonium atoms, so it seemed quite possible that the analogous silicon and germanium compounds might do so as well. Consequently we began a collaboration with the group at Simon Fraser University to investigate muon capture by these molecules, using the muon beam line at the TRIUMF cyclotron in Vancouver BC, Canada. In the spring of 2007 we recorded the TFμSR spectrum of 2 (Figure 3): The first μSR spectrum of a silicon-centered radical. The hyperfine splitting constant Aμ was found to be 235.4 MHz, which is a little less than that for the muon adduct of carbene 1, 286.7 MHz. The saturated silylene 3 gives a similar TFμSR, with Aμ = 154.9 MHz.

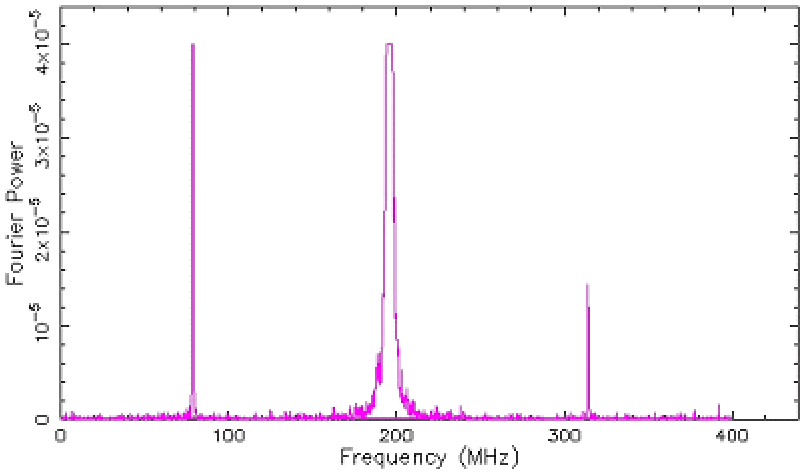


Figure 3. The TF-muSR for silyene 2: The first μSR spectrum for a silicon-centered radical.

In both carbene 1 and silylene 2, the muonium adds to the divalent atom, not to the C=C double bond. The similarity in the TF-μSR for 2 and 3 is one indication that this true. Also consistent with our assignment are the results obtained by the other μSR technique, avoided level crossing muon spin resonance (ALC-μSR). In this experiment the magnetic field is aligned with the muon spin, rather than perpendicular to it. The muon then serves to detect interaction between the unpaired electron and any nearby magnetic nuclei, much as in EPR spectroscopy. Figure 4 displays the ALC-μSR for silylenes 2 and 3. (In this experiment the spectra are presented in a rather different manner.) The spectrum of 2 contains only a single line, indicating equivalent coupling to the two nitrogen atoms. In the spectrum for 3, two overlapping lines appear, consistent with coupling of the unpaired electron to two slightly different nitrogens. Evidently the five-membered ring is somewhat distorted in the muon adduct of 3.

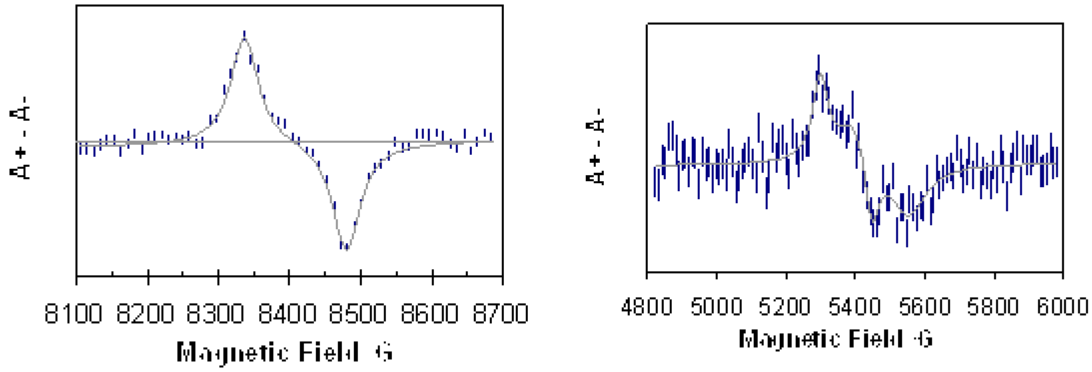


Figure 4. Avoided level crossing μSR for 2 (left) and 3 (right), showing coupling of the unpaired electron to two nitrogen atoms.

We also explored muon capture by stable germylenes. Figure 5 shows the TF−μSR for the unsaturated germylene, 4. The spectrum shows a much larger Aμ value, 649.3 MHz.

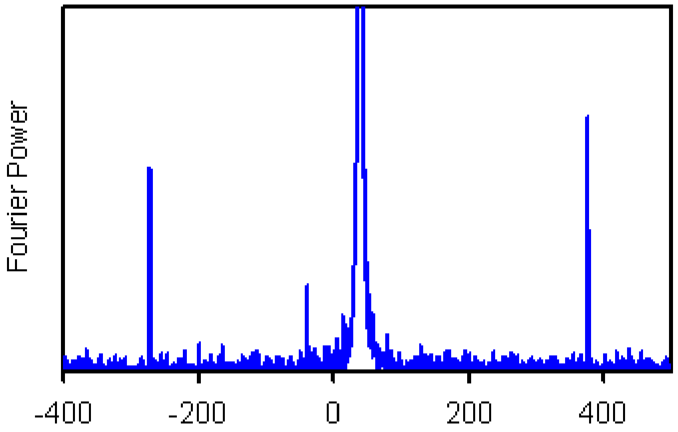
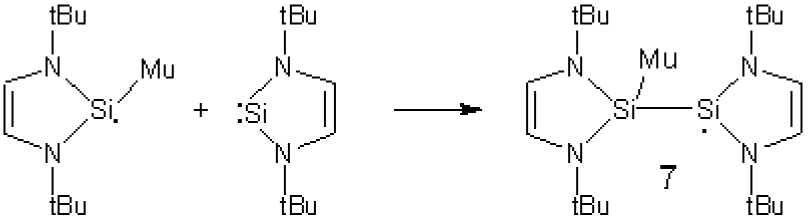


Figure 5. TF−μSR for unsaturated germylene 4: Aμ=649.3 MHz.

The spectra for these muon adducts can also be calculated by density functional theory. The calculation is done for the corresponding hydrogen adduct, and corrected for the difference in the gyromagnetic ratios of H and Mu, and for the difference in their zero point energies. The values for the carbene and germylene, calculated in this manner, are in rather good agreement with the measured values. But for the silylenes, the observed values are far too small. Theory predicts Aμ values near 900 MHz for the silylenes, compared with the observed values near 200 MHz!

Our explanation for this difference is that the recorded Aμ values are not for the silylene, but for a disilicon species, formed by reaction of the original muoniated silylene with a second silylene molecule. This reaction is shown for silylene 2 in Eq. 1.[9] The calculated Aμ value for the dimeric radical 7 is 230 MHz, quite close to the observed value. If our interpretation is correct, these findings



Equation 1. Proposed dimerization of muoniated silylene 2.

represent *the first bimolecular reactions ever observed by μSR*. These reactions are quite unexpected, but there is some precedent. The reactions of silylenes 2 and 4 with several halocarbons also lead to disilane products.[10]

One test of our result would be to determine the μSR spectrum of a disilene. Addition of a muon to the Si=Si bond would produce a radical similar to 7, and this experiment is planned. However we have determined the μSR for a Si=C doubly bonded compound, the silene 8 prepared by Kira and his students.[11]
The TFμSR spectrum, shown in Figure 6, indicates that two different radicals are formed, in relative amounts of 2.2:1. Further ALCμSR spectra for this compound shows that Aμ value 186.7 MHz is due to radical 9 and the smaller value, 137.0 MHz to radical 10. These values are close to those found for the silylenes, and tend to confirm our assignment of the dimer structures.

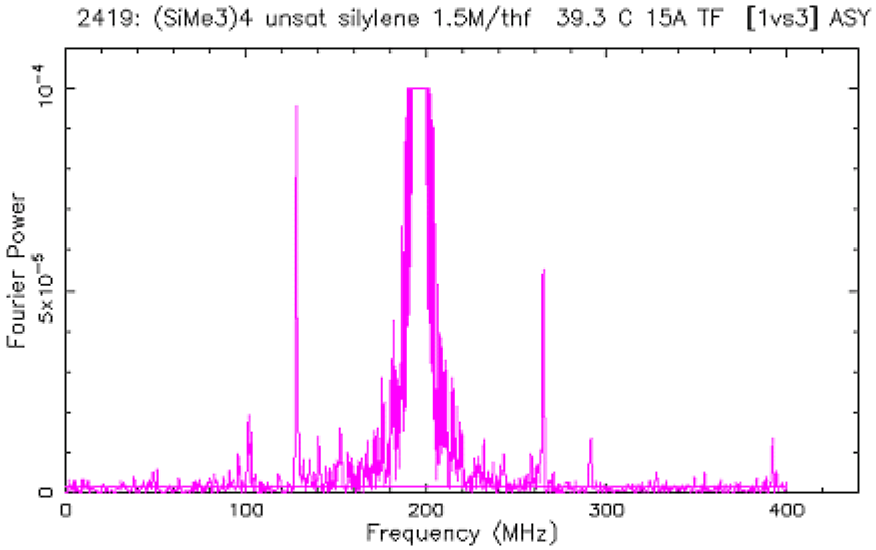
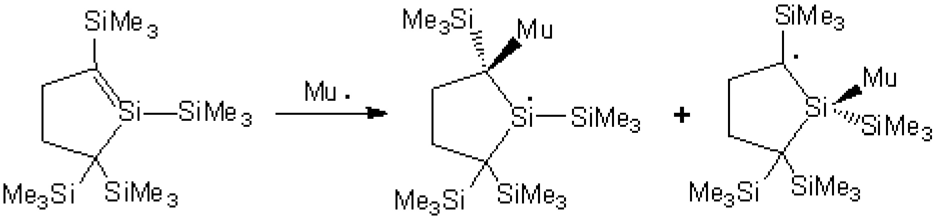


Figure 6. TFµSR for silene 8.



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These initial experiments have opened a new frontier in organosilicon chemistry, and perhaps in organometallic chemistry generally. In Figure 7 are listed a sampling of the unsaturated compounds of silicon which could be studied; all of them can be predicted to display muon spin resonance spectra. And these are just the silicon compounds! Multiply-bonded and unsaturated compounds are know for B, Al, Ga, In, Ge, Sn, Pb, P, As, Sb, S, Se, and Te ? and for virtually all of the transition metals. Studying the µSR for these compounds presents possibilities for years of research.

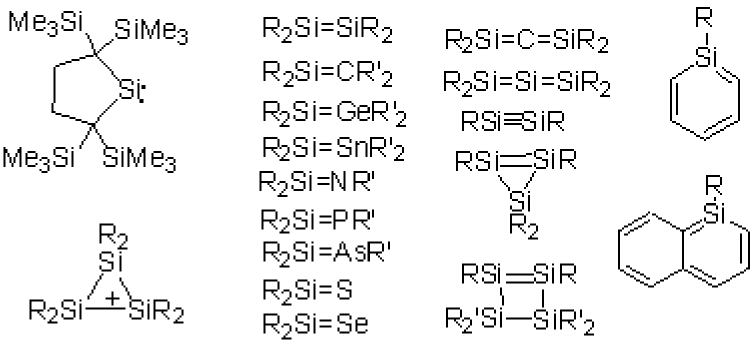

Figure 7. Unsaturated silicon compounds which should show muon spin resonance spectra.

To carry out muon spin resonance spectroscopy, a high intensity proton beam is required to generate an adequate number of muons. Currently three facilities are equipped to carry out muon spin resonance experiments conveniently: TRIUMF, in Vancouver Canada; PES, in Switzerland; and ISIS, in Great Britain. The latter is a cooperative facility between the Rutherford Appleton laboratory and Japan's RIKEN. The pulsed muon source at KEK, Tsukuba, Japan has recently been shut down. However a new accelerator which will provide a suitable source of pulsed muons is under construction within the Japan Proton Accelerator Research Complex, near Tokai. This new facility should be ready to carry out µSR experiments about the time this review is published.

Muon spin resonance requires fairly large samples, 2 to 3 millimoles, and fairly long acquisition times– perhaps an hour for a TFμSR spectrum, and several hours for ALCμSR. Beam time at all facilities must be scheduled well in advance of running spectra. Fortunately the spectra can be determined either on neat liquids, or in solution in ordinary solvents such as hexane or THF, which do not capture muons.

The author invites the participation of chemists in this new exciting field, which he predicts will soon grow substantially.

Acknowledgements: I thank my collaborators at Simon Fraser University: Prof. Paul Purcell, Dr. Jason Clyburne, Dr. Jean-Claude Brodovitch, and Mr. Brett McCollum. Samples for our studies were prepared by my coworkers at the University of Wisconsin: Drs. Adam Tomasik, Amitabha Mitra, and Clemens Krempner.

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社団法人　日本化学会
〒101-8307　東京都千代田区神田駿河台1-5
Tel: 03-3292-6161
Fax: 03-3292-6318