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COMMUNICATION

Synthesis of Vinyl Germylenes

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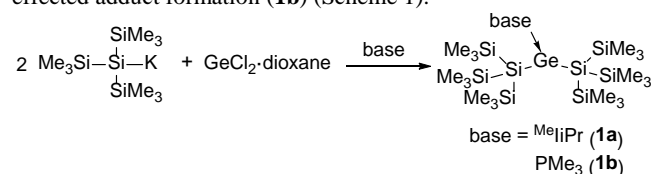
A disilylated germylene phosphine adduct was obtained by reaction of tris(trimethylsilyl)silyl potassium with PMe_3 and $\text{GeCl}_2 \cdot \text{dioxane}$. The adduct reacted with toluene to give a germacyclopropene, while reactions with phenylacetylene occurred by insertion into the Si-Ge bonds giving vinylgermylene adducts. Release of the mono- or divinylgermylenes by base abstraction led to insertion into Si-Si bonds and formation of silagermetes.

Research concerned with heavy carbene analogs (tetrylenes) bearing π -donating substituents has become a flourishing field in recent times.¹ In comparison analogous compounds with bulky aryl or alkyl groups have received less attention.² A likely reason for this diminished interest is a higher intrinsic reactivity of the latter, associated with lacking π -stabilization. Switching from alkyl or aryl to silyl groups even increases the reactivity and frequently such compounds can only be isolated in the form of base adducts,^{3,4} dimers,⁵ or rearrangement products.^{5,6} Our recent work in this field has focused on disilylated plumblylenes,^{7,8} stannylenes^{7,9,10} and germlylenes.¹¹⁻¹³ Most of these studies were concerned with cyclic compounds but earlier work by Klinkhammer^{14,15} and Stalke¹⁶ as well as recent reports by Escudie and Castel¹⁷ and by Jones, Kaltsoyannis, Mountford, and Aldridge¹⁸ demonstrated the versatility of the tris(trimethylsilyl)silyl group as substituent in this context.

Our attempts to employ this bulky silyl group for the synthesis of disilylated germlylenes were guided by Stalke's account¹⁶ reporting rearrangement of bis[tris(trimethylsilyl)silyl]germylene to hexakis(trimethylsilyl)disilagermirane as well as our previous experience with cyclic disilylated germlylenes and stannylenes where the use of trialkylphosphines, or N-heterocyclic carbenes allowed the isolation of base adducts of the respective tetrylenes.⁸⁻¹³

Reaction of two equiv tris(trimethylsilyl)silyl potassium¹⁹ with $\text{GeCl}_2 \cdot \text{dioxane}$ in the presence of the N-heterocyclic carbene 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (^{Me}LiPr)²⁰ afforded the respective bis[tris(trimethylsilyl)silyl]germylene base adduct (**1a**) in close to 80 % yield (Scheme 1). Attempts to repeat the reaction with Et_3P as base revealed that this phosphine is not able to stabilize the

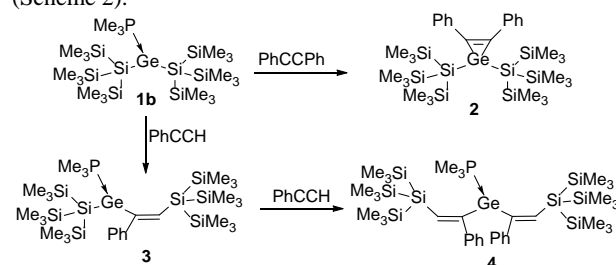
germylene effectively and formation of hexakis-(trimethylsilyl)disilagermirane was observed.¹⁶ However, using the smaller Me_3P and running the reaction at low temperature (-30°C) effected adduct formation (**1b**) (Scheme 1).



Scheme 1 Synthesis of bis[tris(trimethylsilyl)silyl]germylene base adducts

As the reaction of free silylenes and germlylenes with alkynes was found to proceed to silirenes²¹⁻²³ and germirenes²⁴⁻²⁶ we were interested to check for similar reactivity of base adducts **1a** and **1b**.

No conversion was observed in attempts to react **1a** with either toluene or phenylacetylene at ambient or slightly elevated temperature (50°). At higher temperature decomposition of **1a** begins. Adduct **1b** on the other hand, while not stable enough to allow its isolation in solid state, turned out to be suitable to study basic reactivity patterns with alkynes. The reaction with toluene showed formation of germirene **2** and thus supported reaction of **1b** as a germlylene (Scheme 2).



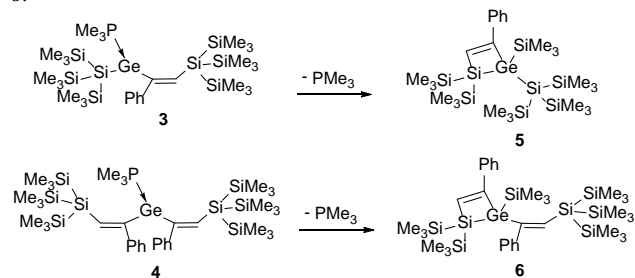
Scheme 2 α -Insertion of phenylacetylene into the Si-Ge bonds of germlylene PMe_3 adduct **1b** vs toluene addition

When switching from toluene to phenylacetylene we were not entirely convinced to expect formation of another germirene. No precedence for this reaction could be found in the literature. Germylene insertion into the rather polar C-H bond was thus considered a plausible alternative pathway. Also, a reaction following a course similar to Wesemann's recent reports of phosphine stabilized stannylenes which upon reaction with phenylacetylene gave the product of alkyne insertion into the Sn-P bond,^{27,28} seemed possible.

However, reaction of **1b** with phenylacetylene did not give any of the anticipated products. Instead the unexpected insertion product **3** (Scheme 2) was observed. Compound **3** was formed by regio- and stereoselective insertion of the alkyne into a Ge-Si bond. It is thus the PMe_3 adduct of a germylene bearing one silyl and one vinyl substituent (Scheme 2). A second reaction step was found to occur in the presence of another equivalent of phenylacetylene yielding again in a regio- and stereoselective way the divinylated germylene adduct **4** (Scheme 2).

Compounds **3** and **4** are interesting as they are stabilized versions of heavy analogs²⁹ of the elusive vinyl carbenes.^{30,31} No stable examples³² of vinyl carbenes are yet known, as they instantaneously cyclize to cyclopropenes. Although this reaction is believed to involve singlet vinyl carbenes³⁰ the free germlynes derived from **3** and **4** do not react analogously. Instead of cyclopropene formation insertion into Si-Si bonds is preferred. We are not aware of any known vinylgermylenes. The fact that they are stable is however in agreement with theoretical work, which states that the parent vinylgermylene is more stable than the isomeric germirene.³³

NMR-spectroscopically the reactions of **1b** with phenylacetylene and toluene are remarkably clean. However, similar to adduct **1b** also compounds **3** and **4** are very reactive and difficult to isolate. This property is likely associated with the rather weak interaction of the germlynes with PMe_3 .¹³ The fact that it is possible to obtain crystals of compounds **3** (although in a low isolated yield) and **4** suggests that the interaction between PMe_3 and the free germlynes of **3** and **4** is stronger than the interaction between PMe_3 and bis[tris(trimethylsilyl)silyl]germylene. The slightly more deshielded ^{31}P resonance of **1b** compared to **3** and **4** is also supportive of this argument. The sole side-products in the isolation attempts of **3** and **4** are those featuring intramolecular insertion of the free germlynes into pendant Si-Si bonds. This reactivity can be triggered deliberately by abstraction of the PMe_3 from **3** and **4** either by application of vacuum or by addition of the Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$ (Scheme 3). In both cases insertion of the respective free germylene occurs into a Si-SiMe₃ in γ -position causing the formation of silagermetes **5** and **6**.¹³



Scheme 3 Rearrangement of germylene PMe_3 adducts **3** and **4** upon loss of PMe_3

The NHC stabilized germylene **1a**, the alkyne addition product **2**, the insertion products **3** and **4**, as well as the intramolecular addition products **5**, and **6** were characterized by single crystal X-ray diffraction analysis. The molecular structures of the germylene adducts **1a** (Figure S-1), **3** (Figure 1), and **4** (Figure S-3) display the characteristic elongated bonds to the low valent germylene atoms.

This is illustrated by comparison of the Si-Ge distances of **1a** (2.4861(11) Å) and **3** (2.4816(8) Å) to those of **2** (2.4049(7) Å) (Figure S-2), **5** (2.4031(6), 2.4220(7), and 2.4354(6) Å) (Figure 1), and **6** (2.3959(8) and 2.4132(8) Å) (Figure S-4). Likewise the Ge-C bonds of **3** (2.031(2) Å) and **4** (2.043(2) Å) are distinctly longer than the related bond in **6** (1.997(2) Å).

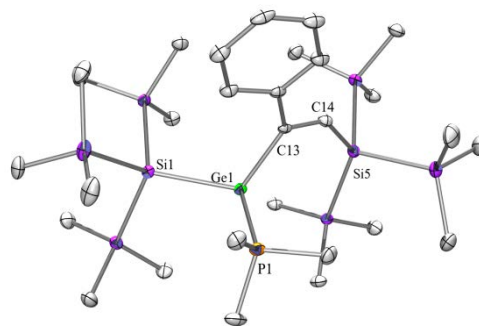


Fig. 1 Molecular structure of phenylacetylene insertion product **3**

The same behavior was previously observed also for the cyclic disilylated germylene adducts.^{11,13} The Ge-P distances of **3** (2.3900(7) Å) and **4** (2.4261(9) Å) are slightly elongated compared to the cyclic disilylated germylene PET_3 adducts,¹¹ but match the value for Power's aryl-germylgermylene PMe_3 adduct.³⁴ Other bond distances such as Si-Si and Si-C bond lengths are within the typically observed ranges. The structures of both **3** and **4** show some alignment of a vinyl π -system with the germylene p-orbital thus indicating a possible conjugative interaction.

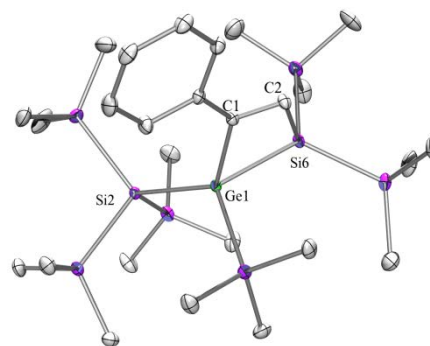


Fig. 2 Crystal structure of silagermete **5**

NMR spectroscopic analysis of the observed compounds proved to be straightforward. The ^{29}Si -NMR resonances of **1a** (δ (ppm) = -8.8 (SiMe_3), -122.9 ($\text{Si}(\text{SiMe}_3)_3$) and **1b** (δ (ppm) = -8.7 (d, SiMe_3 , $^3J_{\text{Si-P}} = 11$ Hz), -119.9 ($\text{Si}(\text{SiMe}_3)_3$) are close to those of **5** (δ (ppm) = -8.4 (SiMe_3), -116.6 ($\text{Si}(\text{SiMe}_3)_3$) and $(\text{Me}_3\text{Si})_3\text{SiGeMe}_3$ (δ (ppm) = -9.7 (SiMe_3), -127.9 ($\text{Si}(\text{SiMe}_3)_3$),^{35,36} thus indicating that the electronic influence of the base stabilized germylene is not much different from that of a germyl group. The ^{29}Si -NMR resonances of the vinylated compounds resemble that of related simpler systems.^{37,38}

^{13}C -NMR spectra of **3**, and **4** show that the resonances of the carbon atoms attached to stabilized germlynes is strongly deshielded to values of $\delta = 173$ and even 177 ppm. However, this large down-field

shift is also present in compound **6**, where the germanium atom is tetracoordinate. Nevertheless compared to related structures^{39,40} this spectroscopic behavior is unusual.

Conclusions

The synthesis of acyclic disilylated germylene base adducts was demonstrated. Reaction of the PMe_3 adduct with phenylacetylene gave vinylated germylene adducts which represent higher analogs of vinyl carbenes. In terms of the current discussion of low valent main group compounds mimicking transition metal complexes^{41–43} one could call such a reaction a migratory insertion. With respect to the mechanism of the vinyl germylene formation we are convinced that the first step of the reaction pathway is germirene formation. Support for this assumption comes from the observation that heating of diphenylgermirene **2** gives a silagermete analogous to **5**.⁴⁴ Computational studies of this unusual reactivity as well as a more comprehensive reactivity study of the germylene adducts are currently under investigation.

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Notes and references

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Electronic Supplementary Information (ESI) available: [Experimental details concerning synthesis and characterization, ORTEP plots of compounds **1a**, **2**, **4**, and **6**, crystallographic details as well as crystallographic information for compounds **1a**, and **2** – **6** in CIF format.] See DOI: 10.1039/c000000x/

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43. We want to thank a reviewer of this manuscript for suggesting to subject germirene **2** to forced conditions.