Functionalization and Cluster Expansion of a Si_6 Cluster (Siliconoids)

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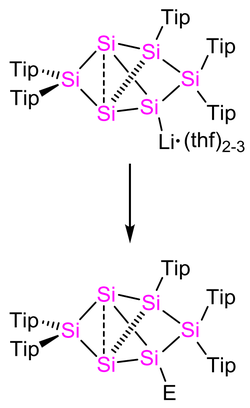
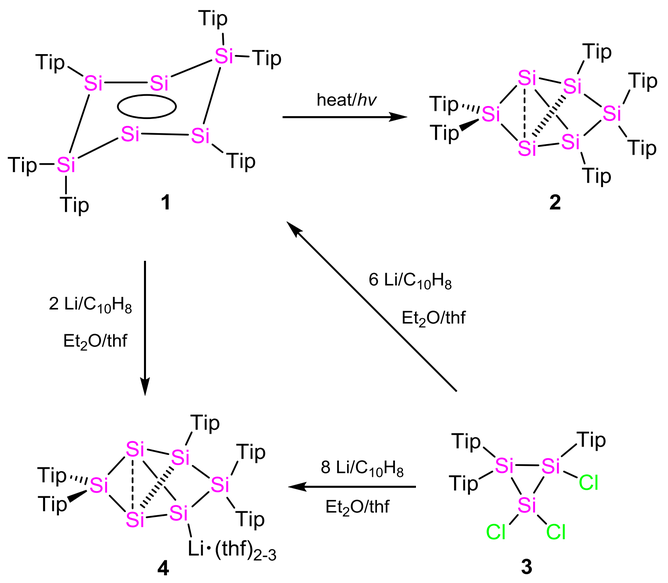
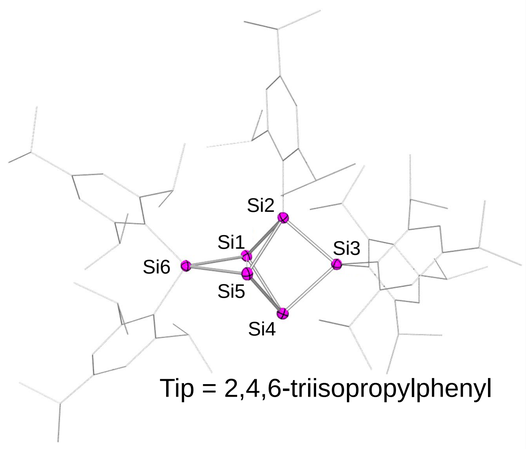
Introduction

Siliconoids are unsaturated, partially unsubstituted neutral silicon clusters[1], which are similar to silicon surface materials at molecular regimes concerning their characteristic structural properties. These clusters typically contain one or several unsubstituted vertices[2], which confers unusually pronounced electronic anisotropies, already known from the dismutational hexasilabenzene isomer[3] **1**. A rearrangement of the silicon atoms leads to the bridged propellane[4] structure **2**. The incorporation into extended systems is currently limited by the scarceness of stable functionalized derivatives. Recently, the synthesis of anionic $Si_6Tip_5^-$ siliconoids and the reaction with different electrophiles under preservation of the cluster's structure was reported[5]. Main attention of this work is the synthesis, isolation and characterization of different functionalized Si_6Tip_5E siliconoids by conversion of an anionic $Si_6Tip_5^-$ siliconoid with suitables electrophiles (E).



E = Electrophile

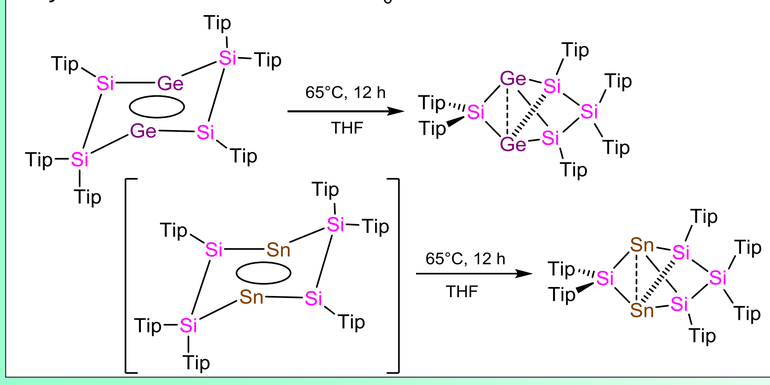




Tip = 2,4,6-triisopropylphenyl

d Si1-Si2 [Å]	2.5506(9)
Si1-Si2-Si3/Si1-Si2-Si4 [°]	107.61
λ [nm]	364

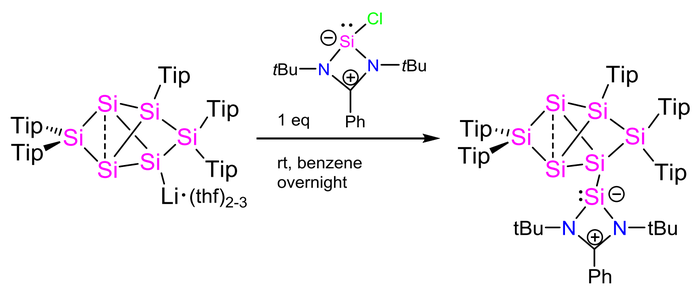
Inspired by the synthesis of dismutational isomer **1**, partially germanium- and tin- substituted species were also investigated in the Scheschkewitz group and were found as Ge_2Si_4 and Sn_2Si_4[6]. In 2013, Fässler et al. published the synthesis of mixed Si/Ge Zintl clusters[7] and here we present the synthesis and structure of a Si_6Ge cluster as a result of a cluster expansion of the Si_6 siliconoid.

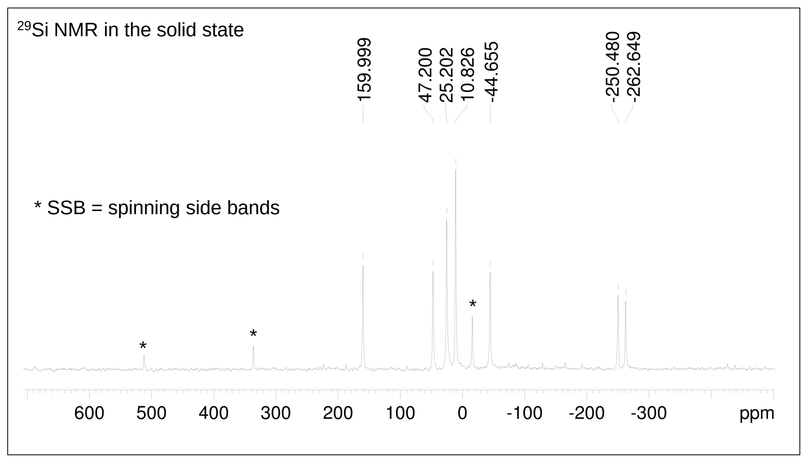


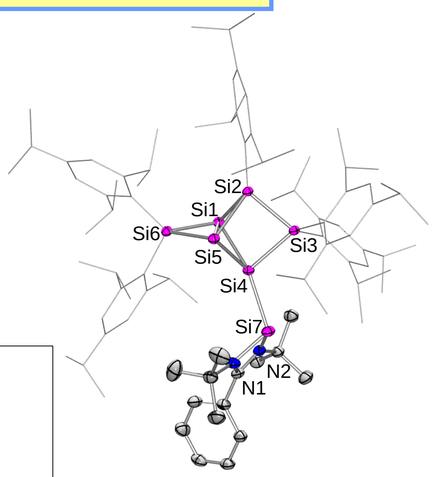
λ_{max} [nm]	518
δ ^{29}Si [ppm] $SiTip_2Ge_2$	236.1
δ ^{29}Si [ppm] SiTip	29.8
δ ^{29}Si [ppm] $SiTip_2Si_2$	14.6

λ_{max} [nm]	679
δ ^{29}Si [ppm] $SiTip_2Sn_2$	284.5
δ ^{29}Si [ppm] SiTip	52.8
δ ^{29}Si [ppm] $SiTip_2Si_2$	23.9

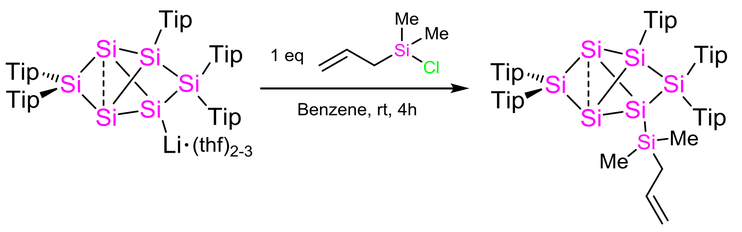
Functionalization of a Si_6 Cluster

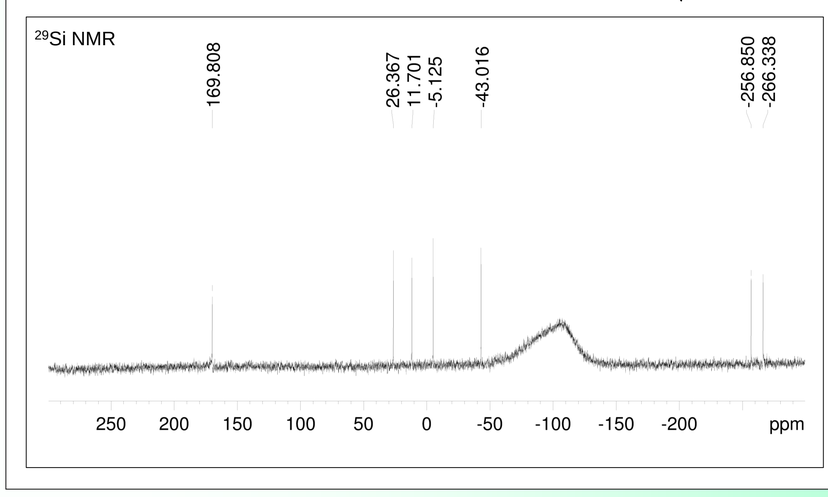


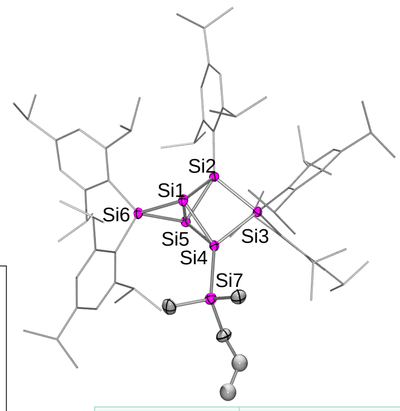




Si atom	δ ^{29}Si [ppm]
Si6	159.9
Si1	−250-5
Si5	−262.7
Si2	25.2
Si4	−44.7
Si3	10.8
Si7	47.2

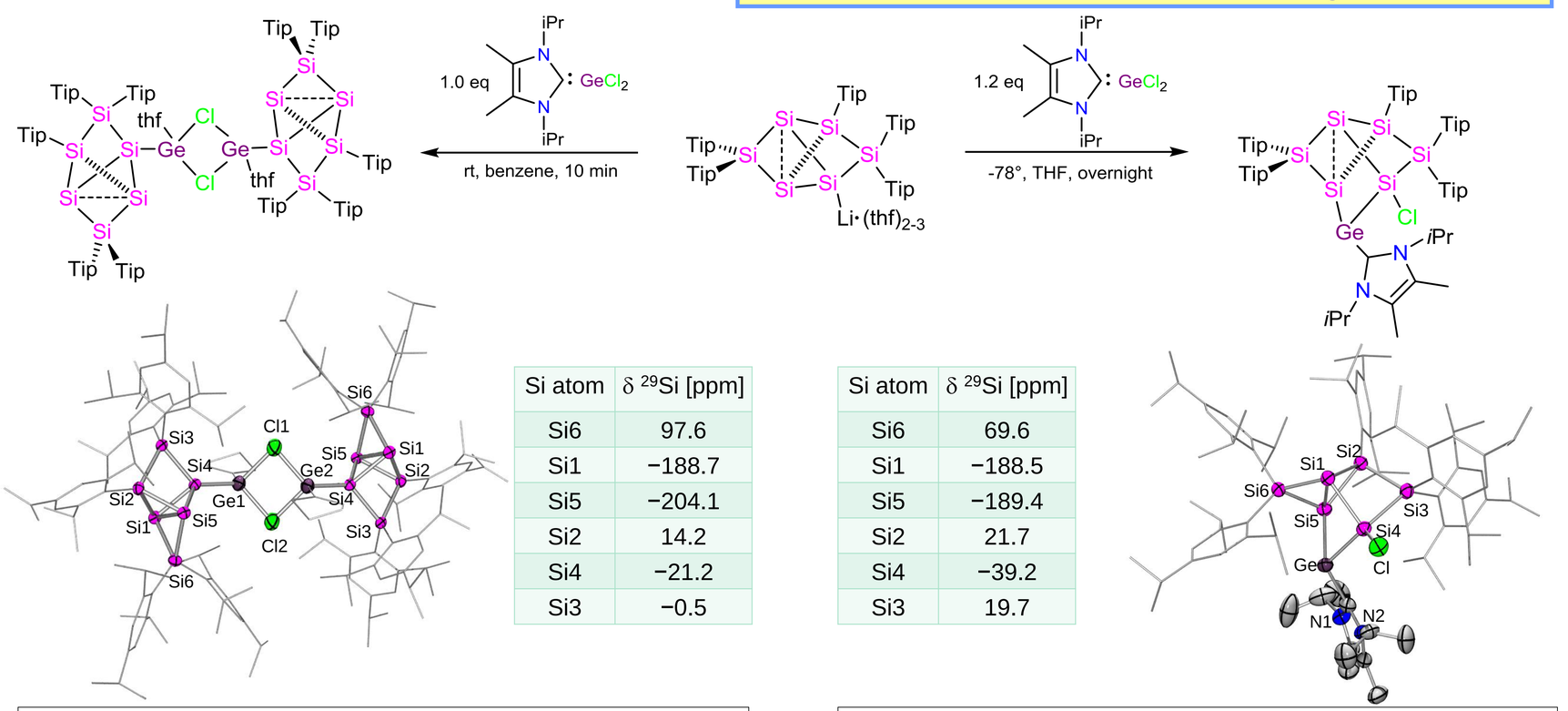






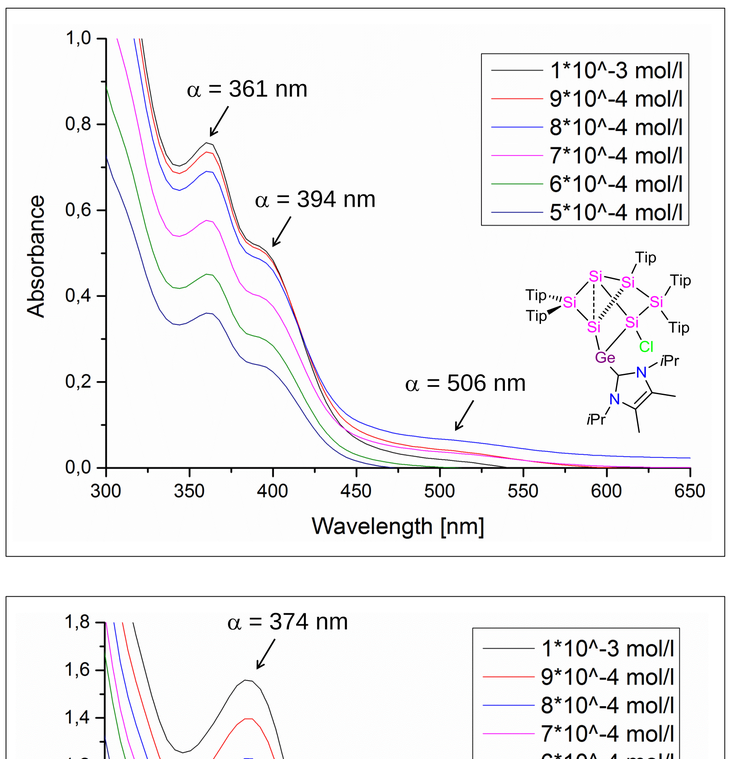
Si atom	δ ^{29}Si [ppm]
Si6	169.8
Si1	−256.9
Si5	−266.3
Si2	26.4
Si4	−43.0
Si3	11.7
Si7	−5.1

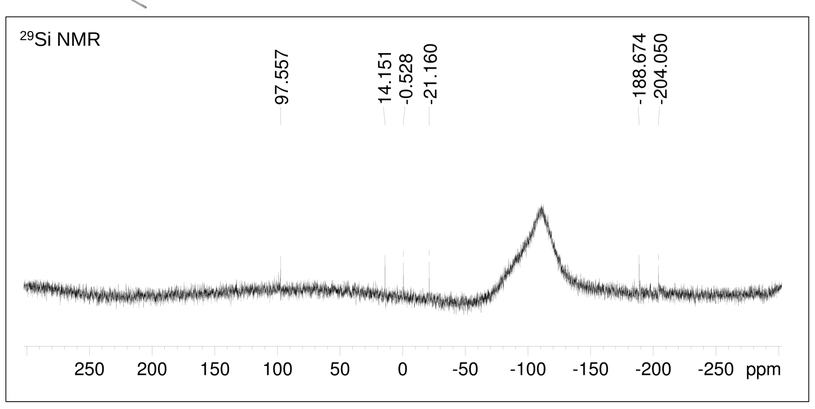
Cluster Expansion of a Si_6 Cluster

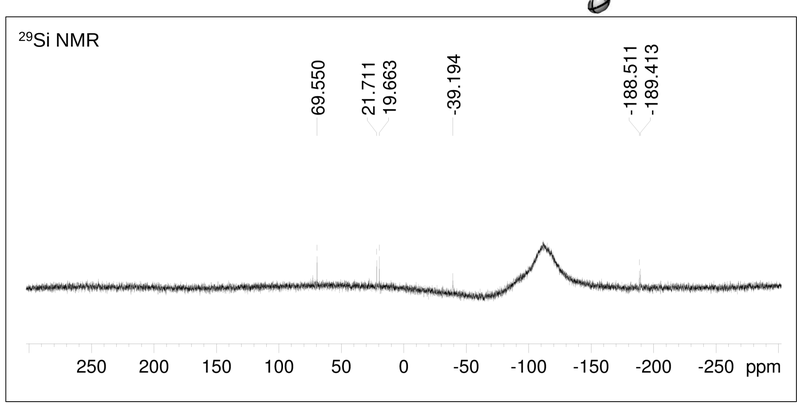


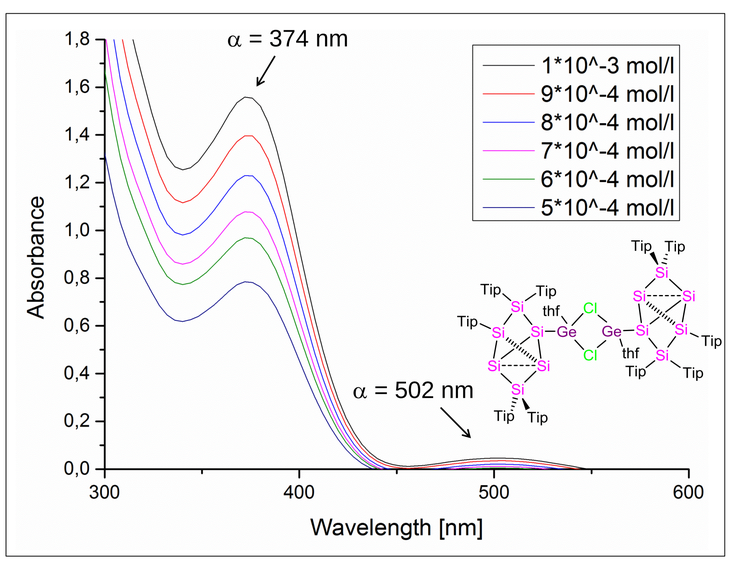
Si atom	δ ^{29}Si [ppm]
Si6	97.6
Si1	−188.7
Si5	−204.1
Si2	14.2
Si4	−21.2
Si3	−0.5

Si atom	δ ^{29}Si [ppm]
Si6	69.6
Si1	−188.5
Si5	−189.4
Si2	21.7
Si4	−39.2
Si3	19.7









Acknowledgements

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