

Vinyl Anion Analogues

A Mixed Heavier Si=Ge Analogue of a Vinyl Anion

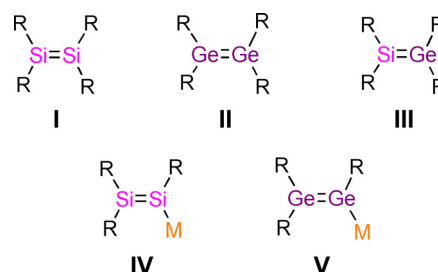
Paresh Kumar Majhi, Volker Huch, and David Scheschkewitz*

Dedicated to Professor Rainer Streubel on the occasion of his 62nd birthday

Abstract: The versatile reactivities of disilenides and digermene, heavier analogues of vinyl anions, have significantly expanded the pool of silicon and germanium compounds with various unexpected structural motifs in the past two decades. We now report the synthesis and isolation of a cyclic heteronuclear vinyl anion analogue with a Si=Ge bond, potassium silagermenide as stable *thf*-solvate and 18-c-6 solvate by the KC_8 reduction of gerylene or digermene precursors. Its suitability as synthon for the synthesis of functional silagermenes is proven by the reactions with chlorosilane and chlorophospane to yield the corresponding silyl- and phosphanyl-silagermenes. X-ray crystallographic analysis, UV/Vis spectroscopy and DFT calculations revealed a significant degree of π -conjugation between $N=C$ and $Si=Ge$ double bonds in the title compound.

Stable unsaturated compounds between two heavier Group 14 elements continue to be a heavily researched topic in contemporary main-group chemistry.^[1] Multiple bonds between the heavier congeners of carbon confer inherently small HOMO–LUMO gaps, conformational flexibility, high reactivity and peculiar bonding situations.^[1] Since the landmark discoveries of a stable digermene by Lappert^[2] and a disilene by West,^[3] a plethora of heavier alkenes ($R_2E=ER_2$, $E=Si-Pb$) **I–III** (Scheme 1) have been synthesized and their unusual structure and properties have been thoroughly investigated.^[1] In comparison with the homonuclear species ($R_2E=ER_2$), the synthetic routes to heteronuclear heavier alkenes ($R_2E=E'R_2$) are limited, but a handful of cyclic^[4] and acyclic silagermenes^[5] **III** have nonetheless been prepared.

The advent of heavier alkenes ($R_2E=ER-M$) with metal-functionality^[6,7] in vinylic position has enabled various transformations under retention of the uncompromised heavier



Scheme 1. Literature-known motifs of unfunctionalized (**I** to **III**) and metalated (**IV** and **V**) heavier alkenes (R = Organic substituent; M = Alkali metal).

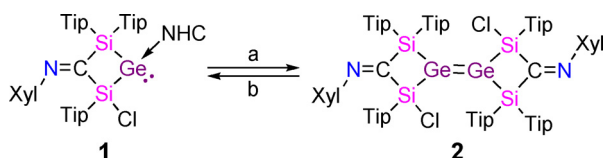
multiple bonds,^[8] but also expanded significantly the repertoire of silicon compounds as starting materials for heteronuclear and functionalized heavier alkenes,^[9,10] heterocycles^[11] and clusters.^[12] Several methods for the preparation of metal disilenides **IV** have been developed in the last two decades,^[6] but only one example of an alkali metal digermene **V** is known.^[7] Vinyl anions consisting of two different heavier Group 14 elements remain elusive, although lithium silenides ($R_2C=SiR-M$) with at least one heavier Group 14 terminus were reported by the Apeloig group.^[13] Tokitoh et al. described germenyl ($R_2C=GeR-M$) and stannenyl anion moieties ($R_2C=SnR-M$) as part of the delocalized germa-phenyl^[14] and stannaphenyl potassium^[15] frameworks.

We selected the NHC-coordinated four-membered gerylene **1** with an exocyclic imino functionality and a chloro substituent in α -position to the germanium center^[16] as precursor for the synthesis of an unprecedented vinyl anion analogue with a Si=Ge double bond, either as silagermenide or as gerasilenide depending on the position of the negative charge in the double bond. Computations predicted the slightly higher stability of silagermenide $[(CH_3)_2Si=Ge(CH_3)]^-$ by $\Delta G = 4.7 \text{ kcal mol}^{-1}$ compared to the positional isomer $[(CH_3)_2Ge=Si(CH_3)]^-$.^[17] The NHC can be reversibly removed from gerylene **1** by BPh_3 to yield the corresponding dimerization product, digermene **2** (Scheme 2). Renewed addition of NHC converts digermene **2** back to the starting gerylene **1**.^[16] Based on the weakness of both the coordinative bond to the NHC and the Ge=Ge double bond thus evident, we anticipated that the $2e^-$ or $4e^-$ reduction of **1** or **2**, respectively, would result in the cleavage to a heavier mixed vinyl anion analogue under concomitant expulsion of a chloride anion. Indeed, the treatment of gerylene **1** with two equivalents of KC_8 in THF affords potassium silagermenide **3**·K(THF) selectively (Scheme 3, route I). The potassium silagermenide **3**·K(THF) can also be synthesized by treatment

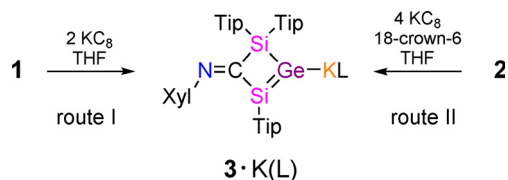
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Scheme 2. Reversible dimerization of germylene **1** to digermene **2**; (a) + BPh₃, [NHC-BPh₃], (b) + NHC^{Pr₂Me₂} (NHC=N-heterocyclic carbene) (Tip = 2,4,6-*i*Pr₃C₆H₂, Xyl = 2,6-Me₂C₆H₃).^[16]



Scheme 3. Synthesis of potassium silagermenides **3** as stable thf-solvate and 18-c-6 solvate (Tip = 2,4,6-*i*Pr₃C₆H₂, Xyl = 2,6-Me₂C₆H₃, L = thf, 18-crown-6).

of digermene **2** with four equivalents of KC₈ and isolated as red crystals in 76% yield (route II). The ²⁹Si NMR spectrum of **3**·K(THF) shows two signals at $\delta = 140.2$ and 12.3 . The former is strongly downfield shifted compared to germylene **1** ($\delta = 5.6, -13.5$) indicating the presence of a low-coordinate silicon atom.^[16] Unfortunately, due to the nuclear spin of ⁷³Ge of $I = 9/2$ paired with its low gyromagnetic ratio meaningful ⁷³Ge NMR spectra can only be obtained in the most symmetrical of cases. A downfield signal in the ¹³C{¹H} NMR spectrum of **3**·K(THF) at $\delta = 222.5$ is assigned to the N=C unit (cf. $\delta = 216.05$ for **1**^[16]) suggesting the integrity of the imine backbone. The liberation of NHC in route I was confirmed by NMR.

In order to study the potassium co-ligands effect on NMR spectroscopic properties, thermal stabilities and the nature of cation-anion interaction, the reduction of **1** was repeated in the presence of 18-crown-6 leading to the isolation of **3**·K(18-c-6) in 65% yield as red crystals (Figure S26b) from benzene (route I). The yield of **3**·K(18-c-6) increases up to 90% with the NHC-free digermene **2** as precursor (route II) by eliminating the need for crystallization to separate the liberated NHC. The potassium silagermenide **3**·K(18-c-6) is thermally surprisingly stable even at 180 °C. The ²⁹Si NMR resonances of **3**·K(18-c-6) are slightly solvent dependent ($\delta = 142.9, 12.4$ in C₆D₆ and $\delta = 138.5, 13.4$ in [D₈]THF) indicative of the varying strength of solvent interaction with the potassium cation. The downfield signal at $\delta = 142.9$ in C₆D₆ served as first indication of the formation of the Si=Ge double bond due to its close proximity to the downfield resonance of the neutral NHC-stabilized silagermenylidene ($\delta^{29}\text{Si} = 158.9$).^[18] The UV/Vis spectrum in THF shows the longest wavelength absorption band at $\lambda_{\text{max}} = 490$ nm ($\epsilon = 8690$ L mol⁻¹ cm⁻¹) for **3**·K(THF) and at $\lambda_{\text{max}} = 495$ nm ($\epsilon = 9200$ L mol⁻¹ cm⁻¹) for **3**·K(18-c-6) both values being red-shifted significantly compared to a lithium disilenide [$\lambda_{\text{max}} = 417$ nm ($\epsilon = 760$ L mol⁻¹ cm⁻¹)]^[6a] and a lithium digermene [$\lambda_{\text{max}} = 435$ nm ($\epsilon = 11800$ L mol⁻¹ cm⁻¹)].^[7] Besides, additional intense absorption bands are present at $\lambda = 413$ nm

($\epsilon = 5470$ L mol⁻¹ cm⁻¹) for **3**·K(THF) and at $\lambda_{\text{max}} = 417$ nm ($\epsilon = 6130$ L mol⁻¹ cm⁻¹) for **3**·K(18-c-6). Two similar UV/Vis absorption bands were observed for a silagermene [(*t*BuMe₂Si)₂Si=Ge(SiMe₂*t*Bu)₂] [$\lambda_{\text{max}} = 413$ nm ($\epsilon = 5000$ L mol⁻¹ cm⁻¹), 359 nm ($\epsilon = 2000$ L mol⁻¹ cm⁻¹)].^[5e]

X-ray diffraction analysis on single crystals revealed that both solvates of silagermenide **3** form coordination polymer in the solid state (Figure 1). The Ge–K bonds in **3**·K(18-c-6) (Ge1–K1 3.5546(3) Å, Ge2–K2 3.5372(3) Å) are longer than those found in digermanyldipotassium salts (3.40–3.52 Å)^[19] and similar to that of the tripotassium salt of the trianion obtained from the KC₈ reduction of a germaanthracene (3.5490 Å).^[20] The Ge1–Si1 bond of 2.2590(3) Å is significantly shorter than the Ge1–Si2 bond (2.4361(3) Å) and of comparable length to those of silagermenes (*t*Bu₃Si)₂Si=GeMes₂ (2.2769 Å; Mes = 2,4,6-Me₃C₆H₂)^[5b] and (*t*BuMe₂Si)₂Si=Ge(SiMe₂*t*Bu)₂ (2.2208 Å).^[5e] clearly reflecting its

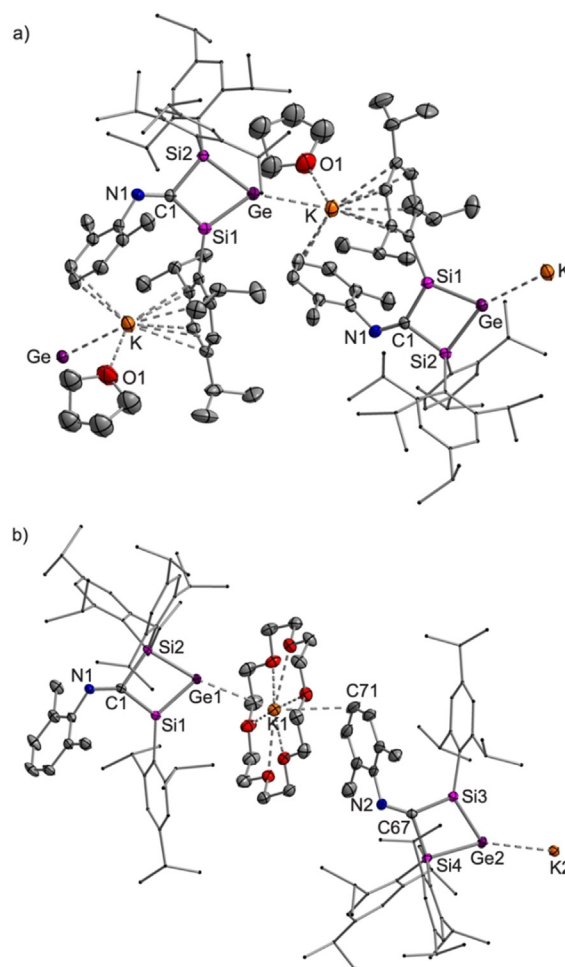


Figure 1. Structures of the two coordination polymer chains [**3**·K(THF)]_n (a) and [**3**·K(18-c-6)]_n (b) in the solid state. Hydrogen atoms and co-crystallized solvent omitted for clarity, thermal ellipsoids at 50% probability. Selected bond lengths [Å]: **3**·K(THF) Ge–K 3.4066(9), Ge–Si1 2.2457(10), Ge–Si2 2.4295(10), Si1–C1 1.855(3), Si2–C1 1.938(3), C1–N1 1.287(4); Si1–Ge–Si2 72.44(3); **3**·K(18-c-6) Ge1–K1 3.5546(3), Ge2–K2 3.5372(3), Ge1–Si1 2.2590(3), Ge1–Si2 2.4361(3), Ge2–Si3 2.2586(3), Ge2–Si4 2.4372(3), Si1–C1 1.8633(11), Si2–C1 1.9261(11), C1–N1 1.2928(13), C71–K1 3.3125(16).

double bond nature. The four-membered ring is almost planar (sum of internal angles = 359.92°) with a torsion angle of Si1-Ge1-Si2-C1 of 1.913(2)°.

The inner angles at the anionic germanium center [Si1-Ge1-Si2 71.793(11)°, Si3-Ge2-Si4 71.816(11)°] are significantly more acute than in germylene **1** (79.22°)^[16] presumably as a consequence of the negative charge at the Ge atom. While the C1-N1 bond of 1.2928(13) Å is slightly longer than that of the germylene precursor **1** (1.276 Å), the Si1-C1 bond of 1.8633(11) Å is discernibly shorter (**1**: 1.979 Å).^[16] A comparable degree of bond equalization had been observed in a phenylene-bridged bis(1,2,3-trisilylcyclopentadiene) and taken as an indication for π -conjugation between both double bonds.^[21] Together with the considerable red shift ($\lambda_{\text{max, exp}} = 495$ nm) in the UV/Vis spectrum a significant degree of π -conjugation between the N=C and Si=Ge double bonds in **3-K**(18-c-6) can be assumed in contrast to opposite conclusions in the cases of a silole-type structure^[4b] with adjacent Si=Ge and C=C double bonds and of a trisilylcyclopentadiene^[22] comprising Si=Si and C=C double bonds.

To gather more insight into the bonding in **3-K**(18-c-6), density functional theory (DFT) calculations were performed at the M06-2X(D3)/def2-SV(P)//BP86(D3BJ)/def2-SVP level of theory. Selected Kohn-Sham orbitals of **3-K**(18-c-6) are depicted in Figure 2. Consistent with the earlier observations for 1,2,3-trisilylcyclopentadiene,^[21] the highest occupied molecular orbital (HOMO) is dominated by the π -orbitals of the Si=Ge double bond, but does show a significant albeit smaller contribution at the imine nitrogen as well. The lowest unoccupied molecular orbital (LUMO) is completely delocalized across the Ge=Si-C=N path thus providing clear evidence for pronounced conjugation. The HOMO-1 shows a partial contribution from the imine (N=C) lone pair in contrast to a lithium digermene^[7] in which the HOMO-1 corresponds to the Ge-Li bond. In **3-K**(18-c-6), the Ge-K bond is identified as the HOMO-2 with contributions from the Si(sp³)-Ge(sp²) σ -bond. Second order perturbation theory (SOPT) confirms strong conjugation between Ge=Si and C=N with an interaction energy of 23.6 kcal mol⁻¹ for $\pi_{\text{GeSi}} \rightarrow \pi_{\text{CN}}^*$.^[23] The increased Wiberg bond index (WBI) of Si1-C1 (0.904) compared to that of Si2-C1 (0.762) further corroborates this interpretation. The TD-DFT simulated UV/Vis spectrum (Figure S31) determines the longest wavelength absorption band to $\lambda_{\text{max, calc}} = 505$ nm in good agreement with the experimental value ($\lambda_{\text{max, exp}} = 495$ nm). As expected, it predominantly arises from the HOMO \rightarrow LUMO transition

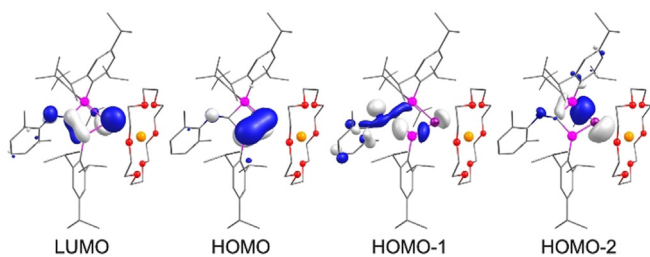
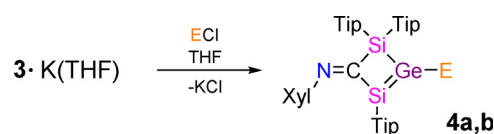


Figure 2. Selected Kohn-Sham molecular orbitals of **3-K**(18-c-6) (Contour value = 0.052).

(82% contribution). Another intense absorption band at $\lambda_{\text{max, calc}} = 382$ nm is blue shifted compared to experimental value of $\lambda_{\text{max, exp}} = 417$ nm and is ascribed to three transitions of comparable oscillator strength at 411, 385 and 373 nm (for details see Supporting Info).

In order to investigate the reactivity of silagermenide **3-K**(THF) and compare it with that of disilenides^[6a] and a digermene,^[7] two nucleophilic substitution reactions were performed as proof-of-principle (Scheme 4). The treatment of **3-K**(THF) with an equimolar amount of Ph₃SiCl at ambient temperature affords silylsilagermene **4a** in 81% yield. The ²⁹Si NMR resonance of **4a** at $\delta = 136.6$, -1.6 and -7.6 is upfield shifted compared to **3-K**(THF). The signal at $\delta = -1.6$ assigned to the Ph₃Si unit is slightly upfield shifted compared to triphenylsilyl substituted digermene (Tip₂Ge=GeTip (SiPh₃); $\delta^{29}\text{Si} = 1.9$).^[24]

The longest wavelength UV/Vis absorption is located at $\lambda_{\text{max}} = 436$ nm ($\epsilon = 10570$ L mol⁻¹ cm⁻¹). The blue-shift in **4a** compared to **3-K**(THF) ($\lambda_{\text{max}} = 490$ nm, for comparison to TD-DFT results see Supporting Info) is reminiscent of similar observations for the reaction of Tip₂Ge=Ge(Tip)Li with the same Ph₃SiCl substrate.^[24] Single-crystal X-ray diffraction analysis confirmed the constitution of **4a** as silyl-substituted silagermene (Figure 3 a). The Ge1-Si1 bond of 2.2020(2) Å is slightly shorter than in **3-K**(18-c-6). Similar to **3-K**(18-c-6), the four-membered ring is almost perfectly planar (sum of internal angles = 359.99°) with torsional angle of Si1-Ge1-Si2-C1 of 0.219(1)°. In the neutral species **4a**, a slight pyramidalization of Ge1 is recovered (sum of angles 357.34°).



Scheme 4. Syntheses of silylsilagermene **4a** and phosphanylsilagermene **4b** (Tip = 2,4,6-*i*-Pr₃C₆H₂, Xyl = 2,6-Me₂C₆H₃; **4a**: E = SiPh₃; **4b**: E = P(NiPr₂)₂).

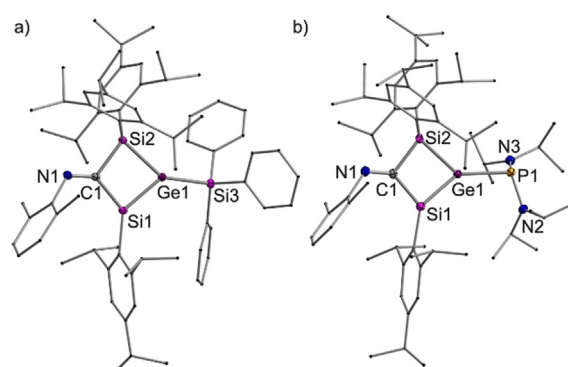


Figure 3. Molecular structure of **4a** (a) and **4b** (b) in the solid state. Hydrogen atoms and co-crystallized solvent omitted for clarity, thermal ellipsoids at 50% probability. Selected bond lengths [Å]: **4a** Ge1-Si1 2.2020(2), Ge1-Si2 2.3613(2), Ge1-Si3 2.3544(3), Si1-C1 1.8869(8), Si2-C1 1.9437(8), C1-N1 1.2824(11). **4b** Ge1-Si1 2.2252(4), Ge1-P1 2.3645(4), Ge1-Si2 2.3861(4), Si1-C1 1.8839(15), Si2-C1 1.9269(14), C1-N1 1.2853(18).

Finally, the reaction of **3**-K(THF) with an equimolar amount of $(iPr_2N)_2PbCl$ furnishes phosphanylsilagermene **4b** in 79% yield (Scheme 4). The ^{31}P NMR resonance at $\delta = 94.9$ is downfield-shifted compared to a reported bis(diisopropylamino)phosphanyl disilene ($\delta = 58.4$).^[9b] In the ^{29}Si NMR spectrum, two sets of doublets are observed at $\delta = 104.5$ and -6.8 . Interestingly, the $^2J_{P,Si}$ coupling constant magnitude for the sp^2 hybridized silicon atom (9.8 Hz) is smaller compared to the sp^3 hybridized silicon atom (14.6 Hz) in **4b**. The red color of **4b** is due to the longest wavelength UV/Vis absorption at $\lambda_{max} = 453$ nm ($\epsilon = 11\,710$ L mol $^{-1}$ cm $^{-1}$), which is very similar to that of a phosphanyldisilene ($\lambda_{max} = 441$ nm)^[9b] (for calculated values see Supporting Info). The single-crystal X-ray analysis of **4b** confirmed the molecular constitution of a phosphanylsilagermene (Figure 3b). The Ge1–Si1 bond of 2.2252(4) Å is slightly shorter than in **3**-K(18-c-6) reflecting the trend discussed above.

In conclusion, we have established the synthesis and structural characterization of the first silagermenides as stable thf-solvate [**3**-K(THF)] and 18-crown-6 solvate [**3**-K(18-c-6)]. Their suitability as synthons for the synthesis of functional silagermenes was demonstrated by reactions with electrophiles such as Ph_3SiCl and $(iPr_2N)_2PbCl$. X-ray crystallography, UV/Vis and DFT calculations revealed a significant degree of π -conjugation between the N=C and Si=Ge double bonds in potassium silagermenide. The silagermenide could therefore also be regarded as heavier analogue of a butadienide anion, an example of which was recently documented,^[25] but not structurally characterized due to decomposition above $-50^\circ C$. Reactions of the silagermenide **3**-K(THF) with a variety of other electrophiles and small molecules are currently underway.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: anions · double bonds · functional groups · germanium · silicon

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