Muoniated Free Radicals formed from some Novel Silylenes

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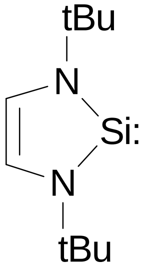
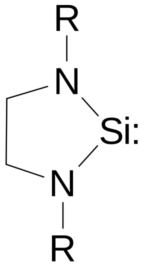
Introduction

Silylenes are generally considered highly reactive species, and are indispensable building blocks for the synthesis of organosilanes. It was only in 1994 that the first synthesis of an isolable silylene (1) was accomplished [1].



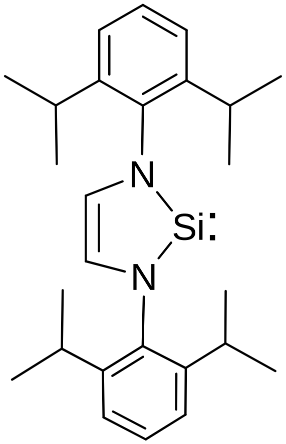
(1)



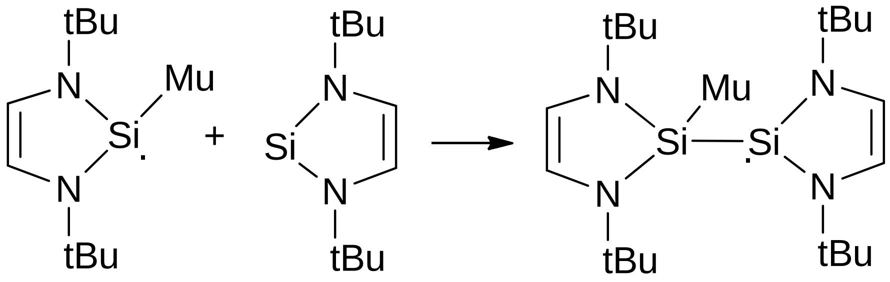
(2)

Unsaturated N-heterocyclic silylenes benefit from π-donor stabilization of the silicon (II) atom by the nitrogen atoms, as well as pseudoaromaticity in the ring. The latter factor is absent from the corresponding saturated N-heterocyclic silylenes (2) and they are indeed less stable.

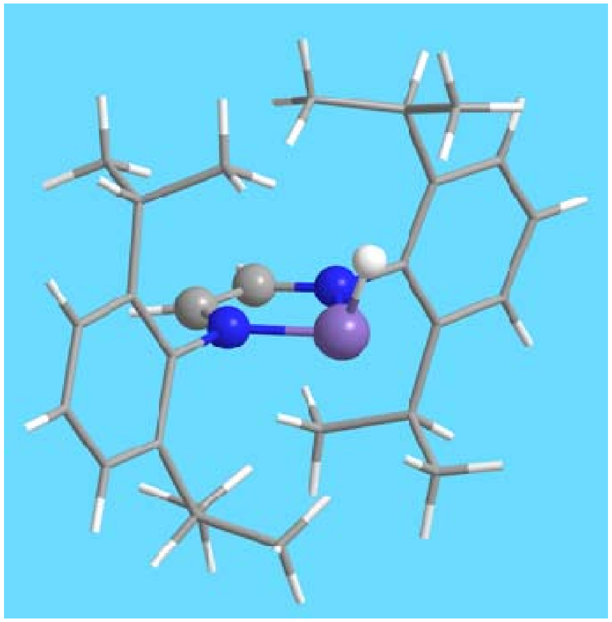
An additional, kinetic, factor in the reactivity of silylenes is steric protection of the reaction centre by bulky substituents (e.g. diisopropylphenyl) on the nitrogen atoms. We have explored the reactivity of silylenes by studying the free radicals formed by muonium addition.



At first we could not reconcile the muon hyperfine constants (hfcs) of the radicals formed from silylenes with the predictions of quantum calculations. The explanation lies in coupling of the primary muonium adduct with a second silylene, so that the disilanyl product radical is observed [2].

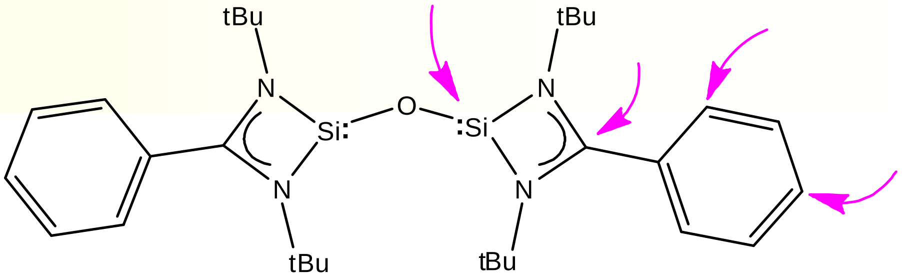


This was confirmed in an experiment on a series of NHC silylenes with different substituents on the nitrogens. The largest substituent (diisopropylphenyl) served to slow the silyl coupling reaction so that we were able to detect the primary silyl radical, as evident from the record high muon hfc (931 MHz) [3].



This poster reports unpublished results on various novel silylenes.

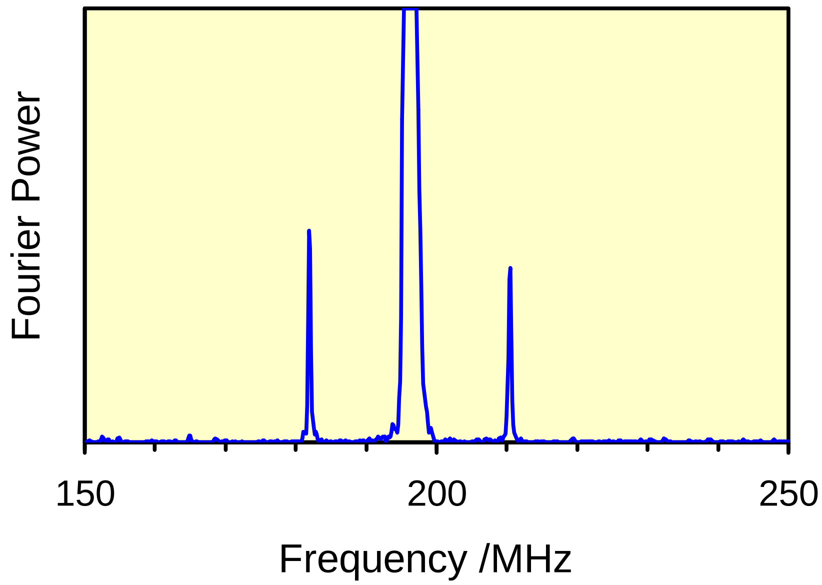
Bis-silylene oxide



This remarkable compound was first synthesized in 2010 [4]. Potential sites of reaction include the tricoordinate silicon atoms, the carbon atoms at the opposite corner of the rings, and the phenyl substituents, most likely at the ortho and para positions. Examples are shown by arrows in the diagram.

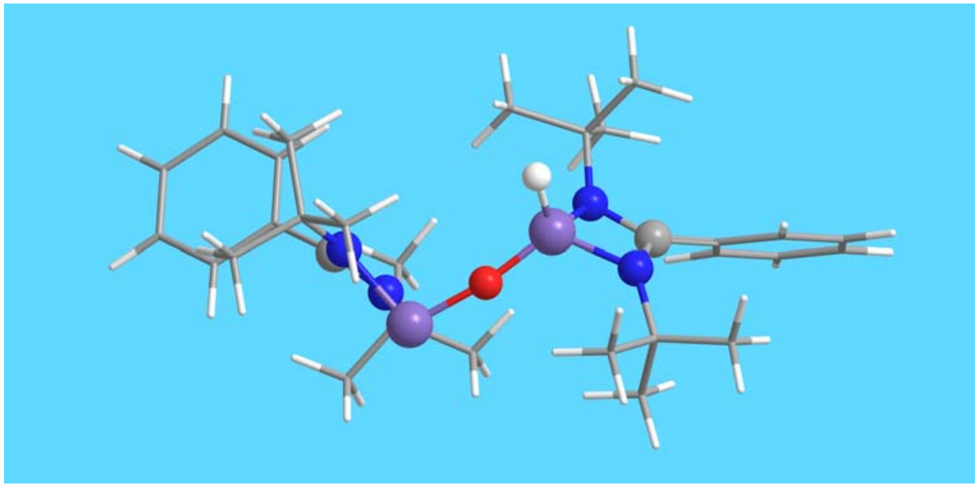
Computation suggests that H atom addition to the 4-ring is preferred over addition to the phenyl substituent. In any event, formation of a muoniated cyclohexadienyl-type radical would give a large muon hfc (380 MHz for the para position), which is not observed.

Mu addition to a 4-ring could occur at either Si or C. Computation of the two radical isomers shows that H addition to Si is favoured, consistent with distribution of the unpaired spin density from the 4-ring C to the phenyl group. The predicted muon hfc (16.1 MHz without isotope effect) is more consistent with the experimental value than the alternative (6.8 MHz for addition at C).


TF-µSR spectrum at 39°C,14.5 kG

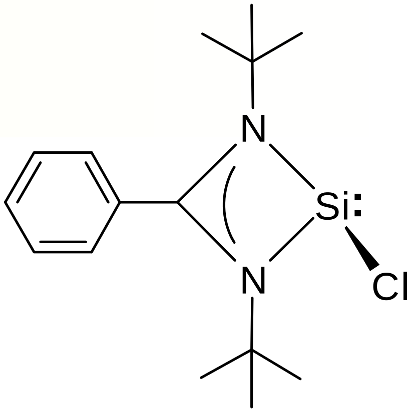
T / °C	muon hfc /MHz
7.4	28.38 ± 0.03
25.3	28.49 ± 0.02
38.7	28.49 ± 0.02
53.0	28.57 ± 0.02

Calculations on the optimized structure predict phenyl proton hfcs which might be detectable by µLCR.



(sample provided by the group of Matthias Driess, T.U. Berlin)

A cyclic chlorosilylene



This N-heterocyclic silylene is the first example of a system stable at room temperature that contains a Si^{II}–Cl bond [5]. The puckered ring has two potential sites of reaction, at C and Si.

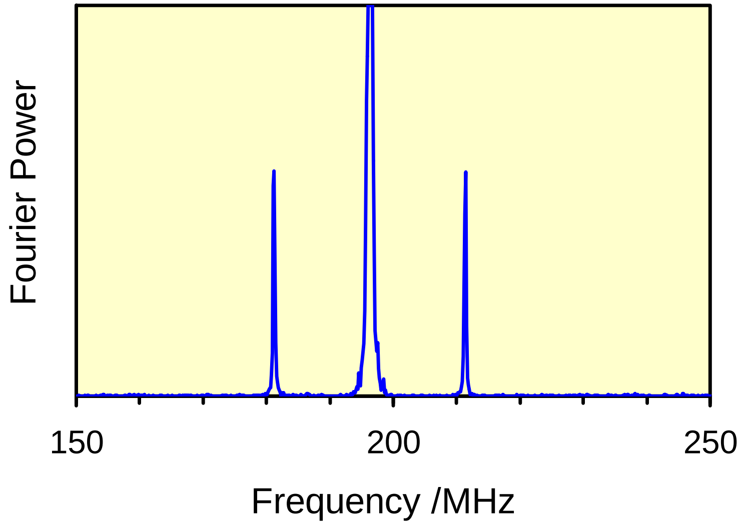
Of particular interest for muon spin spectroscopy is the presence of the spin-active Cl (76% ^{35}Cl and 24% ^{37}Cl, both $I = 3/2$).

As found for the bis-silylene oxide, computation shows that H addition at Si results in some unpaired spin delocalization onto the phenyl substituent. However, despite this, the radical formed by H addition to the 4-ring C is predicted to be more stable.

The μLCR spectrum is a key factor in the radical assignment, because it is sensitive to the relative signs of the muon hfc and that of the interacting nucleus. Cl is particularly useful because the two isotopes provide a characteristic intensity pattern.

(sample provided by the group of Herbert Roesky, Göttingen)

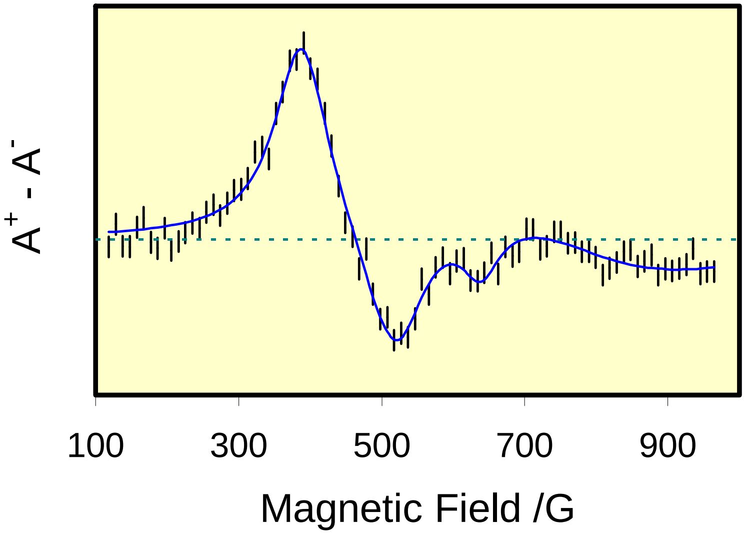
TF-μSR spectrum at 25°C,14.48 kG

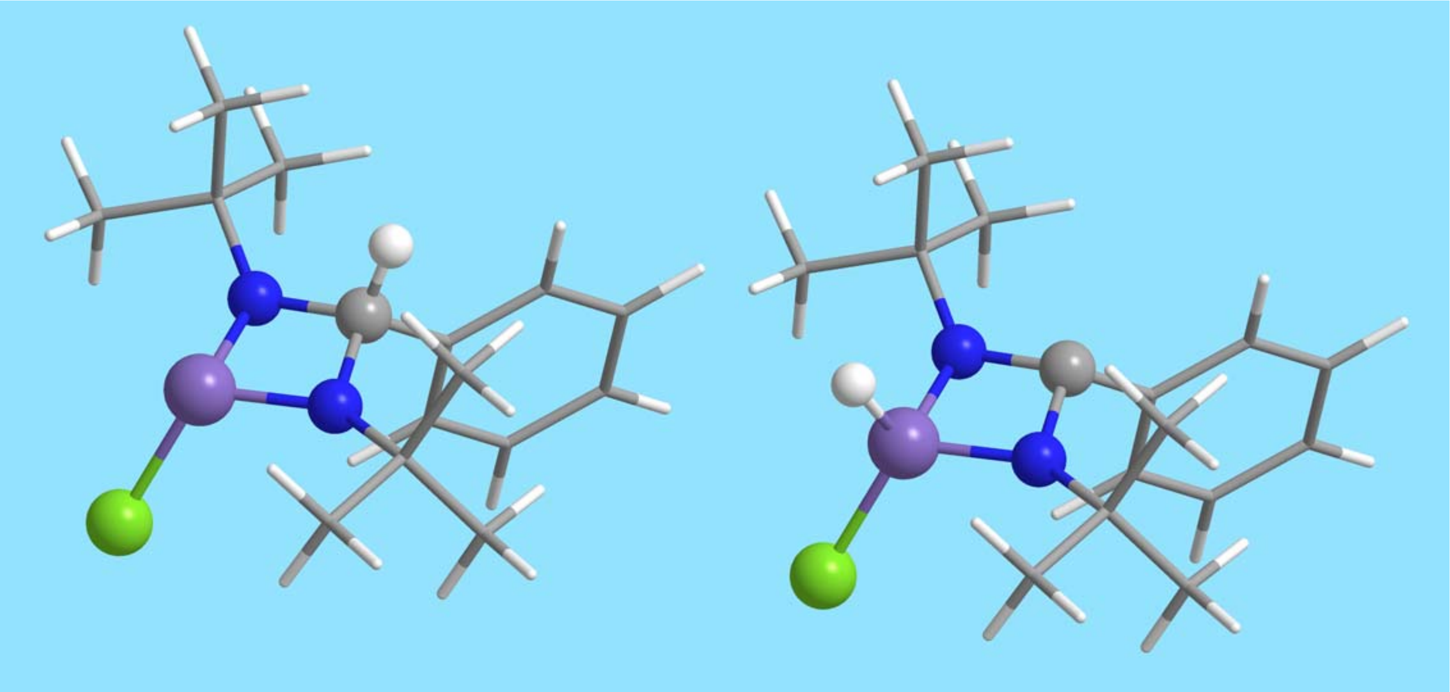


T / °C	A_μ /MHz
7.1	29.61 ± 0.01
25.2	30.18 ± 0.01
52.0	30.95 ± 0.01

T /°C	LCR/G	A_μ/MHz	nucleus	A_k /MHz
7.1	407	29.6	Cl-35	18.7
7.1	538	29.6	Cl-37	15.6
52.0	452	31.0	Cl-35	18.8
52.0	576	31.0	Cl-37	15.7

μLCR spectrum at 52°C

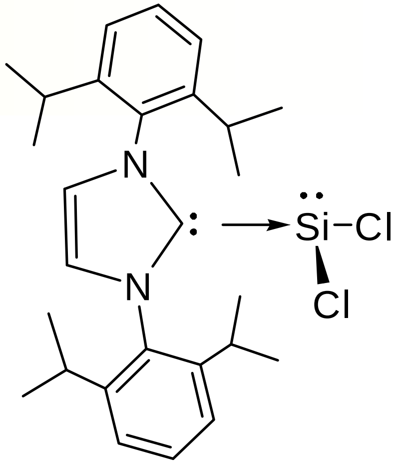




more stable	less stable
positive muon hfc	negative muon hfc
positive Cl hfc	positive Cl hfc
✓	✗

Steric interaction forces the phenyl into a perpendicular orientation to the 4-ring, which inhibits spin delocalization.

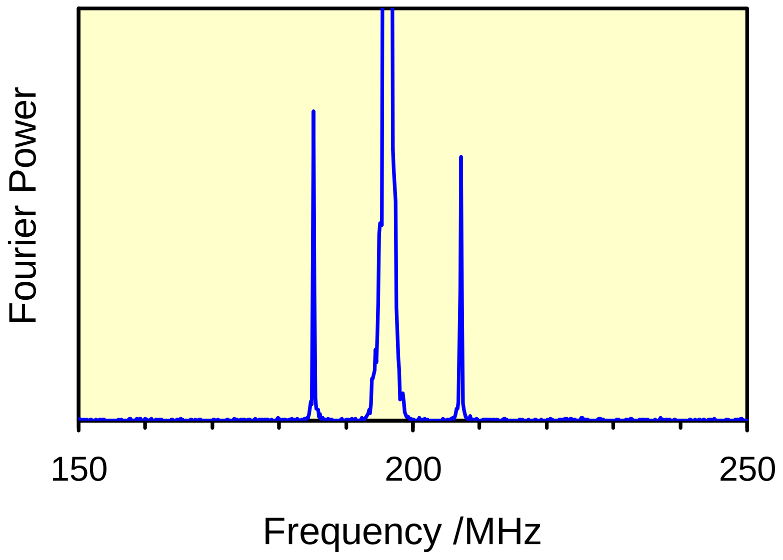
Carbene-stabilized dichlorosilylene



Although dichlorosilylene :CCl$_2$ is known in the gas phase, it condenses at room temperature to a polymer. However, it has recently been possible to stabilize this reactive species by forming a complex with a N-heterocyclic carbene [6]. We know that Mu adds readily to individual carbenes [7], and similar behaviour is expected from the silylene [8], but how does their association affect the reactivity? Strong bonding between C: and Si: might be expected to result in a silene (C=Si). We have previously studied a silene and found that Mu adds to both atoms, with a preference for the carbon [9]. On the other hand, Ghadwal et al [6] describe the carbene-silylene complex as “electrostatic interaction of the Lewis base carbene ligand and the electronically depleted silicon atom”. This results in side-on coordination of the carbene ligand, as indicated in the structure diagram, leaving the silylene as the more exposed reactive centre.

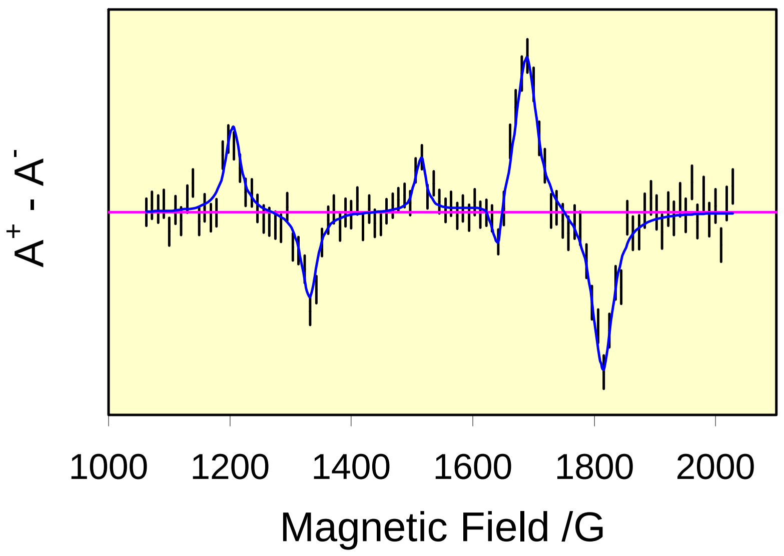
(sample provided by the group of Herbert Roesky, Göttingen)

TF-μSR spectrum at 25°C,14.5 kG



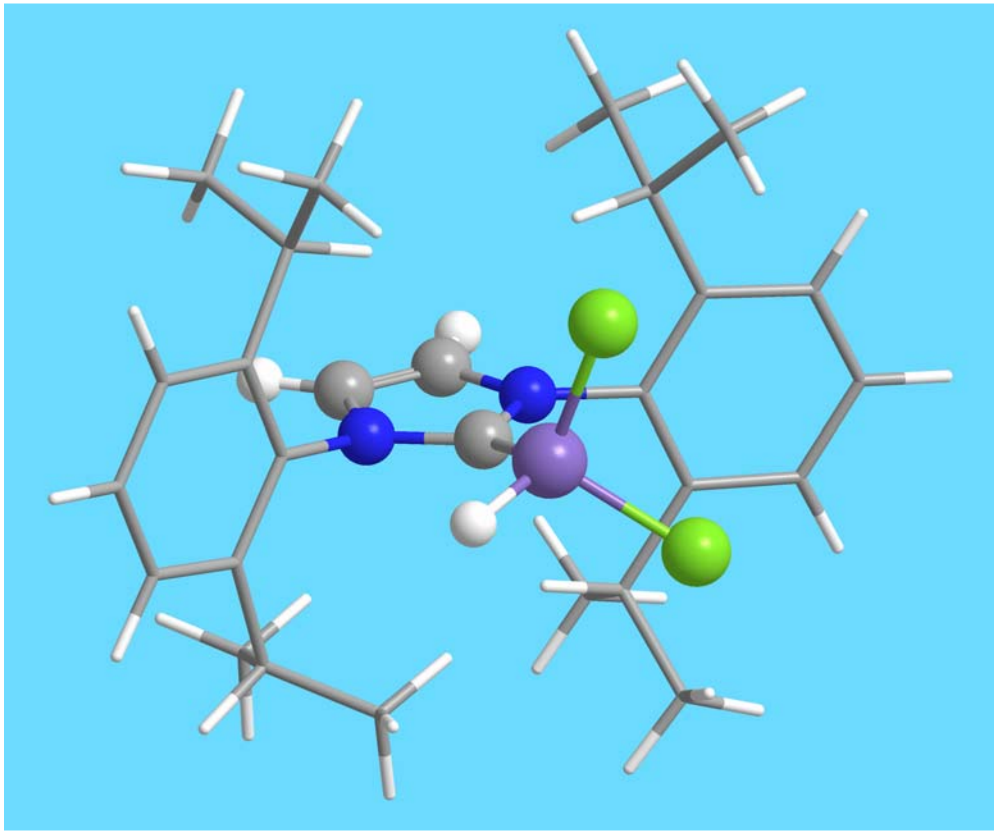
T / °C	muon hfc /MHz
7.1	23.52 ± 0.01
25.2	22.04 ± 0.01
52.7	19.73 ± 0.01

μLCR spectrum at 53°C



T /°C	LCR/kG	A_μ/MHz	nucleus	A_k /MHz
7.1	-1.919	-23.5	Cl-35	26.9
7.1	-1.737	-23.5	Cl-37	22.4
7.1	-1.414	-23.5	N-14	14.0
25.2	-1.851	-22.0	Cl-35	26.6
25.2	-1.672	-22.0	Cl-37	22.1
25.2	-1.347	-22.0	N-14	13.7
52.7	-1.751	-19.7	Cl-35	26.3
52.7	-1.575	-19.7	Cl-37	21.9
52.7	-1.270	-19.7	N-14	14.0

Preliminary results are consistent with Mu addition at Si, as shown below.



Rotational motion of the –$SiMuCl_2$ “propeller” may be the cause of the temperature dependence of the muon hfc.

References

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Molecular geometries were optimized at the UB3LYP/6-31G(d) level using Gaussian09 running on the WestGrid computing network; hyperfine coupling constants were computed for the UB3LYP/cc-pVDZ basis set.