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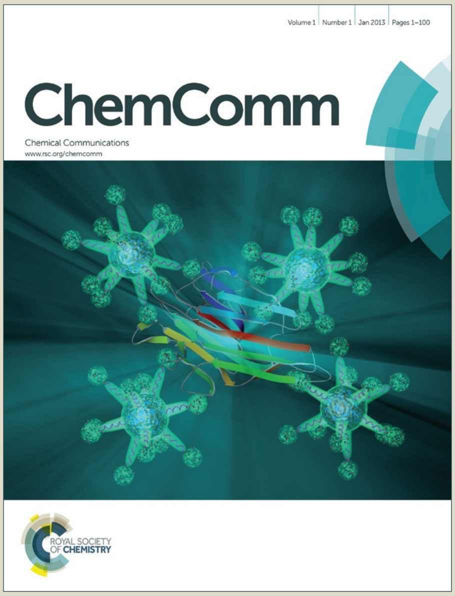

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Dimerization of a marginally stable disilenyl germylene to tricyclic systems: evidence for reversible NHC-coordination

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Tetrasiladigermatricyclohexanes in two isomeric forms (chair and doubly-bridged tetrahedron) are obtained by the reaction of MeLi with an α-chlorosilyl functionalized NHC-stabilized silagermenylidene. ^{29}Si NMR at low temperature proves the initial formation of a monomeric NHC-adduct of a disilenyl germylene followed by cyclisation to the isomeric heavy cyclopropene. Addition of an excess of NHC stabilizes the both intermediates and demonstrates the reversibility of rate-determining initial equilibria involving NHC dissociation. Finally, a mixture of two isomeric tricyclic Si_4Ge_2 species is obtained: at elevated temperature the chair isomer converts to the doubly edge-bridged tetrahedron.

Low-valent and multiply-bonded systems play an important role as transients in processes from molecules towards the elemental bulk and have therefore been subject of various theoretical and experimental studies with a considerable focus on stabilization and isolation.[1] The recently emerged concept of stabilization of such species by coordination with N-heterocyclic carbenes (NHCs) has enabled the characterization of various otherwise inaccessible species.[2] In particular, the seminal discoveries of stable adducts of $Si(0)_2$[3] and $Ge(0)_2$[4] with two equivalents of NHC provided a considerable impetus. More recently, NHC adducts of heavier vinylidenes were isolated[5] and have shown to be versatile precursors due to their high degree of functionality.[6] The question of reversibility of NHC coordination is of central importance in the light of the ongoing debate on the relative contributions of donor-acceptor bonding and covalent interactions in such complexes.[7] As we have argued, the presence of equilibria is at least a powerful indication for a donor-acceptor-interaction of the reactive species with the stabilizing NHC. Strong hints at reversible coordination of Lewis bases to low valent Group 14 systems were provided by the abstraction of NHCs[6b,8] or an isonitrile[9] by Lewis acids.

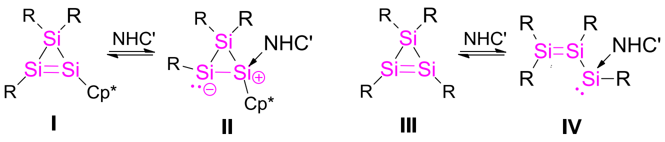
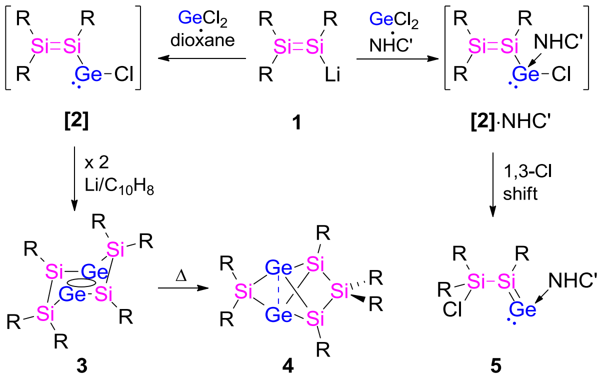


Chart 1 Cyclotrisilenes **I** and **III** in equilibrium with NHC' adducts **II** and **IV**, respectively (R = Tip = 2,4,6-$iPr_3C_6H_2$, NHC' = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene, Cp* = C_5Me_5).

Direct spectroscopic proof for equilibrium reactions with NHCs was obtained in case of the cyclotrisilenes **I** and **III**. While **I** coexists with the NHC-adduct to the Si=Si double bond **II**,[10] the homoleptic cyclotrisilene **III** gives rise to reversible ring opening by the NHC to disilenyl silylene **IV**. The cyclic adduct corresponding to **II** is only observed upon shock-freezing a solution of **III** and **IV** (Chart 1).[11] The related reaction of cyclotrisilenes with isonitriles[12] and carbon monoxide[13] were also suggested to be reversible.



Scheme 1 Reaction of disilenide **1** with $GeCl_2$·NHC' via **[2]**·NHC' to NHC-stabilized silagermenylidene **5** and reaction of disilenide **1** with $GeCl_2$·1,4-dioxane via **[2]** to dismutational Ge_2Si_4 isomer **3** which is thermally converted in **4** (R = Tip = 2,4,6-$iPr_3C_6H_2$, NHC' = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene).

Attempts to prepare a disilenyl-substituted germylene have so far not met with success: we had proposed the disilenyl-substituted germanium(II)chloride **[2]** as an unstable intermediate of the reaction of disilenide **1** with $GeCl_2$·dioxane adduct. Although no spectroscopic evidence for **[2]** was forthcoming, the *in situ*-reduction with lithium/naphthalene yielded the unsaturated heteronuclear

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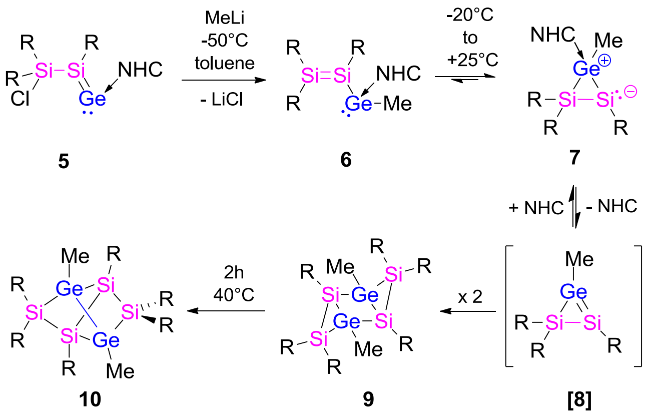
† Electronic Supplementary Information (ESI) available: Experimental details, NMR and X-ray crystallographic data (CIF) for **9** (CCDC-1439296) and **10** (-1439297). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

cluster **3**, which in turn slowly rearranges to the thermodynamically more stable **4**.[14] The related NHC-adduct **[2]**·NHC' was invoked as transient intermediate that undergoes a 1,3-chlorine shift to afford the NHC-complex of silagermenylidene **5**.[5b] Here, we report the conceptual reversal of this approach: reaction of **5** with MeLi allows for the spectroscopic observation of two unsaturated intermediates in a chain of reversible equilibria prior to the irreversible formation of saturated tricyclic Ge_2Si_4 species: a surprisingly stable NHC-complex of a disilenyl-substituted germylene as well as the isomeric cyclopropene-analogue.

The chloro functionality of the proposed germylene intermediates **[2]** and **[2]**·NHC' with its high propensity for migration is likely the key to their instability. We therefore sought to substitute the chloro group by an electronically and sterically innocent methyl group. As discussed previously in the context of the reactivity of **5** with bulkier nucleophiles such as mesityl lithium, nucleophilic attack can either occur at the germanium centre, the chlorosilyl group or the formal sp^2-silicon centre.[6a] If the nucleophilic attack took place at the Ge(II)-center, a subsequent LiCl elimination would result in a Si-Si double bond and thus give access to the NHC-stabilized disilenyl germylene **6** (Scheme 2).



Scheme 2 Reaction of **5** with MeLi to NHC-coordinated disilenyl germylene **6** (R = Tip = 2,4,6-$iPr_3C_6H_2$, NHC' = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene).

A solution of MeLi (3.0 M) was added to a precooled solution of **5** in toluene-d_8. At −60°C only starting material was detected (Fig. S1a in ESI), but upon warming to −40°C two new ^{29}Si NMR signals appeared at δ = 90.07 and 85.40 ppm in an approximate ratio of 1:1 (Fig. S1b in ESI), which is consistent with the presence of a Si=Si double bond. Almost full conversion was reached at −20°C (Fig. S1c in ESI). A multiplet at 5.75 ppm in the ^1H NMR (for comparison **5**: septet at 5.41 ppm for $CHCH_3$ of NHC) and a ^{13}C NMR resonance at δ = 175.22 ppm are indicative of the coordination of the NHC to the Ge(II)-center.[5] These spectroscopic data (Fig. S4-S6 in ESI) strongly support the formulation of the initial reaction product as an NHC-coordinated disilenyl germylene **6**. All attempts to isolate **6** failed, even when the entire workup of the crude reaction mixture was carried out at −10°C. When a sample is further warmed to room temperature, new ^{29}Si NMR signals at δ = −64.92 and −66.51 ppm (Fig. S1d in ESI) start growing in, in accordance with the formation of a three-membered ring. A characteristic ^{13}C NMR signal at δ = 175.90 ppm (Fig. S9 in ESI) proves the coordination of NHC to the germanium centre (see above). On the basis of the spectroscopic data it is concluded that the product corresponds to **7**, the NHC-adduct of a 2,3-disilagermirene analogous to the previously reported stable example with the bulkier mesityl group in place of methyl.[6a,15] Stable disilagermirenes without base-coordination, but with sterically demanding substituents at all three ring atoms have been reported.[16]

Well before complete conversion to **7**, however, an additional set of signals at higher field starts appearing in the ^{29}Si NMR at δ = −82.55 and −96.42 ppm (Fig. S1d in ESI) with concomitant formation of free NHC. We thus speculated that the addition of excess NHC' may slow down this secondary process. Indeed, in a separate NMR experiment in the presence of 3.8 eq of NHC' only ^{29}Si NMR signals at δ = −64.73 and −66.49 ppm (Fig. S2b in ESI) were observed even after heating of the mixture to 50°C for 5h (Fig. S3 in ESI).

Keeping the mixture at room temperature overnight in the absence of more than one equivalent of NHC' results in the complete disappearance of the ^{29}Si NMR signals of **7**. In addition to the two sharp resonances at δ = −82.60 and −96.58 ppm, a second set of broad signals at δ = 21.97 and −37.74 ppm in the integrated ratio of 3:3:2:2 (Fig. S12 in ESI) is observed together with a small amount of an unknown CH-insertion product (^{29}Si NMR: δ = −65.94 ppm, ^1H NMR: characteristic singlet for SiH at δ = 5.57 ppm see Fig. S10 in ESI). Insertion into CH bonds is typically observed for highly reactive species. The ^1H and ^{13}C NMR spectra prove the formation of considerable amounts of free NHC'; we therefore conclude that the formation of the products responsible for the new signals is preceded by the reversible dissociation of NHC' from **7** to give the transient (and unobservable) base-free heavier cyclopropene **[8]**. In case of the homonuclear cyclotrisilene **III** the species corresponding to **6** and **[8]** coexist at room temperature, which can be attributed to the higher stability of isolable **III** due to sterically more demanding substitution pattern. Interestingly, the stability of the disilenyl germylene **6** is similarly increased by excess NHC' (Fig. S2a in ESI).[11]

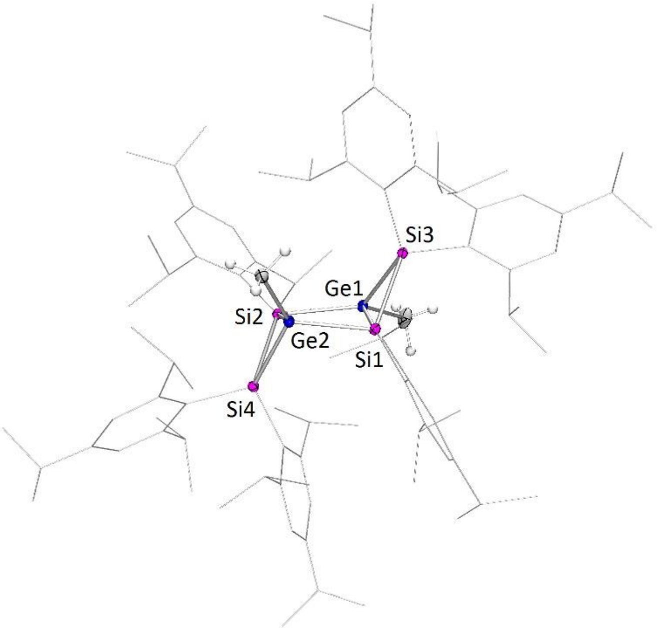


Fig. 1 Molecular structure of **9**·C_7H_8 in the solid state (ellipsoids are at 30%, hydrogen atoms, co-crystallised toluene and disorder omitted for clarity). Selected bond lengths [Å]: Ge1-Si1 2.4099(8), Ge1-Si2 2.4174(8), Ge1-Si3 2.4596(8), Ge2-Si1 2.3725(8), Ge2-Si2 2.4163(8), Ge2-Si4 2.4568(8), Si1-Si3 2.3395(10), Si2-Si4 2.3881(10).

After removal of free NHC by sublimation, crystallisation from toluene at −26°C afforded a few pale red crystals of **9**, co-crystallised with a large amount of colourless crystals of **10**. The X-ray diffraction study on the pale red crystals established the connectivity of the chair-like tetrasila-2,5-digermatricyclohexane **9** (Fig. 1). The central four-membered ring contains the two methyl-substituted germanium centres in 1,3-position with no apparent Ge-Ge bonding (Ge1-Ge2: 3.1984(4) Å). The Ge-Si bond distances (between 2.3725(8) Å and 2.4174(8) Å) of the central four-membered Si_2Ge_2 ring (folding angle: 165.38°) are similar to those of the unsaturated version **3** with "naked" germanium atoms.[14]

The X-ray diffraction study of the colourless crystals reveals a different tricyclic system with a remarkable change in connectivity. The tetrasila-4,5-digermatricyclo$[2.2.0.0^{2,5}]$hexane **10** is best described as a doubly edge-bridged tetrahedron with a direct bond between the two germanium atoms (Fig. 2). The Ge1-Ge2 distance is with 2.4534(5) Å within the typical range of a single bond.[17,18] The Si1-Si2 bond in **10** (2.4809(11) Å) is significantly longer than in analogous homonuclear silicon systems, be they unsaturated[19] or saturated.[20-22]

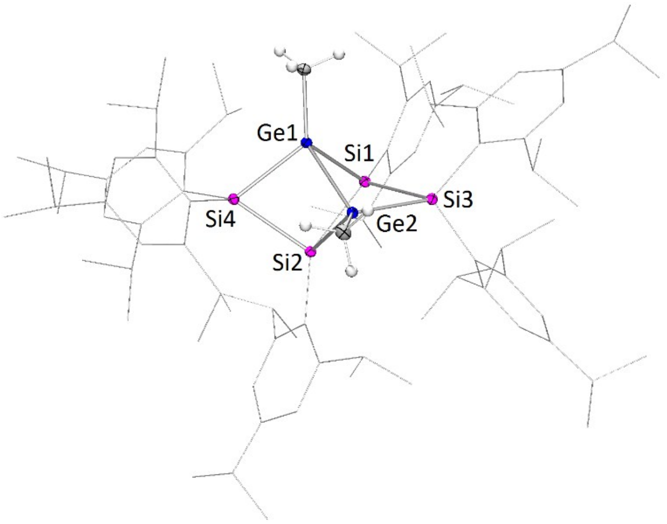


Fig. 2 Molecular structure in the solid state of $\mathbf{10}\cdot 0.5\ C_7H_8$ (thermal ellipsoids are drawn at 30%, hydrogen atoms and co-crystallised half toluene molecules and disorder are omitted for clarity). Selected bond lengths [Å]: Ge1-Si4 2.4072(8), Ge1-Si1 2.4344(8), Ge1-Ge2 2.4534(5), Ge2-Si3 2.3956(8), Ge2-Si2 2.4398(8), Si1-Si3 2.3993(11), Si1-Si2 2.4809(11), Si2-Si4 2.4464(11).

The chair-like isomer **9**, the apparent kinetic product of the dimerization of the transient heavier cyclopropene **[8],** is unstable in solution and therefore a clean sample could not be obtained yet. Full conversion of **9** is achieved by heating the mixture to 40°C for two hours, affording predominantly **10**. A similar, albeit photochemical isomerisation has been reported for a homonuclear Si_6R_8 derivative (R = Si^tBuMe_2) by Kira and co-workers.[21] In the present heteronuclear case, the change in connectivity of the germanium atoms from 1,3 in **9** to 1,2 in **10** is in stark contrast to the case of the 1,4-digermatetrabenzene isomer **3**, which is thermally converted into the likely global minimum isomer **4** without such a change in connectivity (Scheme 1).[14] A pure sample of **10** was obtained by crystallization in 63 % yield. The comparison of the ^{29}Si NMR data of pure **10** with the reaction mixture of **9** and **10**, shows that the broad signals at δ = 21.97 and −37.74 ppm (Fig. S14 in ESI) belong to **10** and that the shifts at δ = −82.60 and −96.58 ppm must consequently be assigned to **9**. The ^{29}Si NMR resonances are comparable to those of homonuclear derivatives of tricyclohexasilane.[20-22]

In order to shed some light on the relative thermodynamic stabilities of **6**, **7**, and **[8]**, we performed DFT calculations on truncated model systems (Me instead of Tip substituents; see ESI for details) at the B3LYP/6-31+G(d,p) level of theory. The calculated gain in free energy from **6-Me** to **7-Me** of $\Delta G = -5.2$ kcal mol^{-1} with an activation barrier of $\Delta G^{\neq} = +8.7$ kcal mol^{-1} is fully in line with the observed equilibrium in favour of **7**. The dissociation of NHC' from **7-Me** to give **8-Me** is strongly endergonic in Gibbs energy ($\Delta G = +21.7$ kcal mol^{-1}), albeit the larger Tip groups would likely decrease this value considerably in the experimental case. Although the dimerization of **8-Me** to **9-Me** is calculated to proceed without apparent barrier with a gain in free energy of $\Delta G = -64.9$ kcal mol^{-1}, **9-Me** is still by $\Delta G = -25.1$ kcal mol^{-1} higher than **10-Me** (see ESI for details), which reflects the experimental observation that **9** is formed as kinetic product prior to its rearrangement to **10**.

In summary, we have gathered spectroscopic evidence for two reactive intermediates on the way towards saturated Ge_2Si_4 dimeric aggregates with saturated scaffolds that structurally resemble the recently reported unsaturated Ge_2Si_4 systems. Initial attack of the sterically innocent methyl anion equivalent at germanium results in formation of an NHC-stabilized disilenyl germylene **6**, followed by ring-closure to an NHC-adduct of a heavier cyclopropene **7**. The reversibility of the NHC coordination to **7** is unambiguously proven. The stabilization by excess NHC is a concept resembling common strategies in the stabilization of catalytically active species in the transition metal series and we conclude that this approach will also have an impact in further developments in main group chemistry.

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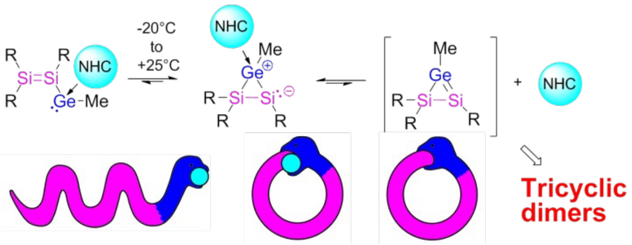
TOC Scheme



TOC Text

Reaction of an α-chlorosilyl functionalised base-stabilised silagermenylidene (heavier version of vinylidene) with MeLi yields a marginally stable disilenyl germylene, which dimerises to two tricyclic isomeric Si/Ge species via an unsaturated three-membered ring species. The stability of the intermediates is increased by the addition of excess N-heterocyclic carbene thus proving the reversibility of its coordination.