Group 14 Chemistry

DOI: 10.1002/anie.201405238

N-Heterocyclic Carbene Coordinated Neutral and Cationic Heavier Cyclopropylidenes**

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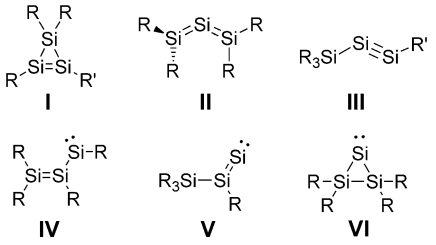
Dedicated to Professor Michael Veith on the occasion of his 70th birthday

Abstract: *Cyclopropylidene is a transient intermediate of the allene–propyne–cyclopropene isomerization. The incorporation of heavier Group 14 elements into the cyclopropylidene scaffold has to date been restricted to the formal replacement of the carbenic carbon atom by a base-coordinated silicon(II) center. Herein we report the synthesis and characterization of NHC-coordinated heavier cyclopropylidenes (Si_2GeR_3X, and Si_3R_3Br; X = Cl, Mes; R = Tip = 2,4,6-$iPr_3C_6H_2$) in which the three-membered ring is exclusively formed by silicon and germanium. In case of the chloro-substituted Si_2Ge-cyclopropylidene, a stable heavier cycloprop-1-yl-2-ylidene cation is obtained by NHC-induced chloride dissociation.*

Cyclopropenes[1] and cyclopropenium cations[2] are iconic compounds of organic chemistry. Even stable homonuclear derivatives of their heavier analogues have been reported.[3] In contrast, the isomeric cyclopropylidenes[4] and cycloprop-1-yl-2-ylidene cations that each feature a carbenic carbon atom have not been isolated to date, although the cyclopropylidenes are established transient intermediates.[5]

Similarly, the heavier trisilacyclopropylidenes have only been studied computationally.[6] On the potential-energy surface of Si_3H_4, six electron-precise isomers were located as minima (**I**–**VI**, R = R′ = H, Scheme 1). Although trisilacyclopropylidene **VI** is considered to be the global minimum at the CCSD/6-311 + G(2df,p) level,[6b] only the persila species **I**, **II**, and **III** are experimentally isolable, stabilized through sterically encumbering substituents. The first cyclotrisilenes **I** were independently disclosed by the groups of Kira (R = SiMe$_2$*t*Bu; R′ = SiR$_3$)[3c] and Sekiguchi (R = R′ = SiMe*t*-Bu$_2$).[3d] Trisilaallenes **II** debuted in work by Kira et al. with the terminal Si atoms incorporated into five-membered carbocycles (R$_2$ = [C(SiMe$_3$)$_2$CH$_2$]$_2$).[7] The first disilynes, reported by Sekiguchi (SiR$_3$ = R′ = Si(*i*Pr)[CH(SiMe$_3$)$_2$]$_2$)[8a] and Wiberg groups (SiR$_3$ = R′ = SiMe(Si*t*Bu$_3$)$_2$),[8b] both bear silyl substituents and hence can be regarded as stable derivatives of Si_3H_4 isomer **III**.

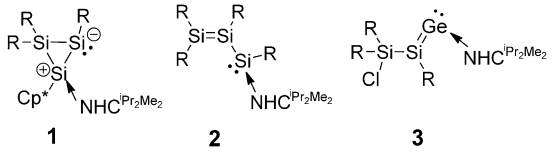


Scheme 1. Isomers of Si_3R_4.

Conversely, in case of silylene-type isomers **IV** to **VI** no stable derivatives have been reported until very recently. Building upon the concept of stabilization of fleeting intermediates by Lewis base coordination,[9] adducts of representatives of **I**, **IV**, and **V** with NHC^{iPr_2Me_2}(NHC^{iPr_2Me_2} = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) were isolated by our group, namely Cp*-substituted (Cp* = C_5Me_5) cyclotrisilene **1**,[10] (disilenyl)silylene **2**,[11] and 2-chlorosilylsilagermenylidene **3** (Scheme 2).[12]

Compound **3** belongs to the class of heavier vinylidenes that we established as novel synthons for Group 14 chemistry.[13] Recently, Robinson et al.[14] and Baceiredo et al.[15] independently reported base-coordinated silacycloprop-1-ylidenes, in which just one heavier Group 14 element is present. We now describe the synthesis of N-heterocyclic carbene (NHC)-coordinated heavier Group 14 cyclopropylidenes and the serendipitous discovery of spontaneous dissociation of a chloride anion to give a cycloprop-2-yliden-1-yl cation.

In light of the current discussion regarding the use of arrows for the representation of donor–acceptor bonding[16]



Scheme 2. NHC coordinated cyclotrisilene **1**, (disilenyl)silylene **2**, and 2-chlorosilylsilagermenylidene **3** (R = Tip = 2,4,6-*i*Pr$_3$C$_6$H$_2$, NHC^{iPr_2Me_2} = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene).

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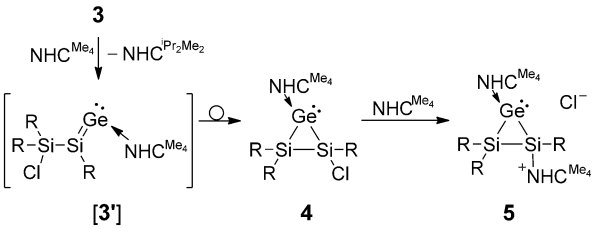
[**] Support by the EPSRC (EP/H048804/1), the COST Action CM1302 (Smart Inorganic Polymers), and the Alfried Krupp von Bohlen und Halbach Foundation is gratefully acknowledged.
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201405238.

we argue that reversible coordination is not just an indication of, but confirmation of a Lewis acid–base complex. Unlike the cases of **1** and **2** with their NMR-spectroscopically demonstrated reversibility of NHC coordination, no such behavior was observed for **3**. We therefore sought to probe this question by the addition of the smaller NHC^{Me_4}, which could plausibly substitute $NHC^{iPr_2Me_2}$ at the germanium center (indicating reversibility of coordination beyond the spectroscopically detectable),[17] or coordinate to the silicon center of the Si=Ge moiety.[18] Computations at the (dispersion corrected, with a continuum solvent field for diethyl ether) ωB97XD/6-311G(d,p) level of theory give $\Delta\Delta G_{298} = -2.99\ kcal\,mol^{-1}$ for the substitution of $NHC^{iPr_2Me_2}$ in **3** by NHC^{Me_4} to yield [**3′**].[19]

Indeed, upon treatment of **3** with one equivalent of NHC^{Me_4}, we observed immediate color change from red to yellow (Scheme 3).[19] ^1H NMR indicates the formation of free $NHC^{iPr_2Me_2}$[20] and concomitant consumption of NHC^{Me_4}; after workup we isolated a yellow amorphous powder in 78% yield. In the ^{13}C NMR the downfield signal at $\delta = 170.81$ ppm



Scheme 3. Syntheses of **4** and **5** (NHC^{Me_4} = 1,3,4,5-tetramethylimidazol-2-ylidene).

suggested coordination of NHC^{Me_4} to the germanium center.[21] The ^{29}Si NMR of the product shows resonances at $\delta = -18.2$ and -71.6 ppm in a 1:1 ratio. The formation of an NHC^{Me_4} stabilized germenylidene of type **3** is ruled out by the absence of the typical downfield signal,[12,13] indicating instead the formation of a three-membered ring, such as the NHC-coordinated heavier cyclopropylidene **4**. Accordingly, $\Delta\Delta G = -4.13\ kcal\,mol^{-1}$ are gained by the cyclization of the undetected intermediate [**3′**] to **4** at the ωB97XD/6-311G(d,p) level of theory.[19] The yellow color of **4** is due to the longest wavelength absorption at $\lambda_{max} = 436$ nm ($\varepsilon = 5370\ L\,mol^{-1}\,cm^{-1}$), which is slightly blue-shifted in comparison to silagermenylidene **3** ($\lambda_{max} = 451$ nm).

In one repeat reaction, we applied an excess of NHC^{Me_4} to **3**, which surprisingly led to the incorporation of a second equivalent of NHC^{Me_4} according to NMR spectra (Scheme 3).[19] In the ^{29}Si NMR, two resonances at $\delta = -68.9$ and -81.9 ppm appeared in a 1:1 ratio. The longest wavelength absorption was observed at $\lambda_{max} = 435$ nm ($\varepsilon = 5020\ L\,mol^{-1}\,cm^{-1}$), similar to that of the product of **3** with one equivalent of NHC^{Me_4} indicative of minimal structural changes upon coordination of the second equivalent. Notably, the ^{29}Si NMR chemical shifts of both products are similar to those of related three-membered silacycles.[10,11] The ωB97XD/6-311G(d,p) level of theory shows that liberation of chloride by the second NHC equivalent is strongly exergonic by $\Delta\Delta G_{298} = -19.83\ kcal\,mol^{-1}$.[19]

Single crystals of **5**, suitable for X-ray diffraction, were obtained at room temperature from a warm saturated THF solution. The determination of the molecular structure confirmed the presence of a cationic three-membered ring (Figure 1).[19] The chloride anion is well-separated from the

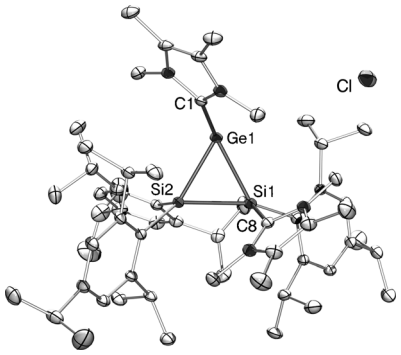
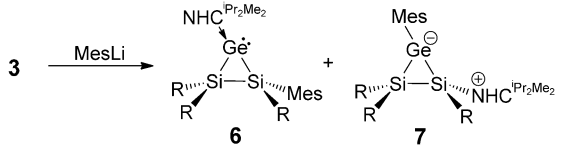


Figure 1. Molecular structure of **5** in the solid state (thermal ellipsoids set at 30% probability; hydrogen atoms and THF molecules omitted). Selected bond lengths [Å]: Ge1-C1 2.035(3), Ge1-Si1 2.4387(10), Ge1-Si2 2.4399(10), Si1-C8 1.934(4), Si1-Si2 2.4127(13).

ring, with distances of 6.342(1) and 6.387(1) Å to Si1 and Ge1, respectively. The two NHC^{Me_4} molecules are coordinated to Si1 and Ge1 in *cis* fashion. The C8–Si1 distance is with 1.934(4) Å not only expectedly shorter than the C1–Ge1 distance with 2.035(3) Å, but also close to a regular C–Si single bond suggesting that the description of **5** as imidazolium salt is more appropriate than as heavier cyclopropylidenylium chloride. Compound **5** was also directly synthesized in 63% from **3** using two equivalents of NHC^{Me_4}.

Prompted by the reaction of **3** with the neutral nucleophile NHC^{Me_4}, we considered anionic nucleophiles, such as mesityllithium. The addition of organolithium reagents to low-coordinate heavier Group 14 compounds has been reported.[22] Notably, in **3**, the attack could either occur at the formal sp^2-silicon center, the germanium center, or the chlorosilyl group. The NMR spectroscopic analysis of the crude mixture from the reaction of **3** with mesityllithium in diethyl ether at room temperature indicates the formation of two compounds in a 3:1 ratio (Scheme 4).[19] The ^{13}C NMR shows two downfield signals at $\delta = 173.47$ and 164.51 ppm indicative of NHC-coordinated germanium and silicon centers, respectively. Similarly, in the ^{29}Si NMR spectrum two sets of resonances with two signals each of equal intensity at $\delta = -63.43$ and -71.91 ppm and $\delta = -56.08$ and -78.10 ppm demonstrate the absence of multiply bonded silicon and suggest a three-membered ring structure similar to that of **4** and **5** instead. Crystallization from *n*-pentane initially yields yellow crystals of **6** as the major product (44%). The yellow color of **6** is due to the longest wavelength absorption in the UV/Vis at $\lambda_{max} = 454$ nm ($\varepsilon = 6420\ L\,mol^{-1}\,cm^{-1}$). X-ray struc-



Scheme 4. Syntheses of **6** and **7** (Mes = 2,4,6-$Me_3C_6H_2$).

ture analysis confirms that NHC^{iPr_2Me_2} is coordinated to the germanium center of **6** (Figure 2).[19]

Keeping the concentrated mother liquor at −20 °C for one week afforded a few orange crystals together with yellow

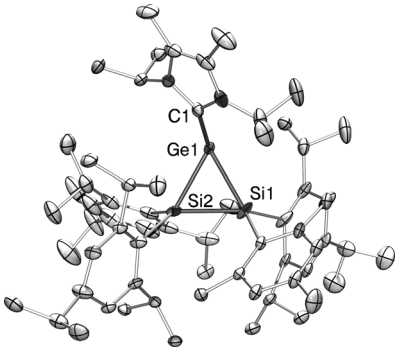
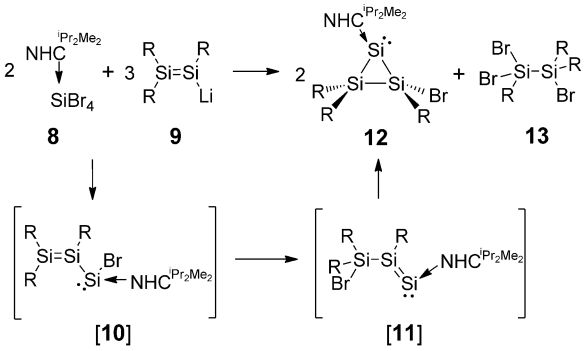


Figure 2. Molecular structure of **6** in the solid state (ellipsoids at 30% probability; hydrogen atoms, pentane and hexane molecules omitted). Selected bond lengths [Å]: Ge1-C1 2.043(3), Ge1-Si2 2.4319(9), Ge1-Si1 2.4320(10), Si1-Si2 2.4448(15).

crystals of **6**. An X-ray diffraction study of the orange crystals confirmed the formation of regioisomer **7**, in which NHC^{iPr_2Me_2} is coordinated to silicon instead of germanium (Figure 3).[19] Compound **7** can be regarded as an NHC^{iPr_2Me_2} coordinated cyclosilagermene;[23] and is thus comparable to the NHC^{iPr_2Me_2} coordinated cyclotrisilene **1**.[10] To date, we were unable to obtain a pure sample of **7**, but the NMR data extracted from spectra of mixtures of **6** and **7** are compatible with the molecular structure determined in the solid state. Based on the observation that the regioisomeric **6** and **7** cannot interconvert, we conclude that the site of initial attack by MesLi determines the outcome of the reaction.

After the successful synthesis of Si_2Ge-cyclopropylidenes (**4**, **6**) and Si_2Ge cycloprop-1-yl-2-ylidene cation (**5**), we focused on the synthesis of a Si_3 scafold of this analogue. To this end, our first choice as a precursor was disilenide **9**,[24] because of its versatile reactivity towards halosilanes.[25]

We anticipated that the reduction of an initial substitution product at the Si^{IV} center would give [**10**], which in analogy to the Si_2Ge system could isomerize via [**11**] to afford **12**. Computations at the ωB97XD/6-311G(d,p) level of theory identified each step of this sequence to be exergonic ([**10**]→[**11**]: $\Delta\Delta G_{298} = -5.84$ kcal mol^{-1}; [**11**]→**12**: $\Delta\Delta G_{298} = -4.00$ kcal mol^{-1}).[19] Surprisingly, from a 1:1 reaction of the NHC^{iPr_2Me_2} adduct of silicon tetrabromide **8** and disilenide **9** we directly obtained a small amount of crystalline compound of **12** together with 1,1,2-tribromodisilane **13**[26] and other unidentified side products indicating that disilenide **9** acts both as a nucleophile and a reducing agent.[25a] Repeating the reaction in the stoichiometrically required 2:3 ratio affords Si_3-cyclopropylidene **12** in 62% yield along with disilane **13** (55%)[26] as the only major side product (Scheme 5).[19] The ^{29}Si NMR spectrum of **12** shows three signals of equal intensity at $\delta = -32.7$, -65.7, and -110.5 ppm. The most upfield shifted resonance is assigned to the NHC^{iPr_2Me_2}-coordinated low-valent silicon by a 2D ^{29}Si-^{1}H spectrum and compares well with that of N-donor-stabilized silacycloprop-1-ylidene ($\delta = -87.5$ ppm).[15] In UV/Vis spectrum **12** shows the longest wavelength absorption at $\lambda_{max} = 466$ nm ($\varepsilon = 7200$ L mol^{-1} cm^{-1}).



Scheme 5. Syntheses of **12** and **13**.

Single crystals of **12** suitable for X-ray structure determination (Figure 4)[19] were obtained from a saturated benzene solution at room temperature. The solid-state structure confirms that the NHC^{iPr_2Me_2} is coordinated to the low-valent silicon in a three-membered ring. The bond between the carbenic carbon (C46) and silicon (Si3) is 1.938(3) Å, which is similar to those of compounds **6** (Si1−C8 1.934(4) Å) and **8** (Si1–C10 1.979(4) Å). The NHC^{iPr_2Me_2}-coordinated silicon center adopts trigonal-pyramidal geometry.

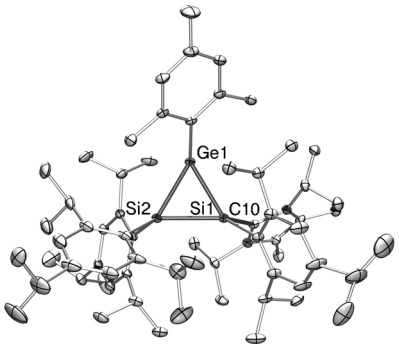


Figure 3. Molecular structure of **7** in the solid state (ellipsoids at 30% probability; hydrogen atoms and half pentane molecules omitted). Selected bond lengths [Å]: Ge1-Si1 2.4250(11), Ge1-Si2 2.4261(11), Si1-C10 1.979(4), Si1-Si2 2.4372(15).

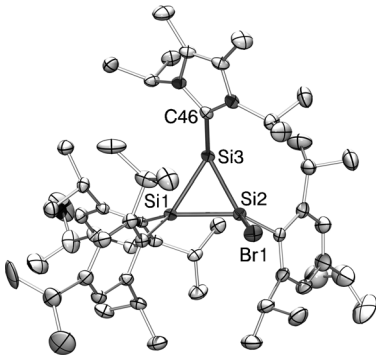


Figure 4. Molecular structure of **12** in the solid state (ellipsoids at 30% probability; hydrogen atoms omitted). Selected bond lengths [Å]: Si3-C46 1.938(3), Si1-Si2 2.3581(12), Si1-Si3 2.3746(12), Si3-Si2 2.2950(12), Br1-Si2 2.3005(10).

In conclusion, by reducing the size of coordinating N-heterocyclic carbenes we have converted heavier vinylidenes into isolable heavier Group 14 cyclopropylidenes that even tolerate residual halide functionality. In one case, the dissociation of a halide anion is prompted by a second equivalent of NHC and affords a heavier NHC-coordinated cycloprop-1-yl-2-ylidene cation. In case of the homonuclear Si_3 species even the larger NHCs directly afford the cyclopropylidene-type isomer.

Received: May 13, 2014
Published online: July 24, 2014

Keywords: cations · germanium · silicon · small rings · subvalent compounds

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[19] Experimental details are supplied in the Supporting Information. Computational details and interactive 3D models are available via the Interactivity Box, DOI: 10.6084/m9.figshare.1016980 and the further digital repository DOIs therein. CCDC 977842 (**5**), 967887 (**6**), 967888 (**7**), 967889 (**12**), 967890 (**13**), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[26] See Supporting Information for the solid state structure of compound **13**.

