Muoniated Free Radicals formed from Germylenes and Silylenes

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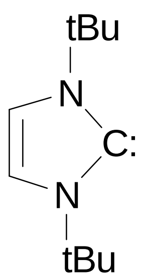
Carbenes, silylenes, and germylenes

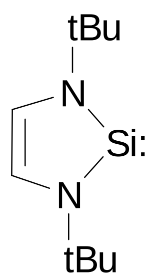
Carbenes, silylenes, and germylenes have

- a neutral dicoordinate group 14 atom and six valence electrons
- singlet or triplet electronic state
- high reactivity

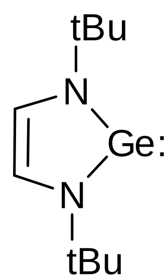
Unsaturated *N*-heterocyclic ylidenes are relatively stable (singlet spin state).



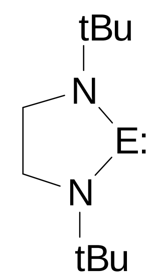
carbene



silylene



germylene



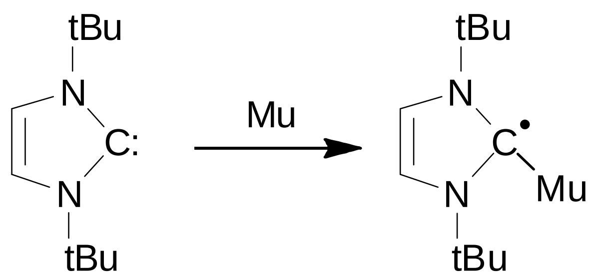
The saturated analogues are somewhat less stable.

Samples are moisture and air sensitive, and some have limited stability.

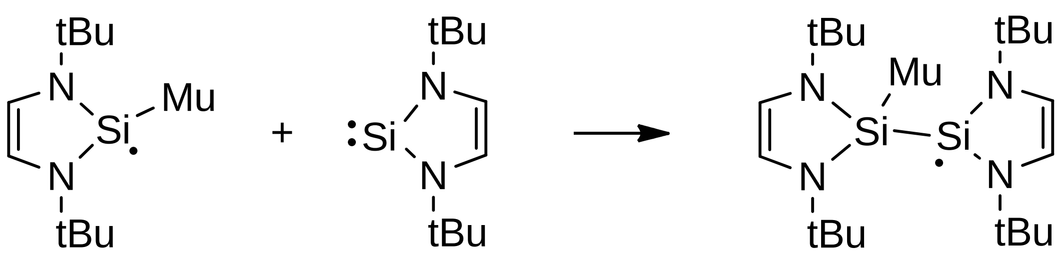
None are commercially available; they are custom-synthesized.

Mu addition to carbenes and silylenes

Mu adds to carbenes



but muoniated silyl radicals undergo further reaction:



Detection of the disilanyl secondary radical product by TF-μSR requires

- fast formation of the primary silyl radical
- fast transformation of the silyl to the disilanyl

to ensure coherent muon spin precession in the product.

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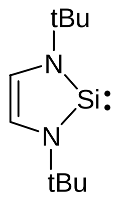
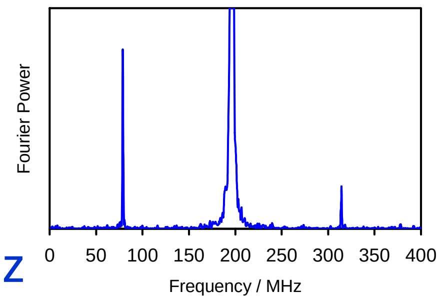
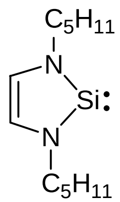
Chemical control of the silyl coupling reaction

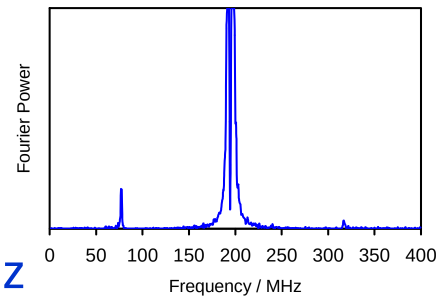


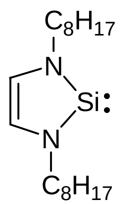
A_μ = 235.4 MHz



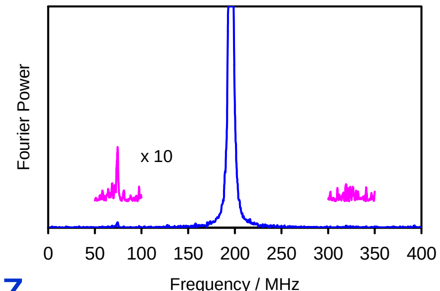


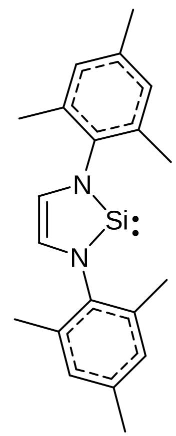
A_μ = 239.6 MHz



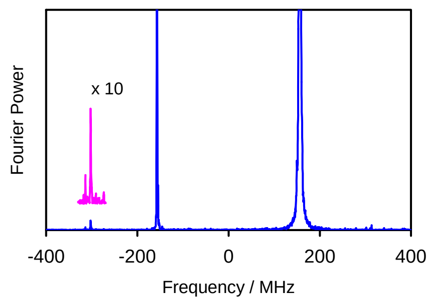


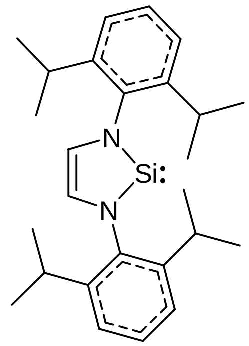
A_μ = 244.3 MHz





no signal



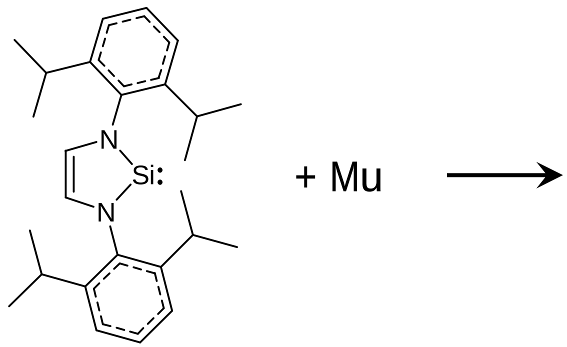


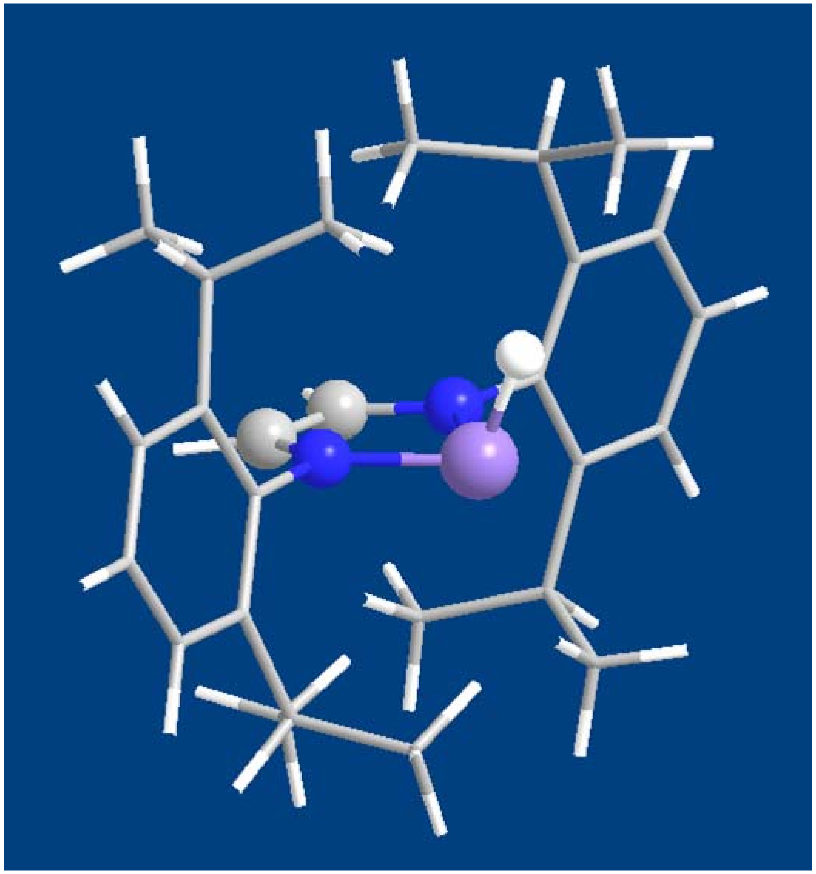
A_μ = 931.3 MHz

Angew. Chem. Int. Ed. 49 (2010) 2893

Mu + N,N'-bis(2,6-diisopropylphenyl)-1,3-diaza-2-silacyclopent-4-en-2-ylidene

The bulky diip groups sterically protect the Si atom.

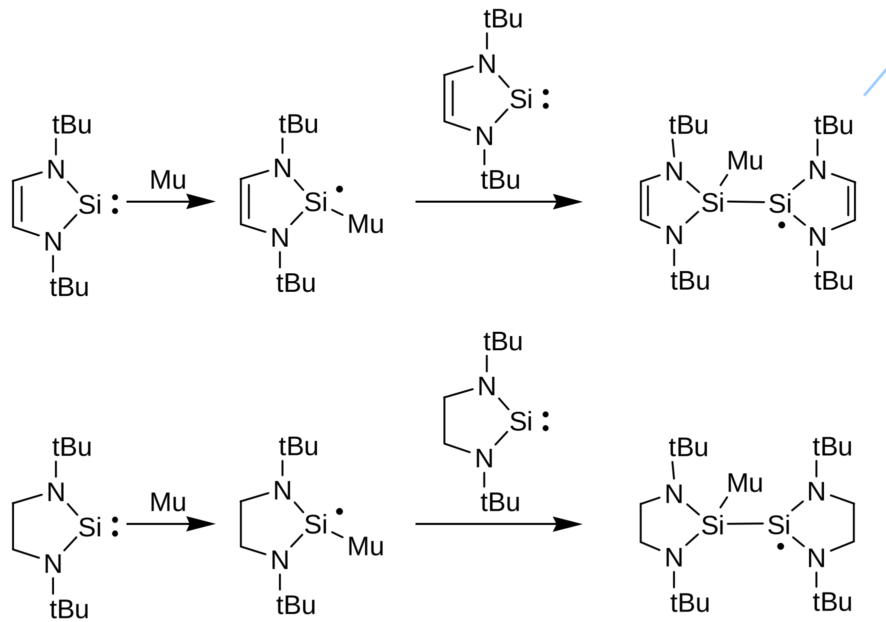


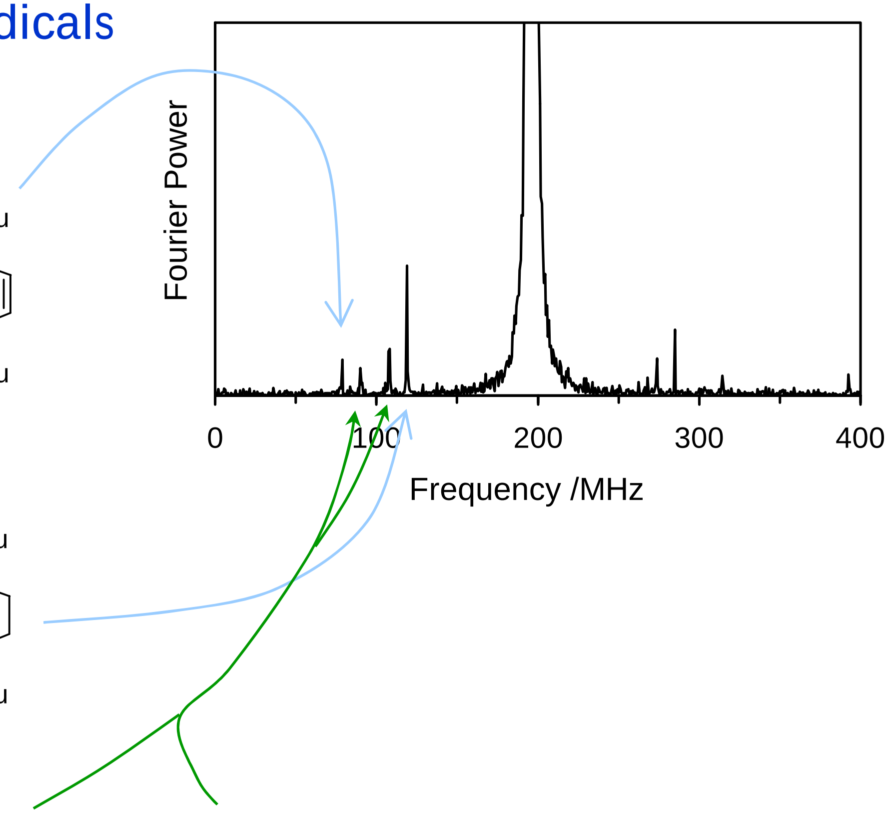


Calc (H)	211 MHz
x 3.183	671 MHz
x 1.4	939 MHz
Experiment	931 MHz

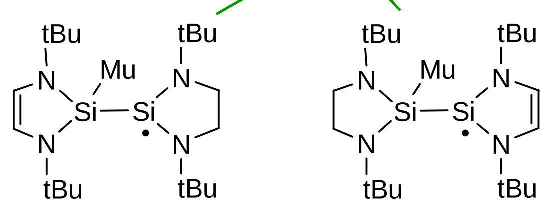
Cross-Coupling from Mixed Silylenes

A mixture of two silylenes gives four radicals





Cross-coupled products:



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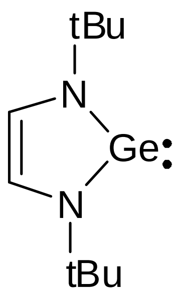
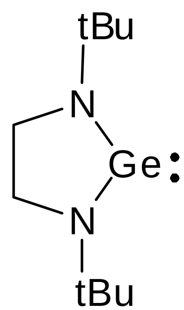
Do germylenes have a similar rich chemistry?

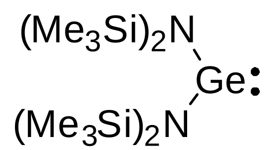
The muon hfcs of the Mu adducts suggest that we detect the primary radicals.



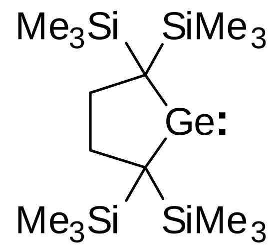
650 MHz



400 MHz



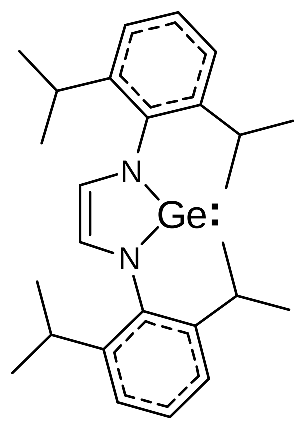
593 MHz



343 MHz

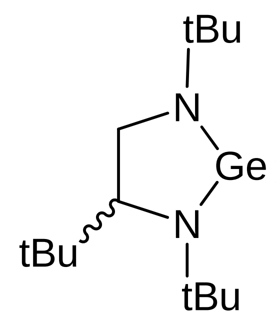
The diip compound also has an intermediate hfc

but why is it less than the Si version?



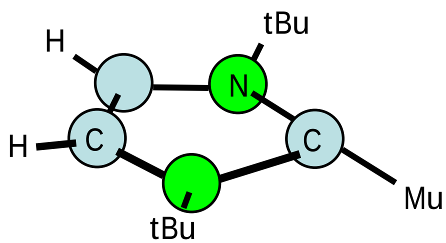
637 MHz

and why is this derivative so different?



947 MHz

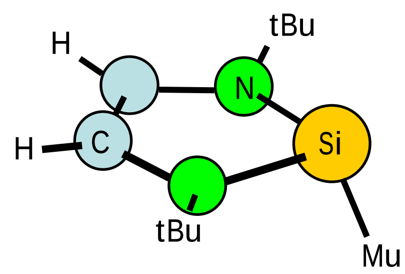
The hfcs depend on the s character of the radical centre



slightly non-planar radical centre

π radical

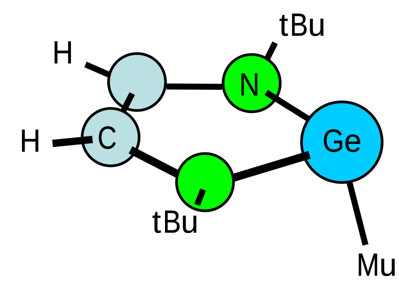
C p_z + small s



~ tetrahedral radical centre

σ radical

Si sp^3



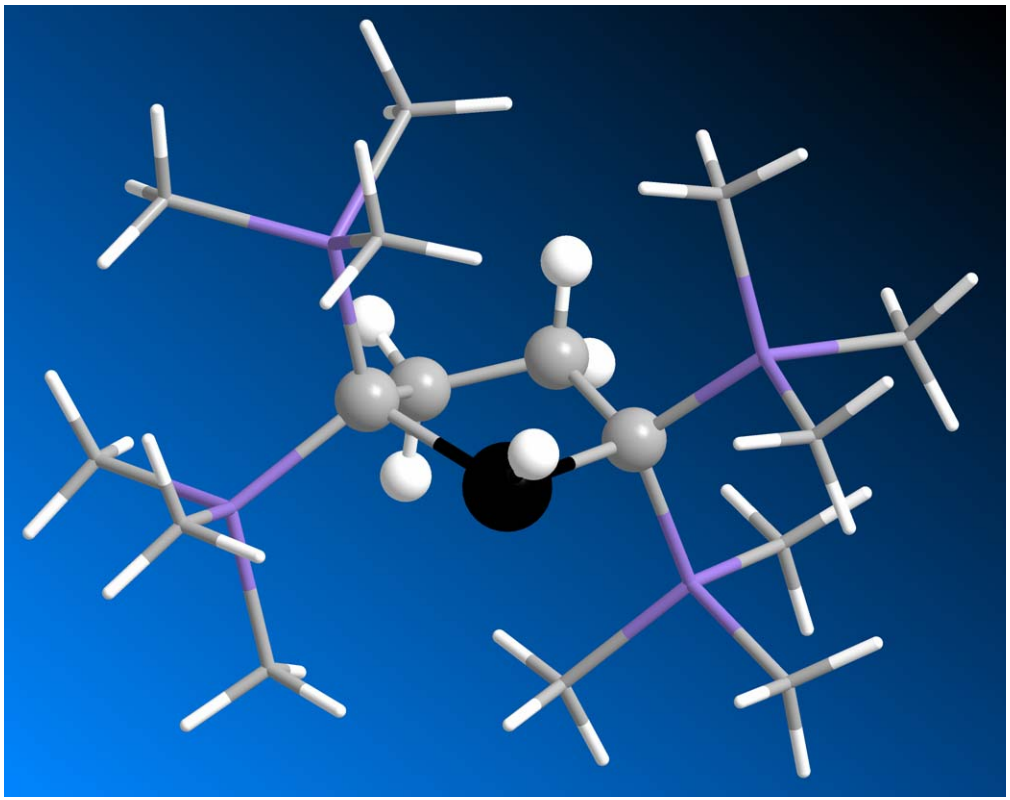
almost perpendicular

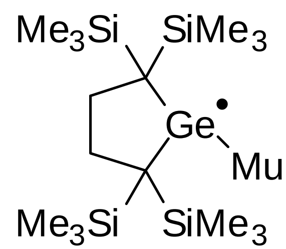
σ radical

Ge sp^3 + d?

Ring geometry also plays a role in bonding

The absence of π delocalization results in a puckered ring.

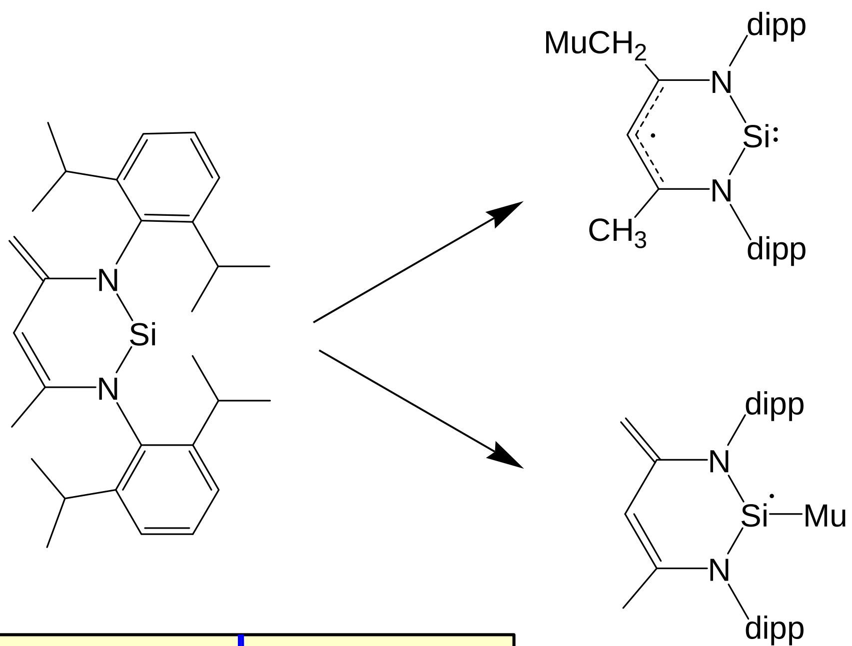




Calc (H)	92	MHz
x 3.183	292	MHz
x 1.2	350	MHz ✓
Experiment	343	MHz

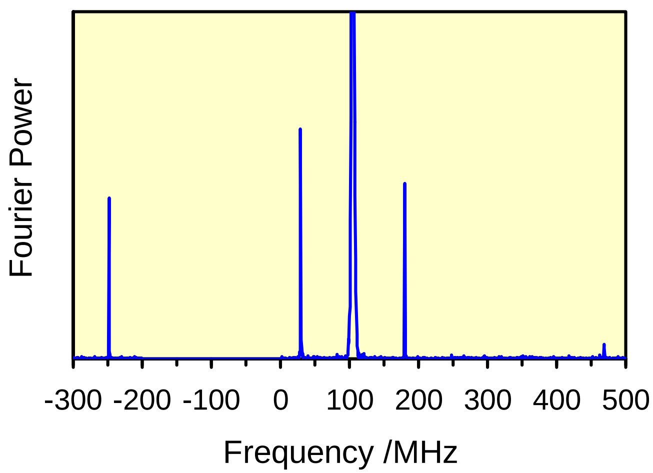
UB3LYP/6-31G(d) for geometry optimization; UB3LYP/cc-pVDZ for hfc

Reactivity studies on the Driess silylene



Mu could add to the *exo*-CH_2

or to the silylene

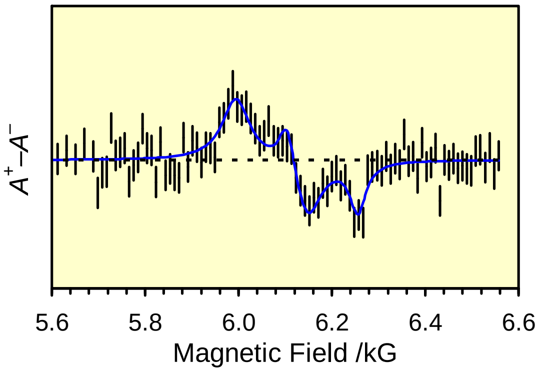


Two pairs of radical precession signals are observed, consistent with the formation of both radicals.

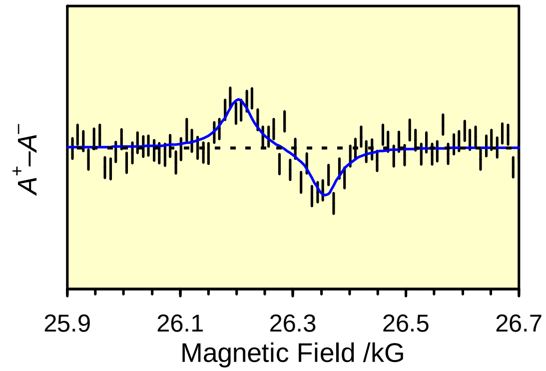
A_μ = 149 MHz, 716 MHz

μLCR signals from the two radical

Protons in CH_2Mu

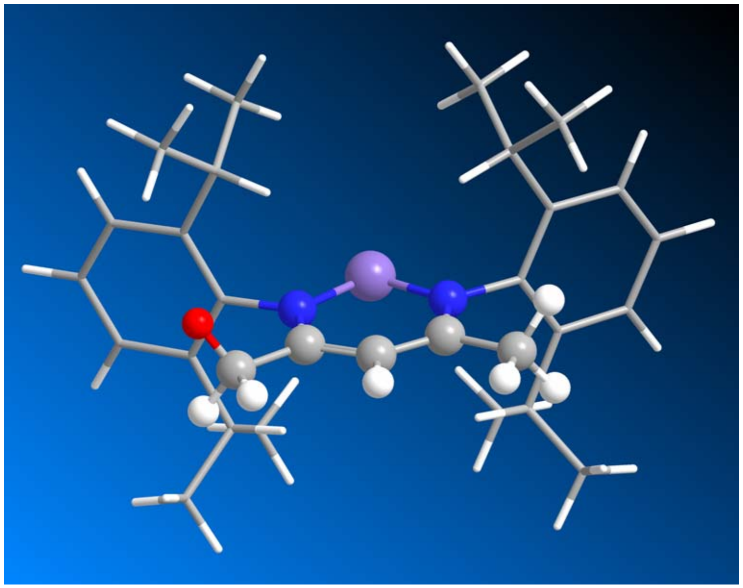


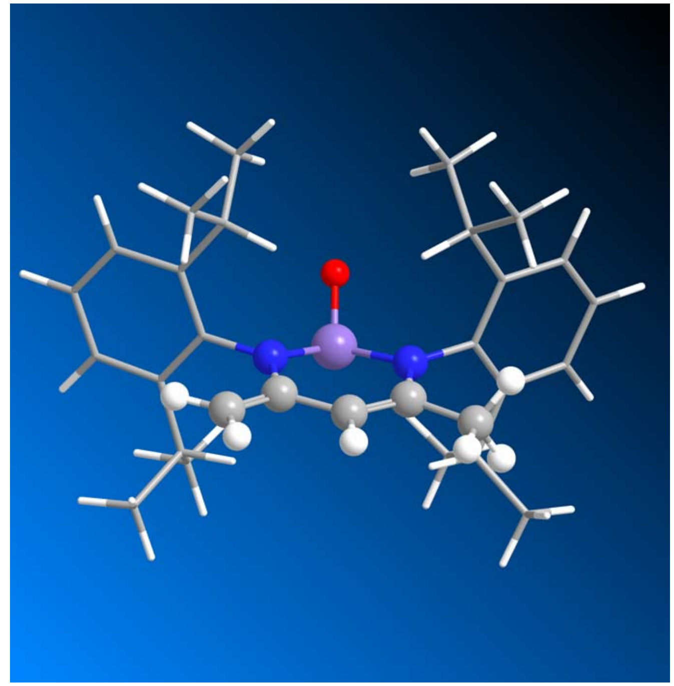
^{14}N in the silyl



T / °C	LCR / kG		nucleus	hfc / MHz				
				A_k		A_μ	A_μ'	$A(CH_2Mu)$
3.3	6.162	6.282	^1H	35.49	33.26	150.67	47.33	38.69
23.3	6.070	6.179	^1H	35.30	33.29	148.77	46.73	38.44
58.0	5.917	6.015	^1H	35.04	33.22	145.66	45.75	38.01
23.3	26.279		^{14}N	16.11		715.75		

Computational predictions agree with our analysis

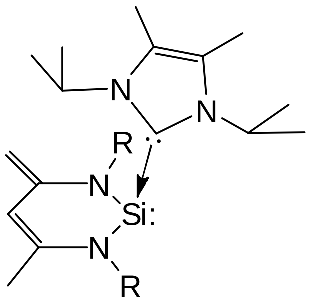


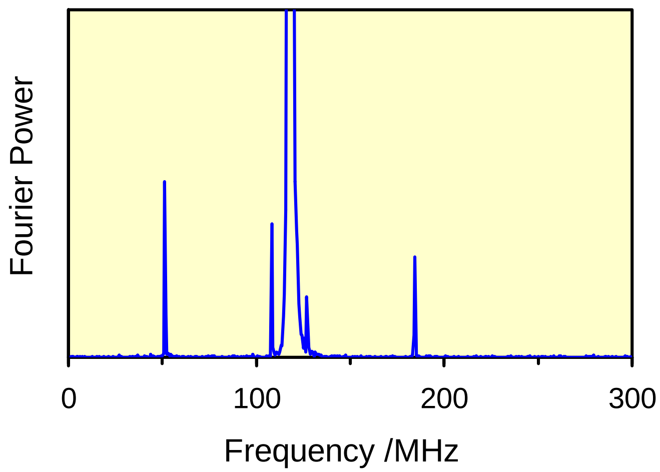


Calc (CH_3)	32	MHz
Experiment	149	MHz
A'_μ	47	MHz
$A(CH_2M_u)$	38	MHz

Calc (H)	187	MHz
x 3.183	596	MHz
x 1.2	715	MHz
Experiment	716	MHz

The spectrum changes when the silylene is complexed



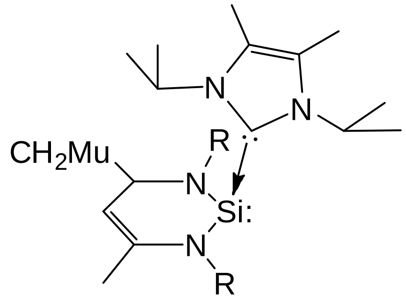


Two radical signals are again observed. A_μ = 19 MHz, 133 MHz

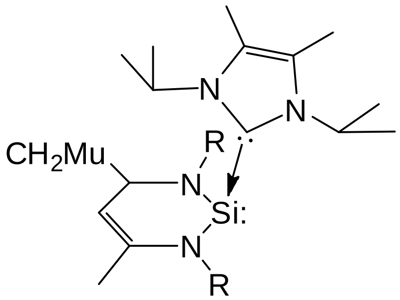
One is consistent with the CH_2 adduct, and there is matching μLCR data,

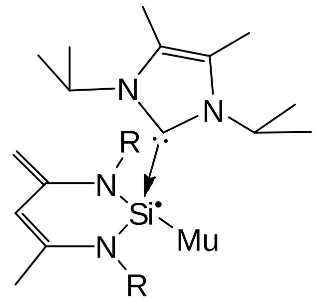
but the other has a much smaller hfc.

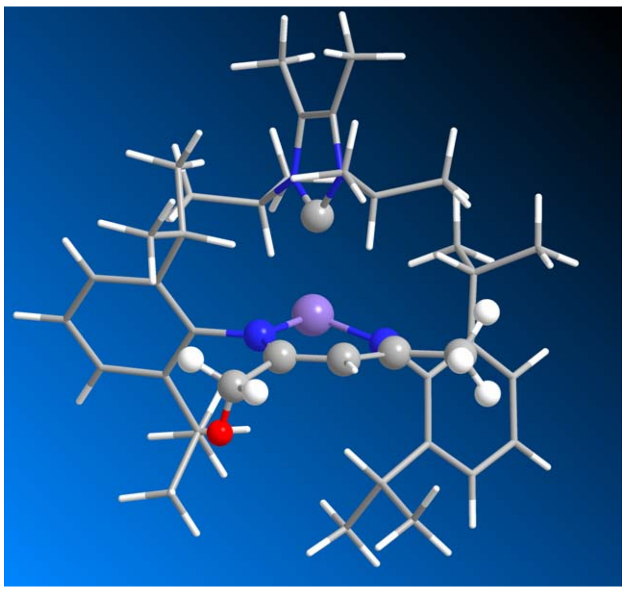
Is it from Mu addition to Si:
or to the carbene?

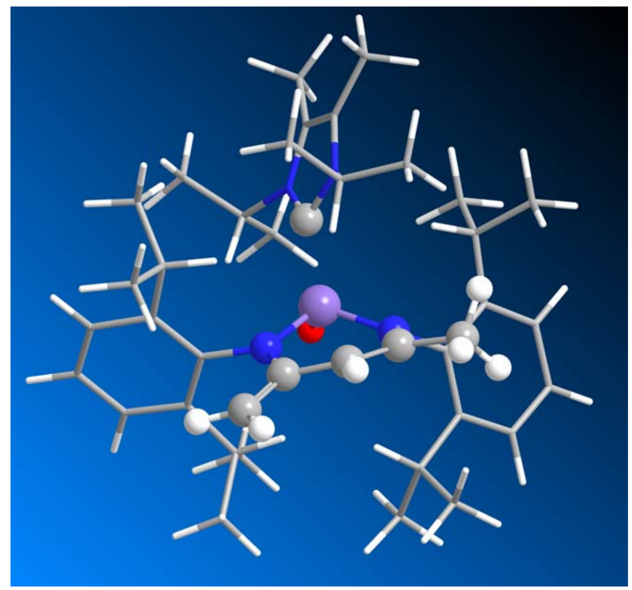


Assignment of complexed radicals









Acknowledgements

The organosilicon samples used in our studies are moisture and air sensitive, and some have limited stability. None are commercially available; they are custom-synthesized by the groups of:

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DFT calculations were carried out with Gaussian 09 running on the WestGrid network.