A Mixed Heavier Si=Ge Analogue of a Vinyl Anion
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Abstract: The versatile reactivities of disilenides and digerme-
nide, 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 hetero-
nuclear vinyl anion analogue with a Si=Ge bond, potassium
silagermenide as stable thf-solvate and 18-c-6 solvate by the
K\textsubscript{C\textsubscript{4}} reduction of germylene or digermene precursors. Its
suitability as synthon for the synthesis of functional silager-
menes is proven by the reactions with chlorosilane and
chlorophospane to yield the corresponding silyl- and phos-
phanyl-silagermenes. X-ray crystallographic analysis, UV/Vis
spectroscopy and DFT calculations revealed a significant
degree of \(\pi\)-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 land-
mark discoveries of a stable digermene by Lappert\(^2\) and
a disilene by West,\(^3\) a plethora of heavier alkenes (R,E=ER\(_2\),
E=Si-Pb) I–III (Scheme 1) have been synthesized and their
unusual structure and properties have been thoroughly
investigated.\(^3\) In comparison with the homonuclear species
(R,R=ER\(_2\)), the synthetic routes to heteronuclear heavier
alkenes (R,E=ER\(_3\)) are limited, but a handful of cyclic\(^4\)
and acyclic silagermenes\(^5\) III have nonetheless been pre-
pared.

The advent of heavier alkenes (R,E=ER-M) with metal-
functionality\(^6,7\) in vinylic position has enabled various trans-
formations under retention of the uncomplexed heavier
multiple bonds,\(^8\) but also expanded significantly the reperto-
ire of silicon compounds as starting materials for hetero-
nuclear and functionalized heavier alkenes\(^9,10\) heterocy-
cycles\(^11\) and clusters.\(^12\) Several methods for the preparation of
disilenides (R, R=SiR-M) with at least one heavier Group 14
terminus were reported by the Apeloig group.\(^13\) Tokitoh
et al. described germényl (R, C=SiR-M) and stannényl anion
moieties (R,C=SnR-M) as part of the delocalized germa-
phenyl and stannaphenyl potassium\(^14\) frameworks.

We selected the NHC-coordinated four-membered germ-
ylene I with an exocyclic imino functionality and a chloro
substituent in \(\alpha\)-position to the germanium center\(^22\) as
precursor for the synthesis of an unprecedented vinyl anion
analogue with a Si–Ge double bond, either as silagermenide
or as germsilenide depending on the position of the negative
charge in the double bond. Computations predicted the
slightly higher stability of silagermenide \([\text{CH}_3_2\text{Si=Ge-}
\text{(CH}_3])]^+\) by \(\Delta G = 4.7\ \text{kcal/mol}^{-1}\) compared to the positional
isomer \([\text{CH}_3_2\text{Ge=Si(CH}_3])]^+\).\(^17\) The NHC can be reversibly
removed from germylene I by BPh\(_3\) to yield the correspond-
ing dimerization product, digermene 2 (Scheme 2). Renewed
addition of NHC converts digermene 2 back to the starting
germylene 1.\(^18\) Based on the weakness of both the coordi-
native bond to the NHC and the Ge–Ge double bond thus
evident, we anticipated that the 2e\(^\rightarrow\) or 4e\(^\rightarrow\) reduction of 1 or 2,
respectively, would result in the cleavage to a heavier mixed
vinyl anion analogue under concomitant expulsion of a chlo-
ride anion. Indeed, the treatment of germylene 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
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 δ = 140.2 and 12.3. The former is strongly downfield shifted compared to germylene 1 (δ = 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 δ = 222.5 is assigned to the N=C unit (cf. δ = 216.05 for 1[19]) 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 (δ = 142.9, 12.4 in C₆D₆) and δ = 138.5, 13.4 in [D₅]THF) indicative of the varying strength of solvent interaction with the potassium cation. The downfield signal at δ = 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 silagermenyldiene (³²⁵Si = 158.9). [30] The UV/Vis spectrum in THF shows the longest wavelength absorption band at λ_{max} = 490 nm (ε = 8690 L mol⁻¹ cm⁻¹) for 3·K(THF) and at λ_{max} = 495 nm (ε = 9200 L mol⁻¹ cm⁻¹) for 3·K(18-c-6) both values being red-shifted significantly compared to a lithium disilene (λ_{max} = 417 nm (ε = 760 L mol⁻¹ cm⁻¹))[30] and a lithium digermenide (λ_{max} = 435 nm (ε = 11800 L mol⁻¹ cm⁻¹)).[31] Besides, additional intense absorption bands are present at λ = 413 nm (ε = 5470 L mol⁻¹ cm⁻¹) for 3·K(THF) and at λ_{max} = 417 nm (ε = 6130 L mol⁻¹ cm⁻¹) for 3·K(18-c-6). Two similar UV/Vis absorption bands were observed for a silagermene [(BuMe₃Si)₂Si=Ge(SiMe₂Bu₂)] [λ_{max} = 413 nm (ε = 5000 L mol⁻¹ cm⁻¹), 359 nm (ε = 2000 L mol⁻¹ cm⁻¹)].[14]

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).[30] The Ge1–Si 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 (tBu₃Si)₂Si= GeMes₂ (2.2769 Å; Mes = 2,4,6-Me₃C₆H₃)[38] and (Bu₂Me₃Si)₂Si=Ge(SiMe₂Bu₂) (2.2208 Å).[40] clearly reflecting its...
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 germeyne 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 germeyne 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-trisilacyclopentadiene) and taken as an indication for π-conjugation between both double bonds.[21] Together with the considerable red shift (λ_{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[40] with adjacent Si=Ge and C=C double bonds and of a trisilacyclopentadiene[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-trisilacyclopentadiene,[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 digermenide[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(sp3) 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 π_{Ge=Si}−π_{C=N}.[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 λ_{max, calc} = 505 nm in good agreement with the experimental value (λ_{max, exp} = 495 nm). As expected, it predominantly arises from the HOMO→LUMO transition (82% contribution). Another intense absorption band at λ_{max, calc} = 382 nm is blue shifted compared to experimental value of λ_{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[6b] and a digermenide,[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 δ = 136.6, −1.6 and −7.6 is upfield shifted compared to 3-K(THF). The signal at δ = −1.6 assigned to the Ph3Si unit is slightly upfield shifted compared to triphenylsilyl substituted digermene (Tip,Ge=GeTip(SiPh3); δ_{29Si} = 1.9).[24]

The longest wavelength UV/Vis absorption is located at λ_{max} = 436 nm (ε = 10570 L mol⁻¹ cm⁻¹). The blue-shift in 4a compared to 3-K(THF) (λ_{max} = 490 nm, for comparison to TD-DFT results see Supporting Info) is reminiscent of similar observations for the reaction of Tip,Ge=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 3a). 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 82% contribution. Another intense absorption band at λ_{max, calc} = 382 nm is blue shifted compared to experimental value of λ_{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).

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![Figure 2](image-url)  
**Figure 2.** Selected Kohn–Sham molecular orbitals of 3-K(18-c-6) (Contour value = 0.052).

![Figure 3](image-url)  
**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 2.3543(4), 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 (iPr2N)PCI furnishes phosphanylsilagermene 4b in 79% yield (Scheme 4). The 31P NMR resonance at δ = 94.9 is downfield-shifted compared to a reported bis(disopropylamino)phosphanyl disilene (δ = 58.4).[96] In the 29Si NMR spectrum, two sets of doublets are observed at δ = 104.5 and −6.8. Interestingly, the J(PS) coupling constant magnitude for the sp3 hybridized silicon atom (9.8 Hz) is smaller compared to the sp3 hybridized silicon atom (14.6 Hz) in 4b. The red color of 4b is due to the longest wavelength UV/Vis absorption at λ_{max} = 453 nm (ε = 11710 Lmol⁻¹cm⁻¹), which is very similar to that of a phosphanyldisilene (λ_{max} = 441 nm)[96] (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 Ph2SiCl and (iPr2N)PCI. 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 silagermide. The silagermide 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°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.

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