Silyl and germyl radicals investigated by muon spin spectroscopy

Brett M. McCollum[1], Jean-Claude Brodovitch[1], Jason A. C. Clyburne[2], Paul W. Percival[1], Adam C. Tomasik[3] and Robert West[3]

[1] *TRIUMF and Department of Chemistry, Simon Fraser University, Burnaby BC, Canada V5A 1S6*

[2] *Department of Chemistry, Saint Mary's University, Halifax NS, Canada B3H 3C3*

[3] *Organosilicon Research Center, University of Wisconsin, Madison WI 53706 USA*

Carbenes, silylenes, and germylenes (R_2E:, E = C, Si, Ge) are molecules containing neutral dicoordinate group 14 atoms with six valence electrons (see Fig.1). Due to their resulting high reactivity, these species play key roles as intermediates in numerous thermal and photochemical reactions, and hence are extremely important in synthetic chemistry. In earlier work we have shown that muonium adds to the carbene centre of stable N-heterocyclic carbenes [1]. We now report the detection of Si- and Ge-centred radicals. There is no equivalent data on H adducts of silylenes and germylenes, but the adducts of larger radicals have been studied by electron spin resonance [2].

Our μSR results for the germyl radicals are consistent with Mu addition to the germanium atom in direct analogy to the carbenes. In particular, the high value determined for the muon hyperfine constant suggests a markedly non-planar radical centre, in agreement with quantum calculations for germyl radicals. On the other hand, the μSR spectra of silyl radicals reveal much smaller muon hyperfine constants, inconsistent with predictions for the simple Mu adducts. We believe that the primary silyl radicals rapidly react with a further silylenes in our highly concentrated samples and that we have detected the secondary radical products. As far as we know, this is the first direct detection of secondary radicals by transverse-field μSR.

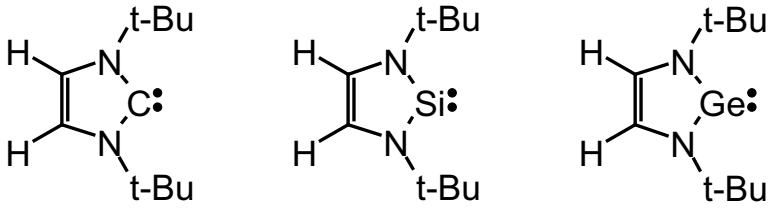

Fig. 1: Examples of an N-heterocyclic carbene, silylene and germylene.

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[2] B. Tumanskii, P. Pine, Y. Apeloig, N.J. Hill, and R. West, J. Am. Chem. Soc. 126, 7786 (2004); 127 (2005) 8248.