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NHC-Stabilized Silagermenylidene: A Heavier Analogue of Vinylidene**

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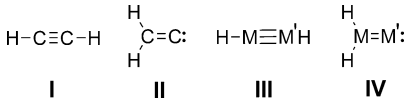
Dedicated to Professor Helmut Schwarz on occasion of his 70th birthday

The chemistry of acetylene (**I**) and its isomerization to vinylidene (**II**) has been an intensely researched topic for theoretical chemists for a long time,[1] which soon prompted interest in the corresponding heavier congeners **III** and **IV** (Scheme 1).[2] To date, neither free vinylidene or its heavier



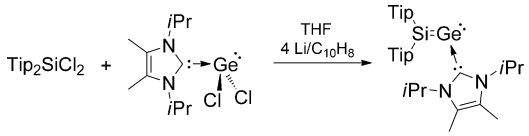
Scheme 1. Chemical structures of acetylene (**I**), vinylidene (**II**), and their corresponding heavier analogues **III** and **IV** (M and M' are heavier Group 14 elements).

analogues have been isolated.[3a–c] The parent vinylidene (**II**) has been detected in matrix experiments.[3d–f] In 1966, Mills et al. reported the first structurally characterized transition-metal complexes of diphenylvinylidene, which were obtained from the reaction of diphenylketene and ironpentacarbonyl.[4a] In the meantime, vinylidene transition-metal complexes have acquired some prominence as catalysts, in particular in alkene and alkyne metathesis.[4b–d] Substituted examples of disilynes (**III**, M = M′ = Si)[5] and digermynes (**III**, M = M′ = Ge)[6] have been isolated as the heavier analogues of alkynes. In neither case, however, was isomerization to the corresponding disilenylidene or digermenylidene of type **IV** observed. In contrast, theoretical calculations on the heteronuclear H_2SiGe potential energy surface predict that silagermenylidene ($H_2Si{=}Ge{:}$) is energetically favored over both silagermyne (HSi≡GeH) and germasilenylidene ($H_2Ge{=}Si{:}$).[7] The stability of $H_2Si{=}Ge{:}$ relative to $H_2Ge{=}Si{:}$ is attributed to the more diffuse orbitals at germanium that accommodate a lone electron pair more easily than in the case of silicon.

For the synthesis of a substituted version of $H_2Si{=}Ge{:}$ we chose an N-heterocyclic carbene (NHC) as a base to coordinate to the low-valent germanium center. NHCs have been shown to stabilize low-coordinate compounds in numerous cases.[8,9] Herein, we now report an isolable NHC-stabilized silagermenylidene. As proof-of-concept for its suitability as a novel synthon to access various low-valent Group 14 compounds, we also demonstrate the formal [2+2]-cycloaddition with phenylacetylene.

The reductive dehalogenation of either diaryl substituted dichlorosilane Tip_2SiCl_2 (**1**; Tip = 2,4,6-*i*Pr$_3$C$_6$H$_2$) or NHC-stabilized germanium(II) dichloride, $NHC^{Dipp}{\cdot}GeCl_2$ (NHC^{Dipp} = C{N(Ar)CH}$_2$, Ar = 2,6-diisopropylphenyl) alone had been shown to afford the homoleptic disilene[10] and an NHC-coordinated digermanium(0) compound,[11] respectively. To obtain the desired cross-coupling product, we figured that a more pronounced discrimination between the two precursors in terms of steric congestion would be beneficial. As a consequence, we chose the less-bulky $NHC^{iPr_2Me_2}{\cdot}GeCl_2$ (**2**; $NHC^{iPr_2Me_2}$ = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene)[12] as starting material alongside **1**.[13]

Indeed, the dropwise addition of four equivalents of freshly prepared lithium/naphthalene (Li/$C_{10}H_8$) to the tetrahydrofuran solution of **1** and **2** (one equivalent each) at −78 °C afforded the target compound, silagermenylidene **3**, along with the known homoleptic disilene, $Tip_2Si{=}SiTip_2$[10] and free $NHC^{iPr_2Me_2}$, 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene as side products.[14] The ^{1}H NMR of the crude reaction mixture indicated the formation of **3** and $Tip_2Si{=}SiTip_2$ in a molar ratio of approximately 2:3 (Supporting Information, Figure S7). From the reaction solution, pure **3** was isolated in 8% yield with respect to Tip_2SiCl_2 by fractional crystallization from hexane as red crystals (mp. 128–130 °C) in a reproducible manner (Scheme 2).[15] The ^{1}H NMR spectrum of a second



Scheme 2. Synthesis of silagermenylidene **3** (Tip = 2,4,6-*i*Pr$_3$C$_6$H$_2$).

crop of crystals obtained from the mother liquor indicated the presence of considerable quantities of $Tip_2Si{=}SiTip_2$[10] and of free $NHC^{iPr_2Me_2}$[14] (Supporting Information, Figure S8).

The ^{29}Si NMR resonance of **3** at δ = 158.9 ppm is shifted significantly downfield compared with those of the disilenes $Mes_2Si{=}SiMes_2$ (63.6 ppm; Mes = 2,4,6-Me$_3$C$_6$H$_2$)[16] and

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$Tip_2Si{=}SiTip_2$ (53.4 ppm);[10] or silagermenes $Mes_2Si{=}GeMes_2$ (80.6 ppm),[17] $(tBu_2MeSi)_2Si{=}GeMes_2$ (22.4 ppm).[18] It is well-established that the chemical shift anisotropy of heavier multiple bonds can be large in the presence of electronically differing substituents at the constituent Group 14 atoms.[19] Not unexpectedly, the dicoordinate Ge^{II} moiety in **3** appears to be more electron-rich than the silylene fragment ($SiTip_2$), resulting in a ^{29}Si chemical shift that is much closer to those of the silyl substituted disilene, $(iPr_3Si)_2Si{=}Si(iPr_3Si)_2$, $\delta =$ 154.5 ppm,[20] but shifted upfield compared with $NHC^{Dipp} \rightarrow Si{=}Si \leftarrow NHC^{Dipp}$ ($\delta = 224.5$ ppm).[21] In the ^1H NMR spectrum, the C*H* protons of the *ortho*-isopropyl groups of **3** result in broadened signals at room temperature, which is presumably due to hindered rotation about the Si–C bonds. Conversely, the *para*-isopropyl groups of the Tip substituents are chemically inequivalent (*cis*/*trans* with regard to $NHC^{iPr_2Me_2}$) and give rise to two different signals even at 25 °C. At −50 °C, individual resonances are observed for most other isopropyl CH moieties as well (Supporting Information, Figure S2).

The molecular structure of compound **3** as determined by X-ray crystallography is shown in Figure 1.[22] Compound **3** crystallizes from hexane in the monoclinic $P2_1/n$ space group. The Si–Ge bond length is 2.2521(5) Å, which matches that of the H-substituted parent silagermenylidene, $H_2Si{=}Ge{:}$, almost

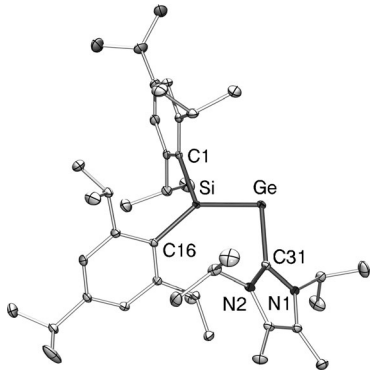
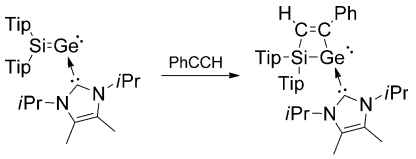


Figure 1. Molecular structure of **3** in the solid state (ellipsoids set at 30% probability; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Si–Ge 2.2521(5), Ge–C31 2.0474(18), C31–N1 1.358(2); C1-Si-C16 110.44(8), C1-Si-Ge 114.97(6), C16-Si-Ge 134.50(6), C31-Ge-Si 98.90(5).

precisely (2.263 Å at the MP2/TZV (2df, 2p) level of theory).[7b] This distance is close to the mathematical average of the bond lengths of $Tip_2Si{=}SiTip_2$ (2.144 Å)[10] and NHC^{Dipp}-stabilized digermanium(0), $NHC^{Dipp} \rightarrow Ge{=}Ge \leftarrow NHC^{Dipp}$ (2.3490(8) Å).[11] The Si atom has an almost perfectly planar coordination environment (sum of the angles at Si: 359.8°). $NHC^{iPr_2Me_2}$ coordinates to the germanium center in a near-orthogonal manner with respect to the Si–Ge bond vector (C31-Ge-Si 98.90(5)°). The torsion angle of C1-Si-Ge-C31 is −176.89°, which allows for efficient π overlap between the Ge and Si centers. The Ge–C31 distance in **3** (2.0474(18) Å) is shorter than that of **2** (2.106(3) Å)[12] although it is similar to the digermanium(0) compound (2.030(3) Å).[11] Taken together these structural features justify the description of compound **3** as an $NHC^{iPr_2Me_2}$-stabilized singlet silagermenylidene. Alternatively, **3** could also be described as a formal germanium(0) species stabilized by silylene and $NHC^{iPr_2Me_2}$ coordination ($Tip_2Si{:}\rightarrow Ge^0 \leftarrow {:}NHC^{iPr_2Me_2}$). A few carbene-stabilized so-called silylones and germylones have been reported.[23] The UV/Vis spectrum of **3** in hexane exhibits absorptions at $\lambda_{max} = 455$ nm ($\varepsilon = 8820\ L\,mol^{-1}\,cm^{-1}$) and at $\lambda_{max} = 365$ nm ($\varepsilon = 8370\ L\,mol^{-1}\,cm^{-1}$), which can possibly be attributed to the π–π* and n–π* transitions.

Because of the presence of the Si–Ge double bond, silagermenylidene **3** has the potential for formal [2+2] cycloadditions, for instance with phenylacetylene. As anticipated, the addition of one equivalent of phenylacetylene to a toluene solution of **3** at room temperature afforded exclusively one regioisomer of the base-stabilized cyclic germylene **4** as yellow crystals (mp. 217–219 °C) in 71% yield of isolated product (Scheme 3).[15] In the reaction



3 **4**

Scheme 3. Formal [2+2] cycloaddition of **3** with phenylacetylene (Tip = 2,4,6-$iPr_3C_6H_2$).

mixture we did not detect any side products, including the conceivable other regioisomer or the product of oxidative addition of an alkynyl C–H bond to the Ge center. In case of silicon(II) compounds such a C–H addition has been reported.[24]

In the ^1H NMR spectrum, the most deshielded signal appears as a singlet at 8.57 ppm, which is assigned to the vinylic hydrogen atom. The upfield-shifted ^{29}Si NMR signal of **4** ($\delta = -39.1$ ppm) in comparison to **3** confirms the absence of a Si–Ge double bond. The UV/Vis spectrum of **4** shows an absorption at $\lambda_{max} = 336$ nm ($\varepsilon = 2524\ L\,mol^{-1}\,cm^{-1}$), which is blue-shifted in comparison to silagermenylidene **3**. The regioselectivity of the reaction is easily explained by a stepwise dipolar addition pathway in which the initial attack occurs at the positively polarized Si atom of **3**. Stepwise reaction pathways are well-established for homo- and heteronuclear heavier double-bond systems.[25]

Single crystals of **4** suitable for an X-ray diffraction study were obtained from a benzene solution at room temperature. The cyclic $NHC^{iPr_2Me_2}$-stabilized germylene crystallizes in the triclinic $P\bar{1}$ space group (Figure 2).[22] The analysis of the solid-state structure clearly indicates a markedly pyramidalized germanium center (sum of angles 270.25°). C1 and C2, Si, and Ge form an almost perfectly planar trapezoid (sum of internal angles 359.96°). The bond length between the carbenic carbon, C33, and germanium is 2.0948(19) Å, which is longer than the corresponding distance observed in **3** (2.0474(18) Å), but very close to the value found in **2** (2.106(3) Å).[12]

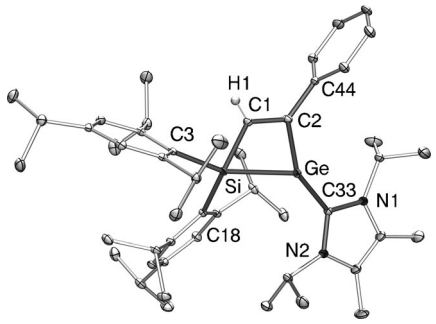


Figure 2. Molecular structure of **4** in the solid state (ellipsoids set at 30% probability; hydrogen atoms are omitted for clarity except the vinylic hydrogen). Selected bond lengths [Å] and angles [°]: Si–Ge 2.4982(6), C1–C2 1.351(3), Si–C1 1.879(2), Ge–C2 2.068(2), Ge–C33 2.0948(19); Si-Ge-C2 68.96(6), Ge-Si-C1 77.45(6), Si-C1-C2 106.62(14).

In conclusion, with silagermenylidene **3** we have isolated the first example of a monomeric base-stabilized vinylidene analogue. Although compound **3** is sensitive to oxygen and moisture, it is stable in the solid state and in solution under argon for at least two months without any decomposition. With the high degree of functionality (double bond, lone pair of electrons, $NHC^{iPr_2Me_2}$ coordination site), silagermenylidene **3** has the potential to act as a valuable novel synthon in low-valent main-group chemistry.[26] As a first proof-of-principle, we have demonstrated the clean conversion of **3** with phenylacetylene to a four-membered base-stabilized cyclic germylene. The scope of this novel access to base-stabilized germylenes, as well as the general reactivity of **3**, are currently being studied in our laboratory.

Experimental Section

3: Li/$C_{10}H_8$ (freshly prepared from 0.215 g (30.97 mmol) of granular Li and 4.76 g (37.17 mmol) $C_{10}H_8$ in 80 mL THF) was added dropwise into a Schlenk flask with **1** (3.916 g, 7.74 mmol) and **2** (2.508 g, 7.74 mmol) in THF (100 mL) at −78 °C. The mixture was slowly brought to 25 °C and stirred overnight. All of the volatiles were removed under vacuum at 65 °C and the solid residue dissolved in hexane (200 mL). The crude reaction mixture contained the product **3** and $Tip_2Si{=}SiTip_2$[10] in an approximate molar ratio of 2:3 as well as free $NHC^{iPr_2Me_2}$ (which could not be quantified owing to signal overlap).[14] After filtration the solution was kept at −78 °C overnight. Occasionally an oily precipitate forms at this stage, from which the solution is separated and concentrated to about 30 mL. After another 15 h at −78 °C red crystals of **3** were obtained (0.430 g, 8%). Mp.: 128–130 °C. ^{1}H NMR (300 MHz, [D$_6$]benzene, TMS, 298 K): $\delta = 7.20$ (br, 2H, Tip-*H*), 7.04 (br, 2H, Tip-*H*), 6.02 (br, 2H, C*H*(CH$_3$)$_2$ of $NHC^{iPr_2Me_2}$), 5.20–3.79 (br, 4H, *o*-C*H*(CH$_3$)$_2$) 2.91–2.70 (m, 2H, *p*-C*H*(CH$_3$)$_2$), 1.62 (br, 6H, CH(C*H*$_3$)$_2$), 1.54 (s, 6H, C*H*$_3$), 1.26 (d, 6H, CH(C*H*$_3$)$_2$), 1.20 (d, 6H, CH(C*H*$_3$)$_2$) 1.30–0.90 ppm (br, 30H, CH-(C*H*$_3$)$_2$). ^{1}H NMR (300 MHz, [D$_8$]toluene, TMS, 223 K): $\delta = 7.44$ (s, 1H, Tip-*H*), 7.19–7.01 (3H, Tip-*H*, masked by [D$_8$]toluene), 6.24 (hept, 1H, C*H*(CH$_3$)$_2$), 5.98 (hept, 1H, C*H*(CH$_3$)$_2$), 5.56 (hept, 1H, C*H*(CH$_3$)$_2$), 4.81 (hept, 1H, C*H*(CH$_3$)$_2$), 3.99–3.85 (m, 2H, C*H*-(CH$_3$)$_2$) 2.94–2.75 (m, 2H, C*H*(CH$_3$)$_2$), 1.92 (d, 3H, CH(C*H*$_3$)$_2$), 1.69 (d, 3H, CH(C*H*$_3$)$_2$), 1.62 (d, 3H, CH(C*H*$_3$)$_2$), 1.58–1.28 (altogether 33H, C*H*$_3$ & CH(C*H*$_3$)$_2$), 0.76 (d, 6H, CH(C*H*$_3$)$_2$) 0.71–0.63 ppm (br, 6H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (75.4 MHz, [D$_6$]benzene, TMS, 298 K): $\delta = 177.85$ (N*C*N), 154.12, 152.73, 148.99, 148.41, 144.21, 142.30 (Ar-*C*$_{quart}$), 126.08 (N*CC*N), 121.51, 121.24 (Ar-*C*H), 54.15 (*C*H(CH$_3$)$_2$ of $NHC^{iPr_2Me_2}$), 36.86, 35.25, 34.73, 34.62 (*C*H(CH$_3$)$_2$), 24.62, 24.29, 24.19, 23.81, (CH(*C*H$_3$)$_2$), 20.73 (CH(*C*H$_3$)$_2$ of $NHC^{iPr_2Me_2}$), 10.01 ppm (*C*H$_3$). ^{29}Si{^{1}H} NMR (59.5 MHz, [D$_6$]benzene, TMS, 298 K): $\delta = 158.92$. UV/Vis (hexane): λ_{max} (ε) 455 (8820), 365 (8370) nm (L mol^{-1} cm^{-1}). Elemental analysis calcd (%) for $C_{41}H_{66}GeN_2Si$: C 71.61, H 9.67, N 4.07; found: C 71.64, H 9.53, N 3.88.

4: A solution of **3** (0.136 g, 0.19 mmol in 1 mL toluene) was added to an NMR tube containing phenylacetylene (22 µL, 0.20 mmol). After 24 h a crystalline compound deposited. The supernatant solution was removed, the remaining solid washed with hexane (2 × 1.5 mL), and dried in vacuum to afford 0.110 g (71%) of **4** as yellow crystals. Mp.: 217–219 °C. ^{1}H NMR (300 MHz, [D$_6$]benzene, TMS, 298 K): $\delta = 8.57$ (s, 1H, vinylic C-*H*), 7.96 (m, 2H, *o*-Ph-*H*), 7.19 (m, 2H, *m*-Ph-*H*), 7.15 (2H, Tip-*H* masked by C_6D_5H), 7.09–7.00 (m and s altogether 3H, *p*-Ph-*H* & Tip-*H*), 5.03 (2H, hept, C*H*(CH$_3$)$_2$ of $NHC^{iPr_2Me_2}$), 4.59 (br, 2H, *o*-C*H*(CH$_3$)$_2$), 3.96 (hept, 2H, *o*-C*H*(CH$_3$)$_2$), 2.93–2.70 (m, 2H, *p*-C*H*(CH$_3$)$_2$), 1.50 (d, 6H, *o*-CH(C*H*$_3$)$_2$), 1.48 (s, 6H, C*H*$_3$), 1.44 (d, 6H, *o*-CH(C*H*$_3$)$_2$), 1.32–1.27 (m, 6H, *p*-CH-(C*H*$_3$)$_2$), 1.24–1.16 (br and m, altogether 12H, *o*- & *p*-CH(C*H*$_3$)$_2$), 1.02 (d, 6H, CH(C*H*$_3$)$_2$ of $NHC^{iPr_2Me_2}$), 0.70–0.63 ppm (m, 12H, six from each *o*-CH(C*H*$_3$)$_2$ & CH(C*H*$_3$)$_2$ of $NHC^{iPr_2Me_2}$). ^{13}C{^{1}H} NMR (75.4 MHz, [D$_6$]benzene, TMS, 298 K): $\delta = 177.88$ (N*C*N), 173.50 (Ph*C*≡*C*), 154.87 (C≡*C*H), 154.10, 154.03, 148.39, 148.14, 147.58, 139.71, 138.65 (Ar-*C*$_{quart}$), 125.98, 125.76 (Ph*C*H), 125.60, (N*CC*N), 121.33, 121.29 (Ar-*C*H), 51.73 (*C*H(CH$_3$)$_2$ of $NHC^{iPr_2Me_2}$), 35.06, 34.46, 34.32, 33.45, (*C*H(CH$_3$)$_2$), 25.72, 24.73, 24.25, 24.16, 24.12, 24.01, 23.86 (CH(*C*H$_3$)$_2$), 21.05, 19.85 (CH(*C*H$_3$)$_2$ of $NHC^{iPr_2Me_2}$), 9.86 ppm (*C*H$_3$). ^{29}Si{^{1}H} NMR (59.5 MHz, [D$_6$]benzene, TMS, 298 K): $\delta = -39.12$. UV/Vis (hexane): λ_{max} (ε) 336 (2520) nm (L mol^{-1} cm^{-1}). Elemental analysis calcd (%) for $C_{49}H_{72}GeN_2Si$: C 74.51, H 9.19, N 3.55; found: C 73.58, H 9.01, N 3.36.

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[15] See the Experimental Section. NMR and UV/Vis spectra of **3** and **4** are provided in the Supporting Information.

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[22] Crystal structure determination at $T = 132(2)$ K on Bruker SMART APEX CCD diffractometer with a Mo-K_α radiation. **3**: red blocks from hexane; $C_{41}H_{66}GeN_2Si$, $M_r = 647.49$, monoclinic, space group $P2_1/n$, $a = 10.9079(9)$, $b = 30.059(3)$, $c = 13.7480(12)$ Å, $\beta = 95.311(2)°$, $V = 4488.4(7)$ Å^3; $Z = 4$, $\rho_{calcd} = 1.064$ g cm^{-3}; crystal dimensions: $0.74 \times 0.50 \times 0.36$ mm^3; $F(000) = 1572$, $\mu = 0.737$ mm^{-1}; $2\Theta_{max} = 54.20°$; 39597 reflections, 9894 independent ($R_{int} = 0.0364$), $R_1 = 0.0360$ ($I > 2\sigma(I)$) and wR_2 (all data) = 0.0931, GooF = 1.046, max/min residual electron density: 0.802/−0.369 e Å^{-3}. **4**: yellow blocks from benzene; $C_{49}H_{72}GeN_2Si$, $M_r = 789.77$, triclinic, space group $P\bar{1}$, $a = 10.0634(11)$, $b = 10.6401(10)$, $c = 22.629(2)$ Å, $\alpha = 91.596$, $\beta = 100.014(4)$, $\gamma = 107.834(4)°$, $V = 2262.9(4)$ Å^3; $Z = 2$, $\rho_{calcd} = 1.159$ g cm^{-3}; crystal dimensions: $0.61 \times 0.23 \times 0.16$ mm^3; $F(000) = 852$, $\mu = 0.737$ mm^{-1}; $2\Theta_{max} = 54.20°$; 34490 reflections, 9906 independent ($R_{int} = 0.0319$), $R_1 = 0.0384$ ($I > 2\sigma(I)$) and wR_2 (all data) = 0.0888, GooF = 1.121, max/min residual electron density: 0.659/−0.466 e Å^{-3}. CCDC 950690 (**3**) and 950691 (**4**) 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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