

## Cyclic Disilylated and Digermylated Germylenes

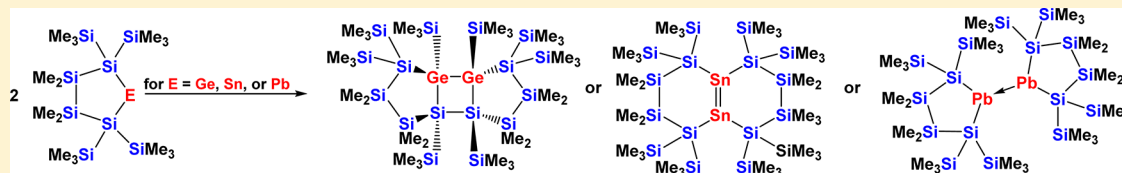
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## Supporting Information



**ABSTRACT:** The preparation of triethylphosphine adducts of cyclic disilylated or digermylated germylenes was achieved by reaction of 1,4-dipotassio-1,1,4,4-tetrakis(trimethylsilyl)tetramethyltetrasilane with  $\text{GeBr}_2 \cdot (\text{dioxane})$  and  $\text{PEt}_3$ . Phosphine abstraction with  $\text{B}(\text{C}_6\text{F}_5)_3$  allowed formation of the base-free germylenes, which undergo 1,2-trimethylsilyl shifts to the germylene atom to form the respective silagermene or digermene, which further dimerize in [2 + 2] cycloadditions to tricyclic compounds. The reasons responsible for the germylenes' completely different reactivities in comparison to the previously studied analogous stannylenes and plumblylenes were elucidated in a theoretical study.

## 1. INTRODUCTION

Over the last few years the advent of stable N-heterocyclic carbenes (NHCs) has revolutionized several branches of chemistry.<sup>1–3</sup> However, even before the first stable carbenes were reported already examples of stable germylenes, stannylenes, and plumblylenes were known.<sup>4</sup> Having a close relationship to NHCs, most of these compounds derive their stability from the  $\pi$ -donation of attached nitrogen substituents, while compounds with more electropositive substituents were found to be much more reactive and thus more difficult to prepare and isolate. Seminal work by Klinkhammer and colleagues has nevertheless shown that stable examples of silylated stannylenes and plumblylenes can be obtained in a straightforward way.<sup>5–7</sup> More recently Escudié, Castel and coworkers have reported that silylated and germylated stannylenes can be stabilized using coordinating NHCs.<sup>8</sup> The same strategy was shown to stabilize also the silylated chlorogermylene  $(\text{Me}_3\text{Si})_3\text{SiGeCl}$ .<sup>8</sup> Previous attempts by Stalke and Heine<sup>9</sup> and by Klinkhammer<sup>10</sup> showed that the reaction of [tris(trimethylsilyl)silyl]lithium with  $\text{GeBr}_2$  did not give bis[tris(trimethylsilyl)silyl]germanium as a stable compound but its isomer hexakis(trimethylsilyl)disilagermirane as the product of a rearrangement reaction. Using  $(\text{Me}_3\text{Si})_3\text{GeLi}$  as the nucleophile, Mallela et al. reported similar chemistry leading to hexakis(trimethylsilyl)germirane.<sup>11</sup>

Recently, we have reported on the synthesis of examples of cyclic disilylated stannylenes<sup>12</sup> and plumblylenes.<sup>13</sup> The difference between the aforementioned work by Klinkhammer<sup>5</sup> and our attempt was that we utilized a 1,4-tetrakis(trimethylsilyl)-tetramethyltetrasilanylene<sup>14,15</sup> unit, which can be considered as

a linked variation of two tris(trimethylsilyl)silyl groups. While we initially expected these compounds to exhibit a chemical behavior similar to that of the acyclic analogues, it turned out that the cyclic nature renders the tetrylene atom more accessible so that dimerization becomes a more facile process.<sup>12,13</sup>

With the elements Pb, Sn, and Ge exhibiting decreasing stability of the divalent state in this order, the respective disilylated tetrylenes reflect this by showing different mechanisms of stabilization. While bis[tris(trimethylsilyl)silyl]-lead<sup>5</sup> was found to be monomeric even in the solid state, for the cyclic plumblylene<sup>13</sup> a dimerization in the crystal was observed (Figure 1). The higher congener bis[tris(trimethylsilyl)silyl]tin was found to be monomeric in solution and dimeric in the solid state,<sup>5</sup> while for the cyclic stannylene<sup>12</sup> dimerization to a distannene in solution and the solid state was observed (Figure

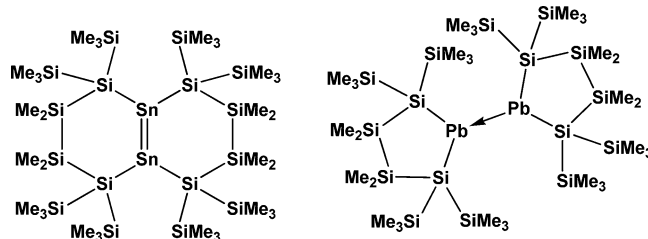
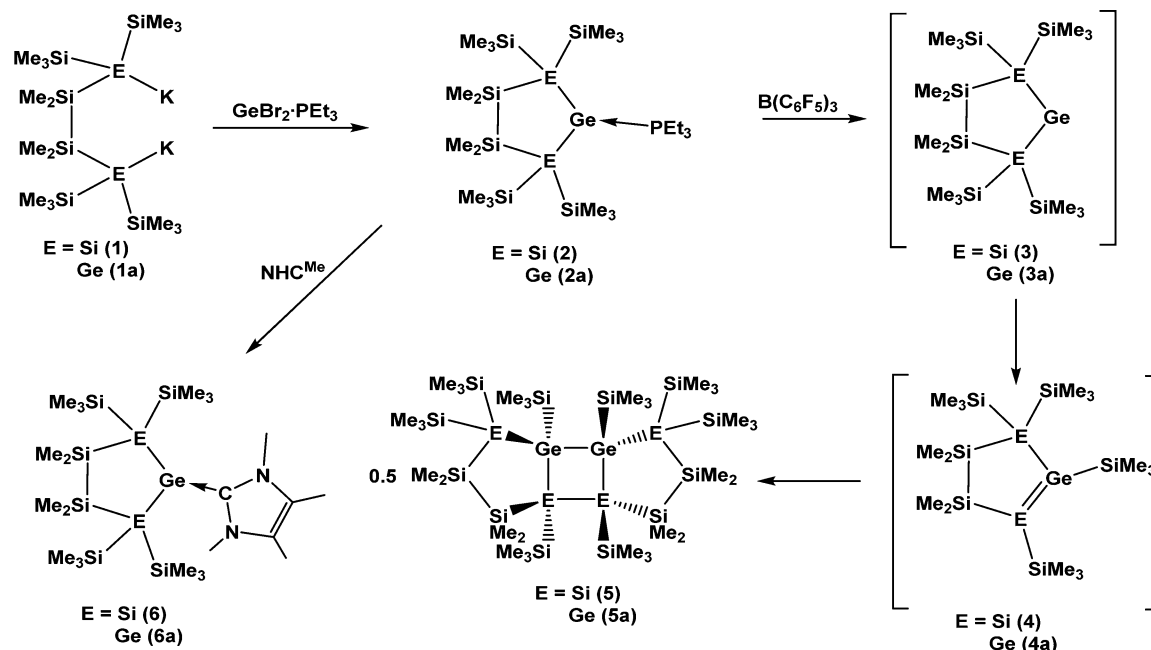


Figure 1. Dimers of cyclic disilylated stannylene and plumblylene.

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Scheme 1. Germylene Adduct Formation, Followed by Abstraction of Base, 1,2-Silyl Shift, and Dimerization



1). The synthesis of adducts of a disilylated germylene in the current study, together with the findings of Stalke<sup>9</sup> and Klinkhammer,<sup>10</sup> show that the decreased stability of disilylated germylenes leads to a different mechanism of stabilization in comparison to analogous stannylenes<sup>12</sup> and plumblylenes.<sup>13</sup> These results are consistent with older work by Klinkhammer<sup>10,16</sup> and a very recent account by Lai, Li, and co-workers.<sup>17</sup>

## 2. RESULTS AND DISCUSSION

**Synthesis.** Reaction of 1,4-dipotassiotetrasilane **1**<sup>14,15</sup> or the respective 1,4-digermanium analogue **1a**<sup>18</sup> with  $\text{GeBr}_2 \cdot (\text{dioxane})$  and  $\text{PEt}_3$  (Scheme 1) led to the clean formation of the germylene- $\text{PEt}_3$  adducts **2** and **2a**. With these precursors in hand, it was possible to release the free germylenes **3** and **3a** by abstracting the phosphane with the strong Lewis acid  $\text{B}(\text{C}_6\text{F}_5)_3$  (Scheme 1). As expected, germylenes **3** and **3a** are not stable but undergo a facile dimerization process. The interesting result is, however, that the dimerization process is not related to that observed for the analogous stannylene.<sup>12</sup> The latter was found to dimerize to a distannene (Figure 1),<sup>12</sup> whereas germylenes **3** and **3a** dimerize to the tricyclic compounds **5** and **5a** (Scheme 1).

For the stannylene dimerization process the first step was found to be the formation of an exocyclic distannene, which then rearranges to its endocyclic isomer.<sup>12</sup> In contrast to this, the first step of the germylene dimerization is a 1,2-trimethylsilyl shift from the  $\alpha$ -position to the germanium atom. The thus formed silagermene (**4**) or digermene (**4a**) undergoes a  $[2 + 2]$  cycloaddition to form **5** and **5a**. The first step of this reaction sequence is likely analogous to what happened in the reactions described by Stalke,<sup>9</sup> Klinkhammer,<sup>10</sup> and Mallela.<sup>11</sup> However, the acyclic examples can react by another 1,2-trimethylsilyl shift to give an isomeric silylene, which eventually inserts into the Si–Si bond, thus forming a three-membered ring. While the cyclic silagermene **4** and digermene **4a** could also undergo an additional 1,2-trimethylsilyl shift, final insertion of the thus formed silylene or

germylene into a Si–Si or Si–Ge bond is not likely, due to the cyclic nature of the molecule. Lacking opportunities for further intramolecular stabilization, **4** and **4a** therefore react in an intermolecular  $[2 + 2]$  cycloaddition.

Reactions of **2** and **2a** with 2,3,4,5-tetramethylimidazol-2-ylidene ( $\text{NHC}^{\text{Me}}$ )<sup>19</sup> proceeded smoothly to exchange  $\text{PEt}_3$  against the carbene ligand and afforded the carbene-stabilized germylenes **6** and **6a** (Scheme 1).

**NMR Spectroscopy.** The NMR spectra of **2** and **2a** do not exhibit very unusual chemical shifts. As the tricoordinated germanium atoms have configurational stability, the respective <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si spectra display different symmetry (vide infra). The <sup>31</sup>P resonances at 14.8 ppm for **2** and 15.0 ppm for **2a** are almost identical. They are interesting in comparison with the analogous stannylene and plumblylene  $\text{PEt}_3$  adducts, for which resonances at –1.0 and –60 ppm, respectively, were observed.<sup>12,13</sup> <sup>29</sup>Si resonances for the trimethylsilyl groups were found at –7.9 ppm for **2** and –2.0 and –4.1 ppm for **2a**, which corresponds to a typical chemical shift difference between  $\text{SiMe}_3$  groups attached to either Si or Ge. In addition, the  $\text{SiMe}_2$  shifts of –22.7 ppm for **2** and –16.9 ppm for **2a** and the resonance of the quaternary Si atom of **2** at –127.1 ppm are perfectly reasonable and do not differ much from the analogous compound with a dimethylgermylene unit in the ring.<sup>20</sup> The <sup>29</sup>Si NMR spectra of **6** and **6a** are fairly similar to those of **2** and **2a**, with all resonances shifted slightly to lower field. The <sup>13</sup>C NMR shifts of the carbene carbon atoms of **6** and **6a** were found at 174.0 and 175.6 ppm, which in comparison to the signal for the free carbene (213.7 ppm)<sup>21</sup> also indicates the substantial Lewis acidity of the germylenes **3** and **3a**.

When  $\text{PEt}_3$  was abstracted from **2** at low temperature, direct NMR spectroscopic observation of silagermene **4** was possible. Especially the  $\text{sp}^2$ -hybridized silicon atom with a chemical shift of  $\delta$  149.6 ppm is quite diagnostic for the detection of this molecule. This resonance is very close to that observed for the related stable silagermene (<sup>t</sup>BuMe<sub>2</sub>Si)<sub>2</sub>Ge=Si(Si<sup>t</sup>BuMe<sub>2</sub>)<sub>2</sub> ( $\delta$  (<sup>29</sup>Si) 144.0 ppm).<sup>22</sup> In addition, <sup>29</sup>Si NMR chemical shift calculations at the MP2/GIAO level predict for the silagermene

**Table 1.** Experimentally Determined and Computed (in Italics>) Activation Parameters of Germylene Donor Complexes **2**, **6**, **2a**, and **6a**

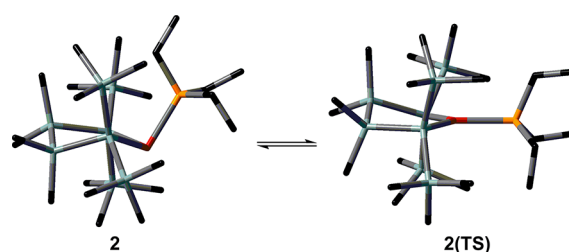
	<b>2</b>	<b>6</b>	<b>2a</b>	<b>6a</b>
$T_{\text{coalescence}}$ (K)	269	293	348	391
$\Delta H^\ddagger$ (kJ mol <sup>-1</sup> )	23.7 ± 3.2	50.2 ± 3.1		
$\Delta S^\ddagger$ (J mol <sup>-1</sup> K <sup>-1</sup> )	-121 ± 10	-34.3 ± 11.6		
$\Delta G^\ddagger$ (kJ mol <sup>-1</sup> )	59.8 ± 6.3 <sup>a</sup> (55.6 ± 6.0) <sup>b</sup>	60.3 ± 6.5 <sup>a</sup> (60.2 ± 6.5) <sup>b</sup>	73.9	78.4
$E_a$ (kJ mol <sup>-1</sup> )	26.2 ± 3.2 <sup>a</sup> (25.9 ± 3.2) <sup>b</sup>	52.6 ± 3.1 <sup>a</sup> (52.6 ± 3.1) <sup>b</sup>		
$\Delta G^\ddagger(\text{calcd})$ (kJ mol <sup>-1</sup> ) <sup>c</sup>	56	61	76	81
BDE (kJ mol <sup>-1</sup> ) <sup>d</sup>	130	173	137	196

<sup>a</sup>For  $T = 298$  K. <sup>b</sup>For  $T = T_c$ . <sup>c</sup>Calculated by M06-2X/def2tzvp (Ge), 6-311+G(d,p) (P), 6-31G(d) (Si, C, H), and PCM methods using the specific parameter for toluene. Free Gibbs energies  $G$  were calculated at the indicated temperature  $T$  and at  $p = 23.71$  MPa (234 atm); see the Supporting Information for further details. <sup>d</sup>BDE denotes the bond dissociation energy of the Ge–P (**2**, **2a**) or Ge–C bond (**6**, **6a**) at 0 K and 0.101 MPa (1 atm).

(Me<sub>3</sub>Si)<sub>2</sub>Ge=Si(SiMe<sub>3</sub>)<sub>2</sub> a silicon NMR chemical shift of  $\delta(^{29}\text{Si})$  158 ppm, which is very close to the experimentally observed values of persilylated silagermenes.<sup>22,23</sup> The tricyclic compound **5** also exhibits an interesting <sup>29</sup>Si NMR spectrum with two resonances at -69.7 and -94.1 ppm. While 4-fold silylated silicon atoms typically resonate around -130 ppm, the incorporation of such units into cyclotetrasilanes is accompanied by a downfield shift of some 40 ppm.<sup>24,25</sup> The presence of strongly branched substituents<sup>28</sup> causes further downfield shift behavior, so that we assign the Si(SiMe<sub>3</sub>) group in the central ring to the resonance at -69.7 ppm, whereas the Si(SiMe<sub>3</sub>)<sub>2</sub> unit is associated with the resonance at -94.1 ppm.

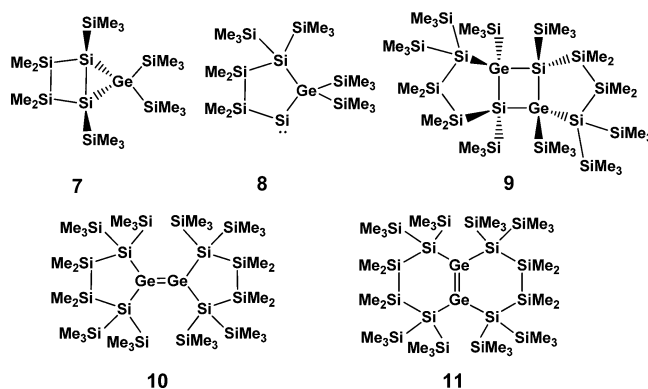
As mentioned above, <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectroscopic analysis of phosphane adducts **2** and **2a** at ambient temperature revealed configurational stability of the germanium atom for **2a**. This is clearly indicated by the presence of well-resolved signal sets for the different sides of the five-membered ring. Under the same conditions compound **2** exhibits broad signals for the trimethylsilyl and methyl groups. The same behavior was observed also for compounds **6** and **6a**. While for the digermylated **6a** configurational stability of the Ge atom at ambient temperature was observed, the same conditions corresponded to the coalescence temperature of **6**. Activation parameters of **2** and **6** were determined by VT-NMR spectroscopic analysis/Eyring plot. For **2a** and **6a** values for  $\Delta G^\ddagger$  are based on the determination of the coalescence temperature (Table 1).

The results of a computational study indicate that the reversible process observed by variable-temperature (VT) NMR spectroscopy for compounds **2**, **2a**, **6**, and **6a** occurs in each case intramolecularly. In this process the configuration at the pyramidalized germanium atom is inverted via a transition state in which the germanium atom adopts a trigonal-planar coordination environment (see Figure 2 for an example). Therefore, this process clearly parallels the well-known inversion processes of isolobal amines and phosphanes. The computed barriers for the intramolecular inversion process are in all four cases very close to the experimentally determined values. The largest deviation,  $\Delta\Delta G^\ddagger$ , was found for the inversion process of compound **2** ( $\Delta\Delta G^\ddagger = 4$  kJ mol<sup>-1</sup>). Moreover, all experimentally determined barriers are significantly smaller than the calculated bond dissociation energy, BDE, of the germanium–donor bond (see Table 1), which discards a dissociation–recomplexation process as a possible alternative.

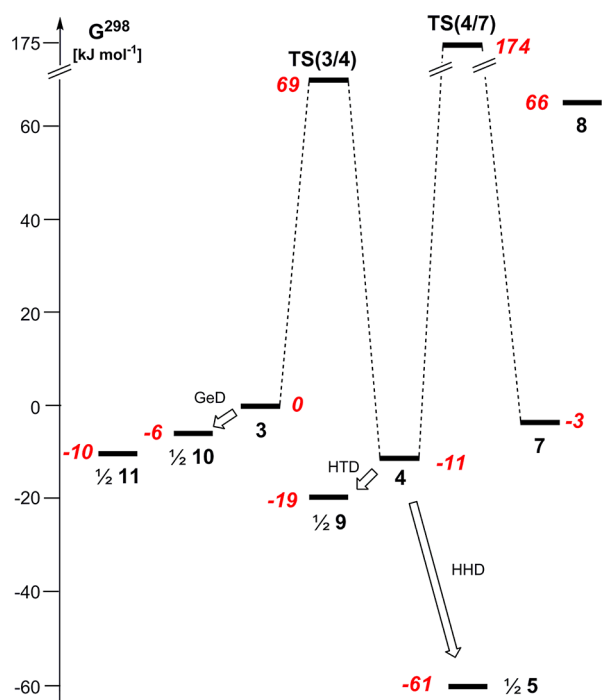


**Figure 2.** Tube representation of the germylene–phosphane complex **2** and its transition state, **2(TS)**, for inversion. (M06-2X/def2tzvp (Ge), 6-311+G(d,p) (P), 6-31G(d) (Si, C, H); hydrogen atoms omitted for clarity; color code Ge (red), Si (gray), P (orange), C (black)).

**Computational Study.** In view of the previous reports by Stalke,<sup>9</sup> Klinkhammer,<sup>10</sup> and Mallela,<sup>11</sup> and in light of our recent and actual experimental results,<sup>12,13</sup> a computational study<sup>26,27</sup> which gives insights into the reactivity of germylene **3** and into the exclusive formation of the head-to-head dimer **5** ought to address possible isomerization reactions of germylene **3** to silagermene **4**, hausane **7**, and silylene **8**. Furthermore, the relative thermodynamic stabilities of different dimers of silagermene **4** and germylene **3**, such as the head-to-tail dimer **9** and the digermenes **10** and **11** need to be evaluated.



The results of our computations suggest that the 1,2 silyl shift which transforms the germylene **3** into the silagermene **4** is slightly exergonic ( $\Delta G^{298} = -11$  kJ mol<sup>-1</sup>) and is connected with a barrier of  $\Delta G^{298 \ddagger} = 69$  kJ mol<sup>-1</sup> (Figure 3). Although the isomeric hausane **7** is also close in energy ( $G_{\text{rel}}^{298} = -3$  kJ mol<sup>-1</sup>), it is separated from the silagermene **4** by a prohibitively



**Figure 3.** Reaction coordinate for the transformation of germylene **3** into silagermene **4** and hausane **7** and their free Gibbs energies at 298.15 K,  $G^{298}$ , relative to their dimers **5** and **9–11** ( $G^{298}$  calculated at M06-2X/def2tzvp (Ge), 6-31G(d) (Si, C, H), are given in red italics): GeD, germylene dimerization; HTD, head to tail dimerization; HHD, head-to-head dimerization.

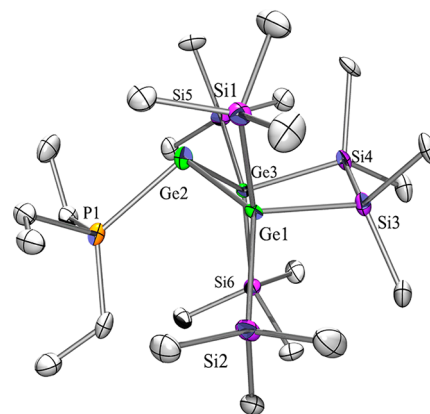
high barrier of  $\Delta G^{298\ddagger} = 185 \text{ kJ mol}^{-1}$  (calculated for the forward reaction  $4 \rightarrow 7$ ) which practically excludes its formation from silagermene **4** under the applied reaction conditions. Similarly, silylene **8** is markedly destabilized in comparison to other investigated isomers ( $G^{298}_{\text{rel}}(\mathbf{8}) = 66 \text{ kJ mol}^{-1}$ ), most probably due to the occurrence of sterically unfavorable vicinal 1,1,2,2-tetrakis(trimethylsilyl) substitution in this compound. This result suggests that silylene **8** is not of further relevance for the discussion.

From a thermodynamic point of view, the dimerization of germylene **3** to give digermene **10** and finally, after skeletal rearrangement,<sup>12</sup> the endocyclic digermene **11** (Figure 3) is practically thermoneutral in comparison to the formation of the silagermene **4**. In contrast, the head-to-tail (HTD) and in particular the head-to-head (HHD, Figure 3) dimerizations of silagermene **4** to the tricyclic compounds **5** (HHD) and **9** (HTD) are strongly exergonic. These computational results suggest that, in agreement with the experimental results, the transient germylene **3** is converted under thermodynamic control preferentially to the head-to-head dimer **5**. The large difference in Gibbs free energies between the HHD isomer **5** and the HTD isomer **9** of  $\Delta G^{298}(\mathbf{5}/\mathbf{9}) = 84 \text{ kJ mol}^{-1}$  is a result of the greater steric congestion in the HTD **9**, as for smaller model systems this marked energy difference is not reflected by the results of the calculations. For example, the calculations for the two different cyclic dimers of  $\text{H}_2\text{Si}=\text{Ge}(\text{H})\text{SiH}_3$  predict an energy difference of merely  $6 \text{ kJ mol}^{-1}$  in favor of the head-to-head dimer.

Quite similar results were obtained for the transformation of the germanium-substituted germylene **3a**. In this case the 1,2-silyl shift proceeds with a slightly smaller barrier ( $\Delta G^{298\ddagger} = 52 \text{ kJ mol}^{-1}$ ) to give the more stable digermene **4a** ( $G_{\text{rel}}^{298}(\mathbf{4a}) =$

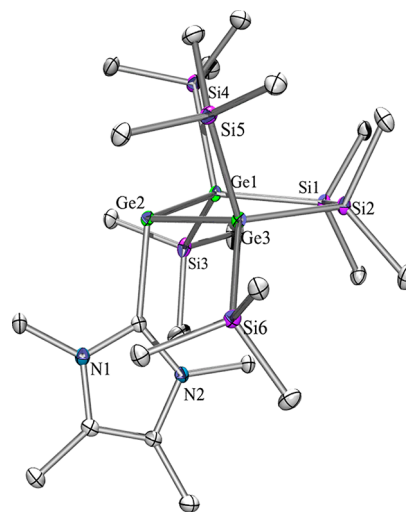
$-13 \text{ kJ mol}^{-1}$ ). Again the dimerization to give the head-to-head dimer **5a** is favored over the formation of the corresponding head-to-tail dimer **9a** ( $\Delta G^{298}(\mathbf{5a}/\mathbf{9a}) = 83 \text{ kJ mol}^{-1}$ ).

**X-ray Crystallography.** Crystal structure analysis provided molecular structures of compounds **2**, **2a**, **5**, **5a**, **6**, and **6a** in the solid state (Table S1, Supporting Information). As expected, compound pairs **2** and **2a**, **5** and **5a**, and **6** and **6a** display isotopic behavior. The structures of **2** (Figure S-1, Supporting Information) and **2a** (Figure 4) feature the five-membered ring



**Figure 4.** Molecular structure of **2a** in the solid state.

in an envelope conformation with one of the  $\text{E}(\text{SiMe}_3)_2$  units out of plane. The base ligands coordinate in an approximately orthogonal way to the plane which is spanned by the divalent tetrel atom and its two neighboring atoms of **2**, **2a**, **6**, and **6a**. For the NHC adducts **6** (Figure S-3, Supporting Information) and **6a** (Figure 5) the angle between the  $\text{EGe}(\text{II})\text{E}$  plane and



**Figure 5.** Molecular structure of **6a** in the solid state.

the base–Ge bond base is more acute (**6**,  $104.9^\circ$ ; **6a**,  $104.2^\circ$ ) in comparison to the  $\text{PEt}_3$  adducts (**2**,  $113.6^\circ$ ). For **6** and **6a** thus almost planar five-membered rings were observed.

The tricyclic compounds **5** (Figure S-2, Supporting Information) and **5a** (Figure 6) are interesting in that sense that they are highly branched. The fact that the  $[2 + 2]$  cycloaddition of the respective silagermene or digermene occurs in a head-to-head fashion leads to a dimer with a Ge–Ge bond with maximum branched atoms in the  $\alpha$ -positions. The steric



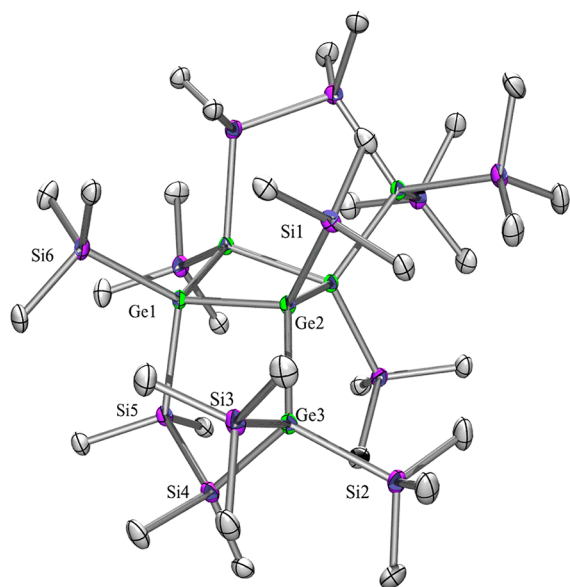


Figure 6. Molecular structure of **5a** in the solid state.

bulk of this arrangement leads to a very long Ge–Ge bond of 2.575(1) Å for **5a**. The direct influence of sterics can be estimated when this bond is compared to the other Ge–Ge bond of the four-membered ring of **5a**, which are with 2.4832(9) and 2.4617(9) Å much shorter. Related structures containing digermene units with silyl or germyl substituents feature Ge–Ge bond lengths ranging from 2.457 to 2.491 Å.

### 3. CONCLUSION

Although the chemistry of germynes has received much attention in recent times, most of the studied compounds are either N-heterocyclic compounds or at least carry  $\pi$ -donating substituents such as amino or alkoxy groups. Tetrylenes with more electropositive substituents are much more reactive, and so far no stable examples of silylated germynes have been reported. Reports dealing with these compounds so far either describe rearrangement reactions of the formed germynes<sup>9,10</sup> or utilize adduct formation of the compounds.<sup>8</sup>

In the current account the preparation of cyclic disilylated and digermylated germynylene  $\text{PET}_3$  adducts was accomplished by reaction of either a 1,4-dipotassiotetrasilane or an analogous digermanide with  $\text{GeBr}_2 \cdot \text{PET}_3$ . Subsequent reaction with an N-heterocyclic carbene led to substitution of the phosphine by the carbene. By treatment of the adducts with  $\text{B}(\text{C}_6\text{F}_5)_3$  the respective germynes could be released. In comparison to analogous stannylenes and plumbylenes, the thus formed free germynes are less stable and achieve stabilization by a different mode of action. For the germynes studied in the current investigation an intermolecular way of stabilization by means of dimerization as digermene is unfavorable. Instead, a 1,2-trimethylsilyl shift from the germynylene's  $\alpha$ -position to the dicoordinated germanium atom leads to a cyclic silagermene or digermene. These compounds, though still not stable, can be detected by NMR spectroscopy before undergoing a dimerization process via a formal [2 + 2] cycloaddition reaction.

### 4. EXPERIMENTAL SECTION

**General Remarks.** All reactions involving air-sensitive compounds were carried out under an atmosphere of dry nitrogen or argon using

either Schlenk techniques or a glovebox. All solvents were dried using a column-based solvent purification system.<sup>29</sup>  $\text{GeBr}_2 \cdot (\text{dioxane})$ ,<sup>30</sup> 1,3,4,5-tetramethylimidazol-2-ylidene,<sup>19</sup> **1**,<sup>14,15</sup> and **1a**<sup>18</sup> were prepared according to literature procedures. Potassium *tert*-butanolate was purchased from Merck. All other chemicals were obtained from different suppliers and used without further purification.

<sup>1</sup>H (300 MHz), <sup>13</sup>C (75.4 MHz), <sup>31</sup>P (124.4 MHz), and <sup>29</sup>Si NMR spectra (59.3 MHz) were recorded on a Varian INOVA 300 spectrometer. If not noted otherwise,  $\text{C}_6\text{D}_6$  was used as the solvent for all samples. To compensate for the low isotopic abundance of <sup>29</sup>Si, the INEPT pulse sequence<sup>30,31</sup> was used for the amplification of the signal.

**X-ray Structure Determination.** For X-ray structure analyses the crystals were mounted onto the tip of glass fibers, and data collection was performed with a Bruker-AXS SMART APEX CCD diffractometer using graphite-monochromated Mo  $K\alpha$  radiation (0.71073 Å). The data were reduced to  $F^2$  and corrected for absorption effects with SAINT<sup>32</sup> and SADABS,<sup>33,34</sup> respectively. The structures were solved by direct methods and refined by full-matrix least-squares methods (SHELXL97).<sup>35</sup> If not noted otherwise, all non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in calculated positions to correspond to standard bond lengths and angles. All diagrams were drawn with 30% probability thermal ellipsoids, and all hydrogen atoms were omitted for clarity. Unfortunately the obtained crystal quality of some substances was poor. This fact is reflected by quite high *R* and low  $\theta$  values.

Crystallographic data (excluding structure factors) for the structures of compounds **2**, **2a**, **5**, **5a**, **6**, and **6a** reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC 866887 (**2**), 866886 (**2a**), 866885 (**5**), 866890 (**5a**), 866889 (**6**), and 866888 (**6a**). Copies of the data can be obtained free of charge at <http://www.ccdc.cam.ac.uk/products/csd/request/>.

**2-Germa-1,1,3,3-tetrakis(trimethylsilyl)-2,2,3,3-tetramethylcyclopentasilan-2-ylidene-Triethylphosphane Adduct (2).** Compound **1** (freshly prepared from  $(\text{Me}_3\text{Si})_3\text{Si}(\text{SiMe}_2)_2\text{Si}(\text{SiMe}_3)_3$  (1.85 g, 3.03 mmol) and  $\text{KO}^t\text{Bu}$  (714 mg, 6.36 mmol) in 10 mL of DME) dissolved in 40 mL of THF/DME (3/1) was slowly added to a mixture of  $\text{GeBr}_2 \cdot (\text{dioxane})$  (1.07 g, 3.33 mmol) and  $\text{PET}_3$  (393 mg, 3.33 mmol) in 20 mL of THF at  $-80^\circ\text{C}$ . The mixture turned orange, and a white precipitate was formed. The mixture was stirred for 12 h and slowly reached ambient temperature. The solvent was removed under reduced pressure, and the dark orange residue was extracted with pentane ( $4 \times 10$  mL). After concentration to 10 mL and storage at  $-20^\circ\text{C}$  yellow crystals of **2** (1.42 g, 71%) were obtained. Mp: 139–144  $^\circ\text{C}$  dec. <sup>1</sup>H NMR ( $\delta$  in ppm): 0.43 (s, 36H,  $\text{SiMe}_3$ ), 0.51 (s, 12H,  $\text{SiMe}_2$ ), 0.82 (m, 9H,  $\text{CH}_3\text{CH}_2$ ), 1.61 (m, 6H,  $\text{CH}_2\text{P}$ ). <sup>13</sup>C NMR ( $\delta$  in ppm):  $-1.2$  ( $\text{SiMe}_2$ ), 3.8 (broad,  $\text{SiMe}_3$ ), 8.3 (d,  $^2J_{\text{C,P}} = 5.7$  Hz,  $\text{CH}_3\text{CH}_2$ ), 19.9 (d,  $^1J_{\text{C,P}} = 19.7$  Hz,  $\text{CH}_2\text{P}$ ). <sup>29</sup>Si NMR ( $\delta$  in ppm):  $-7.9$  (broad, s,  $\text{SiMe}_3$ ),  $-22.7$  (d,  $^3J_{\text{Si,P}} = 9.7$  Hz,  $\text{SiMe}_2$ ),  $-127.1$  (d,  $^2J_{\text{Si,P}} = 15.2$  Hz,  $\text{SiSiMe}_3$ ). <sup>31</sup>P NMR ( $\delta$  in ppm): 14.8. Anal. Calcd for  $\text{C}_{22}\text{H}_{63}\text{GePSi}_8$  (656.03): C, 40.28, H, 9.68. Found: C, 39.36; H, 9.48. UV absorption:  $\lambda_1$  261 nm (shoulder) ( $\epsilon_1 = 2.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ),  $\lambda_2 = 361$  nm ( $\epsilon_2 = 3.7 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ),  $\lambda_3 = 414$  nm ( $\epsilon_3 = 1.9 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ).

**1,2,3-Trigerm-1,1,3,3-tetrakis(trimethylsilyl)-2,2,3,3-tetramethylcyclopentasilan-2-ylidene-Triethylphosphane Adduct (2a).** The procedure for **2** was carried out using **1a** (freshly prepared from  $(\text{Me}_3\text{Si})_3\text{Ge}(\text{SiMe}_2)_2\text{Ge}(\text{SiMe}_3)_3$  (1.40 g, 2.00 mmol),  $\text{KO}^t\text{Bu}$  (471 mg, 4.20 mmol),  $\text{GeBr}_2 \cdot (\text{dioxane})$  (705 mg, 2.20 mmol), and  $\text{PET}_3$  (307 mg, 2.60 mmol). Yellow crystalline **2a** was isolated (710 mg, 48%). Mp: 149–153  $^\circ\text{C}$  dec. <sup>1</sup>H NMR ( $\delta$  in ppm): 0.42 (s, 18H,  $\text{SiMe}_3$ ), 0.51 (s, 18H,  $\text{SiMe}_2$ ), 0.53 (s, 6H,  $\text{SiMe}_2$ ), 0.54 (s, 6H,  $\text{SiMe}_2$ ), 0.85 (m, 9H,  $\text{CH}_3\text{CH}_2$ ), 1.61 (m, 6H,  $\text{CH}_2\text{P}$ ). <sup>13</sup>C NMR ( $\delta$  in ppm):  $-0.5$  ( $\text{SiMe}_2$ ),  $-0.1$  ( $\text{SiMe}_2$ ), 4.0 ( $\text{SiMe}_3$ ), 5.4 ( $\text{SiMe}_2$ ), 8.7 (d,  $^2J_{\text{C,P}} = 5.3$  Hz,  $\text{CH}_3\text{CH}_2$ ), 20.1 (d,  $^1J_{\text{C,P}} = 18.9$  Hz,  $\text{CH}_2\text{P}$ ). <sup>29</sup>Si NMR ( $\delta$  in ppm):  $-2.0$  (d,  $^3J_{\text{Si,P}} = 13.6$  Hz,  $\text{SiMe}_3$ ),  $-4.1$  (d,  $^3J_{\text{Si,P}} = 7.9$  Hz,  $\text{SiMe}_2$ ),  $-16.9$  (d,  $^3J_{\text{Si,P}} = 7.8$  Hz,  $\text{SiMe}_2$ ). <sup>31</sup>P NMR ( $\delta$  in ppm): 15.0. Anal. Calcd for  $\text{C}_{22}\text{H}_{63}\text{Ge}_3\text{PSi}_6$  (745.14): C, 35.46; H, 8.52. Found: C, 35.30; H, 8.36. UV absorption:  $\lambda_1$  259 nm (shoulder) ( $\epsilon_1 = 2.1 \times 10^4$

$M^{-1} \text{ cm}^{-1}$ ),  $\lambda_2$  340 nm ( $\epsilon_2 = 3.9 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ),  $\lambda_3$  421 nm ( $\epsilon_3 = 2.4 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ).

**1,2-Digerma-1,2,3,3,6,7,10,10-octakis(trimethylsilyl)octamethyltricyclo[5.3.0.0<sup>2,6</sup>]deasilane (5).** A solution of **2** (200 mg, 0.305 mmol) was dissolved in 5 mL of pentane and slowly added to a stirred solution of  $B(C_6F_5)_3$  (156 mg, 0.305 mmol) in 5 mL of pentane. The mixture turned orange during the addition, and a colorless precipitate was formed. After 2 h the mixture was hydrolyzed with dilute  $H_2SO_4$  (0.5 M), the organic layer was separated, the aqueous phase was extracted with  $Et_2O$  ( $3 \times 30 \text{ mL}$ ), and the extract was dried over  $Na_2SO_4$ . The solvent was removed under reduced pressure, and the yellowish residue crystallized from hexane, giving colorless crystals (105 mg, 64%) of **5**. Mp: 180–186 °C dec.  $^1H$  NMR ( $\delta$  in ppm): 0.37 (s, 18H, SiMe<sub>3</sub>), 0.41 (s, 18H, SiMe<sub>3</sub>), 0.42 (s, 18H, SiMe<sub>3</sub>), 0.50 (s, 6H, SiMe), 0.57 (s, 6H, SiMe), 0.58 (s, 18H, SiMe<sub>3</sub>), 0.62 (s, 6H, SiMe), 0.74 (s, 6H, SiMe).  $^{13}C$  NMR ( $\delta$  in ppm): 1.0 (SiMe), 1.6 (SiMe), 2.3 (SiMe), 4.6 (SiMe), 5.1 (SiMe<sub>3</sub>), 5.3 (SiMe<sub>3</sub>), 6.1 (SiMe<sub>3</sub>), 7.1 (SiMe<sub>3</sub>).  $^{29}Si$  NMR ( $\delta$  in ppm): -1.5 (SiMe<sub>3</sub>), -6.7 (SiMe<sub>3</sub>), -6.9 (SiMe<sub>3</sub>), -8.7 (SiMe<sub>3</sub>), -17.2 (SiMe<sub>2</sub>), -25.1 (SiMe<sub>2</sub>), -69.7 (SiSiMe<sub>3</sub>), -94.1 (SiSiMe<sub>3</sub>). Anal. Calcd for  $C_{32}H_{96}Ge_2Si_{16}$  (1075.75): C, 35.73; H, 8.99. Found: C, 35.72; H, 8.82. UV absorption:  $\lambda_1$  344 nm ( $\epsilon_1 = 5.2 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ).

**1,2,3,6,7,10-Hexagerma-1,2,3,3,6,7,10,10-octakis(trimethylsilyl)octamethyltricyclo[5.3.0.0<sup>2,6</sup>]deasilane (5a).** The procedure for **5** was carried out using **2a** (224 mg, 0.300 mmol) and tris(pentafluorophenyl)borane (154 mg, 0.300 mmol). Light yellow crystalline **5a** was isolated (85 mg, 45%). Mp: 198–201 °C dec.  $^1H$  NMR ( $\delta$  in ppm): 0.40 (s, 18H, SiMe<sub>3</sub>), 0.44 (s, 18H, SiMe<sub>3</sub>), 0.45 (s, 18H, SiMe<sub>3</sub>), 0.52 (s, 6H, SiMe), 0.58 (s, 24H, SiMe<sub>3</sub>/SiMe), 0.66 (s, 6H, SiMe), 0.82 (s, 6H, SiMe).  $^{13}C$  NMR ( $\delta$  in ppm): 1.2 (SiMe), 1.8 (SiMe), 2.6 (SiMe), 5.2 (SiMe), 5.2 (SiMe<sub>3</sub>), 5.6 (SiMe<sub>3</sub>), 6.4 (SiMe<sub>3</sub>), 6.8 (SiMe<sub>3</sub>).  $^{29}Si$  NMR ( $\delta$  in ppm): -0.7 (SiMe<sub>3</sub>), -1.0 (SiMe<sub>3</sub>), -1.3 (SiMe<sub>3</sub>), -1.8 (SiMe<sub>3</sub>), -11.6 (SiMe<sub>2</sub>) -21.0 (SiMe<sub>2</sub>). Anal. Calcd for  $C_{32}H_{96}Ge_2Si_{12}$  (1253.97): C, 30.65; H, 7.72. Found: C, 30.61; H, 7.82. UV absorption:  $\lambda_1$  262 nm ( $\epsilon_1 = 2.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ),  $\lambda_2$  338 nm ( $\epsilon_2 = 4.4 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ).

**2-Germa-1,1,3,3-tetrakis(trimethylsilyl)-2,2,3,3-tetramethylcyclopentasilan-2-ylidene-NHC Adduct (6).** Compound **2** (66 mg, 0.10 mmol) and 1,3,4,5-tetramethylimidazol-2-ylidene (13 mg, 0.10 mmol) were dissolved in pentane (4 mL) and stirred for 10 min. The orange solution was filtered to remove residual  $K_2S$  precipitate from the NHC synthesis. The filtrate was evaporated under reduced pressure. The yellow residue was dissolved in pentane (3 mL) and stored at -35 °C for 3 days, affording yellow prismatic crystals of **6** (60 mg, 90%). Mp: 147–153 °C dec.  $^1H$  NMR ( $\delta$  in ppm, toluene- $d_8$  at 25 °C): 0.38 (s, very broad, 36H, SiMe<sub>3</sub>), 0.59 (s, 12H, SiMe<sub>2</sub>), 1.38 (s, 6H, CH<sub>3</sub>C), 3.56 (s, 6H, CH<sub>3</sub>N).  $^{13}C$  NMR ( $\delta$  in ppm, toluene- $d_8$  at 25 °C): -0.6 (broad, SiMe<sub>2</sub>), 3.7 (broad, SiMe<sub>3</sub>), 8.0 (MeC), 36.4 (MeN), 105.0 (NCC), 174.0 (NCN).  $^{29}Si$  NMR ( $\delta$  in ppm, toluene- $d_8$  at 25 °C): -18.8 (SiMe<sub>2</sub>), -120.0 (SiSiMe<sub>3</sub>). Anal. Calcd for  $C_{23}H_{60}GeN_2Si_8$  (662.06): C, 41.73; H, 9.13; N, 4.23. Found: C, 41.41; H, 8.88; N, 4.24. UV absorption:  $\lambda_1$  287 nm (shoulder) ( $\epsilon_1 = 2.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ),  $\lambda_2$  377 nm ( $\epsilon_2 = 4.0 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ).

**1,2,3-Trigerma-1,1,3,3-tetrakis(trimethylsilyl)-2,2,3,3-tetramethylcyclopentasilan-2-ylidene-NHC Adduct (6a).** The procedure for **6** was carried out using **2a** (75 mg, 0.10 mmol) and 1,3,4,5-tetramethylimidazol-2-ylidene (12 mg, 0.10 mmol). Yellow crystals of **6a** (66 mg, 88%) were obtained. Mp: 180–184 °C dec.  $^1H$  NMR ( $\delta$  in ppm): 0.19 (s, 18H, SiMe<sub>3</sub>), 0.56 (s, 6H, SiMe<sub>2</sub>), 0.60 (s, 18H, SiMe<sub>3</sub>), 0.62 (s, 6H, SiMe<sub>2</sub>), 1.27 (s, 6H, CH<sub>3</sub>C), 3.46 (s, 6H, CH<sub>3</sub>N).  $^{13}C$  NMR ( $\delta$  in ppm): 0.2 (SiMeSiMe), 0.8 (SiMeSiMe), 4.4 (SiMe<sub>3</sub>), 4.8 (SiMe<sub>3</sub>), 8.3 (MeC), 36.5 (MeN), 105.3 (MeC), 175.6 (NCN).  $^{29}Si$  NMR ( $\delta$  in ppm): -2.8 (SiMe<sub>3</sub>), -3.9 (SiMe<sub>3</sub>), -13.2 (SiMe<sub>2</sub>). Anal. Calcd for  $C_{23}H_{60}GeN_2Si_8$  (751.17): C, 36.78; H, 8.05; N, 3.75. Found: C, 36.90; H, 7.85; N, 7.46. UV absorption:  $\lambda_1$  278 nm (shoulder) ( $\epsilon_1 = 2.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ),  $\lambda_2$  371 nm ( $\epsilon_2 = 3.9 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ).

## ■ ASSOCIATED CONTENT

### Supporting Information

CIF files, tables, and figures giving crystallographic data for compounds **2**, **2a**, **5**, **5a**, **6**, and **6a** as well as details of the theoretical study. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### Notes

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