VIP **Ge–Ge Double Bonds** | **Very Important Paper**

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A Multiply Functionalized Base-Coordinated Ge^{II} Compound and Its Reversible Dimerization to the Digermene**

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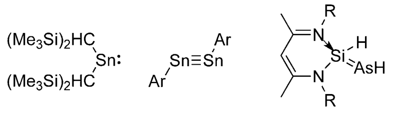
Dedicated to Professor Kaspar Hegetschweiler on the occasion of his 60th birthday

Abstract: *Stable compounds with a Ge=Ge bond are usually prepared under relatively harsh reaction conditions that are incompatible with many functional groups. In particular, unsaturated functionalities are not tolerated owing to their facile reaction with low-coordinate germanium compounds. We now report the synthesis of an imino-functionalized germanium(II) species, stabilized by coordination of an N-heterocyclic carbene (NHC), by reaction of an isonitrile with a heavier NHC-coordinated vinylidene. Removal of the NHC by a Lewis acid results in dimerization to the corresponding digermene with a Ge=Ge bond. The reversibility of this process is demonstrated by addition of two equivalents of NHC to the isolated digermene.*

Stable multiply bonded species play a pivotal role in the chemistry of heavier main-group elements.[1] The unique properties of heavier element double bonds (inherently small HOMO–LUMO gap, conformational flexibility and high reactivity) render the idea of their incorporation into conjugated systems an exciting prospect. Prompted by the successful preparation of P=P- and P=C-containing conjugated polymers,[2] intense efforts towards analogous Group 14 systems followed, but are to date restricted to model compounds with two heavier element double bonds.[3] These difficulties mainly arise from the low selectivity of suitable preparative procedures in the presence of multiple reactive sites. Synthetic methods to selectively (and possibly reversibly) generate multiple bonds between heavier Group 14 elements under mild conditions are therefore urgently needed. Encouraging proofs-of-principle reactions include the equilibrium between Lappert's stannylene **I** and its dimer,[4] the reversible reaction of distannynes of type **II** with ethylene,[5] and the reversible formation of the arsasilene **III** (Scheme 1).[6] In his remarkable 2010 Review, Power identified reversibility as one of the conceptual similarities between main-group and transition metals.[7] In the case of germanium, there are numerous reports on germylene–digermene equilibria in solution,[8] but in general a lack of residual functionality prevents the further exploitation of this behavior for the creation of extended systems. Compounds with Ge=Ge bonds are usually obtained from either nucleophilic substitution reactions, photolysis of germanes, or reductive dehalogenation of 1,1-dichlorogermanes.[9]



I **II** **III**

Scheme 1. Selected examples of low-valent Group 14 compounds formed by reversible reactions (**II**: Ar = terphenyl-type substituent, **III**: R = 2,6-iPr$_2$C$_6$H$_3$).

As a consequence, digermenes with residual functionality in the periphery of the double bond are rare: a 1,2-dibromodigermene was reported by Tokitoh et al.[8f] and a lithium digermenide, albeit not fully characterized, has been described by the groups of Masamune and later Weidenbruch.[10] We now disclose the synthesis of an cyclic N-heterocyclic carbene(NHC)-coordinated germanium(II) compound with no less than two different residual functionalities: an exocyclic imino group and a chloro substituent. Decomplexation of the NHC by triphenylborane (BPh$_3$) results in dimerization to the corresponding digermene, a process which is reversed by adding anew two equivalents of the NHC.

The concept of the stabilization of low-valent main-group species by the coordination of strong bases has allowed the isolation of various compounds with otherwise inaccessible structural motifs.[11] In particular in the case of germanium, numerous low-valent species have been obtained employing this strategy.[11d,12] We recently reported the synthesis of silagermenylidenes **1**[13] and **2**[14] (Scheme 2) and established the formal [2+2] cycloaddition of **1** with phenylacetylene as well as the donor ability of **2** towards the Fe(CO)$_4$ fragment. Subsequently, we disclosed that an NHC exchange in **2**

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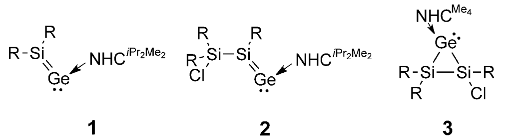
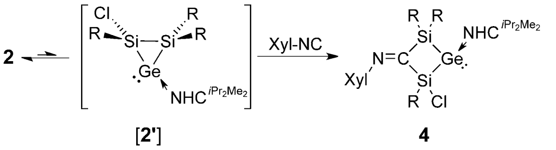


Scheme 2. Heavier vinylidenes **1** and **2** as well as cyclopropanylidene analogue **3** (R = Tip = 2,4,6-$i\mathrm{Pr_3C_6H_2}$, $\mathrm{NHC}i^{\mathrm{Pr_2Me_2}}$ = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene, $\mathrm{NHC^{Me_4}}$ = 1,3,4,5-tetramethylimidazol-2-ylidene).

prompts ring closure to give the heavier cyclopropanylidene species **3** (Scheme 2).[15] This observation encouraged us to investigate the reactivity of **2** towards isonitriles. Isonitriles react with both $\mathrm{Ge^{II}}$ centers,[16] and Si=Ge bonds,[17] as well as facile insertion into Si–Si bonds[18]—in case of strained cyclic compounds and double bonds even in the absence of a catalyst.[19]

The stoichiometric reaction of xylylisonitrile and **2** at 65 °C affords the four-membered cyclic germanium(II) species **4** isolated in 58 % yield as a purple solid (Scheme 3).[20]



Scheme 3. Synthesis of **4** (R = Tip = 2,4,6-$i\mathrm{Pr_3C_6H_2}$, Xyl = 2,6-$\mathrm{Me_2C_6H_3}$).

The purple color of compound **4** is due to the longest wavelength absorption at $\lambda_{\max} = 499$ nm ($\varepsilon = 1330\,\mathrm{L\,mol^{-1}\,cm^{-1}}$), which is red-shifted in comparison to silagermenylidene **2** ($\lambda_{\max} = 451$ nm). In general, the colors of cyclic bis(silyl)imines almost cover the entire range of the visible spectrum.[19a,21]

The multinuclear NMR data of the crude reaction mixture of **4** indicate that $\mathrm{NHC}^{i\mathrm{Pr_2Me_2}}$($\mathrm{NHC}^{i\mathrm{Pr_2Me_2}}$ = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) is still coordinated (^{13}C NMR: $\delta = 169.8$ ppm).[12d] The two silicon ring atoms show ^{29}Si chemical shifts in line with tetracoordination (^{29}Si NMR: δ = 5.6 and 13.5 ppm).[22] In the ^{13}C NMR spectrum of **4** the lowest-field resonance appears at $\delta = 216$ ppm, which is very close to those of known bis(silyl)imines ($\delta \approx 213$–231 ppm).[18,21]

Single-crystal X-ray structural analysis (Figure 1) confirms the formation of an $\mathrm{NHC}^{i\mathrm{Pr_2Me_2}}$-coordinated cyclic four-membered germylene[23] with an exocyclic imino functionality and a residual chloro substituent. The distance between the carbenic carbon and the germanium center (Ge–C46 1.986(6) Å) is at the short end of the usual range observed for NHC coordination to germanium (1.96–2.34 Å).[11d] The germanium center is strongly pyramidal with the sum of bond angles at $\Sigma = 313.07°$.

To gain more insight into the mechanism of the formation of **4** we performed computations at the ωB97XD/6-311G(d,p) level of theory with a continuum solvent model for toluene. The cyclization free energy of **2** to the cyclopropylidene isomer [**2′**] is calculated as $\Delta\Delta G_{298} = -0.6\,\mathrm{kcal\,mol^{-1}}$ (Scheme 3). Considering that the apparent overestimation of the stability of [**2′**] is well within the error margin of the method, [**2′**] is a plausible—albeit experimentally unobserved—initial product formed in equilibrium, prior to the insertion of isonitrile to the Si–Si bond yielding **4**.[15] The cyclization energy in the case of [**2′**] is significantly less exergonic than that of the $\mathrm{NHC^{Me_4}}$ analogue **3** ($\mathrm{NHC^{Me_4}}$ = 1,3,4,5-tetramethylimidazol-2-ylidene) ($\Delta\Delta G_{298} = -4.1$ kcal mol^{-1}), in line with experimental observations. Possible alternative scenarios, such as isonitrile insertion into the Si–Si single bond of **2** or addition to the Si=Ge bond would both involve more endergonic intermediates (Scheme 4: $\Delta\Delta G_{298} = +18.9\,\mathrm{kcal\,mol^{-1}}$ for [**4′**]; $\Delta\Delta G_{298} = +13.9\,\mathrm{kcal\,mol^{-1}}$ for [**4″**] relative to **4**).[20]

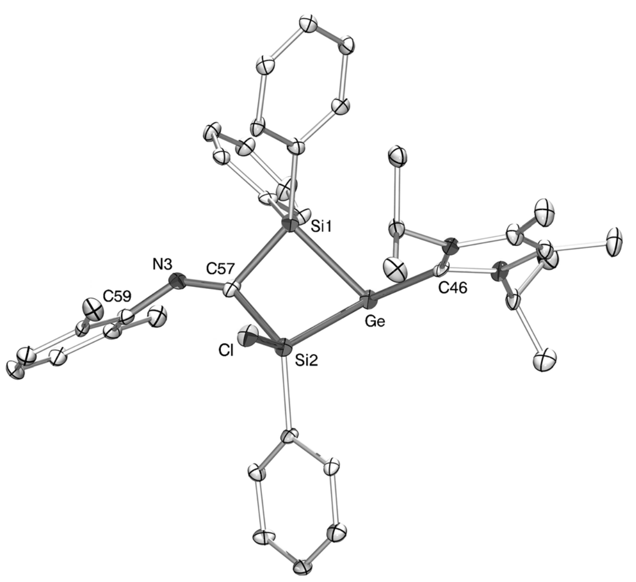
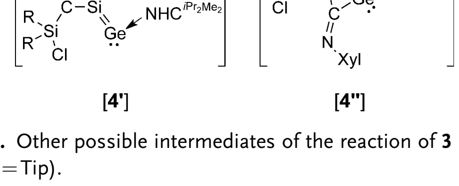


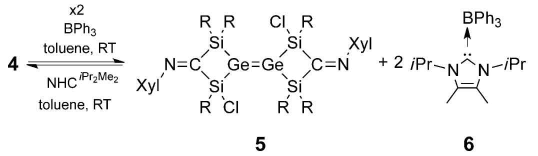
Figure 1. Crystal structure of **4** (thermal ellipsoids at 30 %, isopropyl groups of Tip substituents, hydrogen atoms, and co-crystallized solvent molecules omitted for clarity). Selected bond lengths [Å] and angles [°]: Ge-C46 1.986(6), Ge-Si2 2.365(2), Ge-Si1 2.420(2), Si2-C57 1.979(7), Si1-C57 1.946(7), C57-N3 1.276(8), N3-C59 1.402(8); C46-Ge-Si2 120.7(2), C46-Ge-Si1 113.15(19), Si2-Ge-Si1 79.22(7), C57-Si2-Cl 101.2(2), C57-Si2-Ge 86.4(2), Cl-Si2-Ge 128.66(10), C57-Si1-Ge 85.6(2).



Scheme 4. Other possible intermediates of the reaction of **3** and XylNC (R = Tip).

Compound **4** is stable in solution and in the solid state for months in inert atmosphere at ambient temperature. Moreover, in solution even at 65 °C we did not observe any dissociation of the NHC from the germanium center. We therefore decided to employ an external Lewis acid, $\mathrm{BPh_3}$, as an NHC scavenger.[24]

The 1:1 reaction of **4** with $\mathrm{BPh_3}$ at room temperature leads to the complete consumption of **4** cleanly affording a new product **5** (Scheme 5).[20] We isolated **5** as a brown red solid in



Scheme 5. Reversible reaction of **4** with triphenylborane under formation of digermene **5** (R = Tip).

62 % yield, which was characterized by ^{1}H NMR, UV/Vis spectroscopy, elemental analysis, and X-ray diffraction. ^{13}C and ^{29}Si NMR spectra could not be obtained owing to the low solubility of **5** in benzene, toluene, hexane, or thf. The remaining filtrate contained NHC$^{i\text{Pr}_2\text{Me}_2}$·BPh$_3$ (**6**), as confirmed by spectroscopic data in the literature.[25] The longest wavelength absorption of **5** in the UV/Vis spectrum is observed at $\lambda_{\max} = 507$ nm ($\varepsilon = 19170$ L mol^{-1} cm^{-1}), which is slightly red-shifted in comparison to germylene **4** ($\lambda_{\max} = 499$ nm) and tetrasilyl substituted acyclic digermene, $(i\text{Pr}_3\text{Si})_2\text{Ge=Ge}(\text{Si}i\text{Pr}_3)_2$ ($\lambda_{\max} = 472$ nm).[26] Conversely, the absorption is blue-shifted compared to that of the twisted tetrasilyl-substituted digermene, $(t\text{Bu}_2\text{MeSi})_2\text{Ge=Ge}(t\text{Bu}_2\text{MeSi})_2$ ($\lambda_{\max} = 618$ nm).[27]

Compound **5** crystallizes in the monoclinic *I*2/*a* space group together with one benzene molecule. The center of inversion is situated in the middle of the Ge–Ge bond (Figure 2). This solid-state structure is also reflected in the ^{1}H NMR spectrum in solution with only one set of signals for the xylyl and Tip substituents. The Ge–Ge bond length is 2.2944(4) Å, which is typical of Ge=Ge double bonds, for example, $\text{Dis}_2\text{Ge=GeDis}_2$ ($\text{Dis} = \text{CH(SiMe}_3)_2$) 2.347(2) Å.[28] The exocyclic C1–N1 bond distance is 1.272(2) Å, which is similar to that of C=N in **3** (1.276(8) Å). The sum of angles at Ge is $\Sigma = 334.52°$ and the geometry thus *trans*-bent with a *trans*-bent angle of $\theta = 37.73(2)°$, in the typical region for digermenes.[1c]

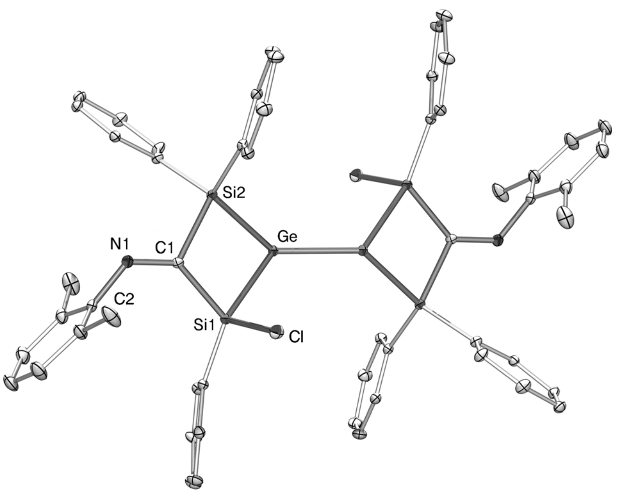


Figure 2. Crystal structure of **5** (thermal ellipsoids at 30 %, isopropyl groups of aryl substituted, hydrogen atoms, and benzene molecule as solvent are omitted for clarity). Selected bond lengths [Å] and angles [°]: Ge-Ge′2.2944(4), Ge-Si1 2.4126(5), Ge-Si2 2.4518(5), Si1-C1 1.9410(17), Si2-C1 1.9666(17), N1-C1 1.272(2), N1-C2 1.419(2); Ge′-Ge-Si1 122.236(16), Ge′-Ge-Si2 131.336(17), Si1-Ge-Si2 80.950(16), C1-Si1-Ge 85.52(5), C1-Si2-Ge 83.90(5), C1-N1-C2 126.93(15), N1-C1-Si1 132.91(13), N1-C1-Si2 116.88(13), Si1-C1-Si2 107.81(8).

With four stereogenic centers (Ge, Si1, Ge′, and Si1′) in **5** the theoretical number of diastereomers is eight; however we selectively obtained only the centrosymmetric and thus achiral *E*-isomer. Even though we do not have definite proof for the integrity of **5** in solution, the computed free energy of the reaction in Scheme 5 is strongly exergonic ($\Delta\Delta G_{298} = -31.4$ kcal mol^{-1}; ωB97XD/6-311G(d,p)/toluene).[20] We therefore discount the possibility of any discernible dissociation of **5** in solution although the limited solubility of **5** in common organic solvents prevents further investigations in this regard. Nonetheless, the integrity of **5** in solution is supported by the absence of any rearranged product, in contrast to the behavior of Marschner's Et$_3$P-stabilized five-membered germylene.[29] Indeed, despite the presence of both unsaturated functionalities (imino groups) and competent leaving groups (chloro substituents), the digermene **5** is stable in the solid state for several weeks.

In a study by Baines et al., NHC-coordinated dimesityl germylene had been obtained by treatment of the corresponding digermene with NHC$^{i\text{Pr}_2\text{Me}_2}$.[30] Similarly, reaction of **5** with two equivalents of NHC$^{i\text{Pr}_2\text{Me}_2}$ at room temperature afforded **4** almost quantitatively (Scheme 5).

In conclusion, we have established the synthesis of an NHC-coordinated four-membered germylene with two peripheral functionalities—an exocyclic imino moiety and a chloro substituent in α-position to the Ge$^{\text{II}}$ center. Its suitability as a synthon for digermene synthesis was demonstrated by removal of the stabilizing NHC under very mild conditions. Notably, this reaction can be reversed by adding NHC again leaving the functional groups untouched. Combined in a single compound, these features create unprecedented opportunities for the creation of extended systems such as polymers incorporating Ge=Ge moieties as repeat units.

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[20] Experimental details are in the Supporting Information. Computational details are available by the Interactivity Box published at http://dx.doi.org/10.6084 m9.figshare.1115056 and the further digital repository links therein. CCDC 977840 (**4**), 977841 (**5**) 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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