



## 1,2-Insertion Reactions of Alkynes into Ge–C Bonds of Arylbromogermylene

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## ARTICLE

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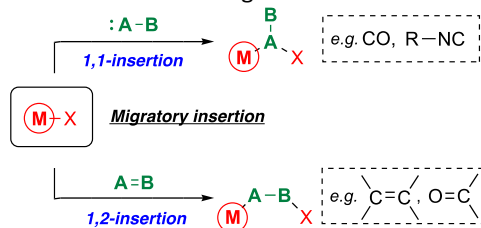
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*1,2-Insertion reactions of alkynes into the Ge–C bonds in dibromodigermenes afford stable crystalline bromovinylgermylenes. In contrast to previously reported Lewis-base-supported vinylgermylenes, the bromovinylgermylene obtained from reaction of the bromogermylene with 3-hexyne via such an 1,2-insertion is a donor-free monomer. A feasible reaction mechanism, proposed on the basis of the observed experimental results in combination with theoretical calculations, suggests that the [1+2]-cycloadduct and the insertion product are the kinetic and thermodynamic product, respectively.*

### Introduction

Transition metals such as palladium and rhodium exhibit ligand-dependent oxidation states, which enables the facile catalytic transformation of small inert molecules such as CO or C<sub>2</sub>H<sub>4</sub>.<sup>1</sup> Representative reactions in this area include insertion reactions of an organic π-bond into M–X bonds (M = transition metal; X = halogen or organic group) bonds. These so-called migratory insertions are attractive, as they simultaneously create two new σ-bonds.<sup>2</sup> The insertion of the A=B π-bond of a small inert molecule into the M–X bond of a transition-metal complex to afford the *cis*-product M–(AB)–X proceeds *via* two predominant pathways of insertion: (i) 1,1-insertion and (ii) 1,2-insertion (Chart 1). In case of the former (*e.g.* AB = CO), M and X end up on the same atom of AB, while in case of the latter (*e.g.* AB = C<sub>2</sub>H<sub>4</sub>), M and X are attached to adjacent atoms. Especially, the 1,2-insertion of alkenes into M–R (R = H or organic group) bonds, which leads to the corresponding alkylated metal species, represents a key step in a variety of

catalytic reactions such as the Mizoroki-Heck reaction.<sup>3,4</sup> Therefore, the reaction mechanism of such 1,2-insertion reactions has been well investigated.<sup>5</sup>



**Chart 1.** Migratory insertion reactions (M = transition metal; X = *e.g.* H, alkyl, or aryl; AB = small molecule with an AB multiple bond).

Recent developments in the area of main-group-element chemistry have allowed using low-coordinated heavier group-14 elements instead of transition-metal complexes to activate unsaturated small molecules.<sup>6,7</sup> Furthermore, isolable low-coordinated compounds of heavier group 14 elements, such as π-bonding species (>E=E< or E≡E, E = Si, Ge, Sn, Pb) and tetrylene species (>E:), were found to engage in migratory insertion reactions into their E–H or E–X (X = heteroatom) bonds in the absence of any transition metal.<sup>8–16</sup> For example, Roesky and co-workers have reported remarkable 1,2-additions of unsaturated molecules such as alkynes and CO<sub>2</sub> to the E–H bonds of Ge<sup>II</sup>/Sn<sup>II</sup> hydrides.<sup>10</sup> The groups of Jones<sup>11</sup> and Power<sup>12</sup> have independently reported reactions of 1,2-dihydrodigermenes with olefins, yielding the corresponding 1,2-insertion products. Power *et al.* have demonstrated a C–H bond metathesis including a stannylene, which could be considered as a 1,2-insertion of a C–H bond into a Sn–C bond.<sup>13</sup> Overall, such insertions into E<sup>II</sup>–H (E = Ge or Sn) bonds exhibit a reactivity akin to that of transition metals. In contrast to the cases of such insertion reactions into a E–heteroatom

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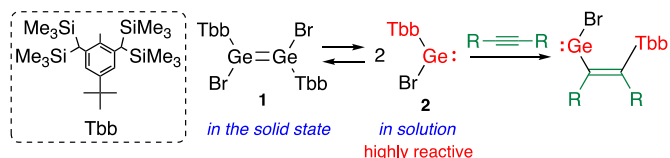
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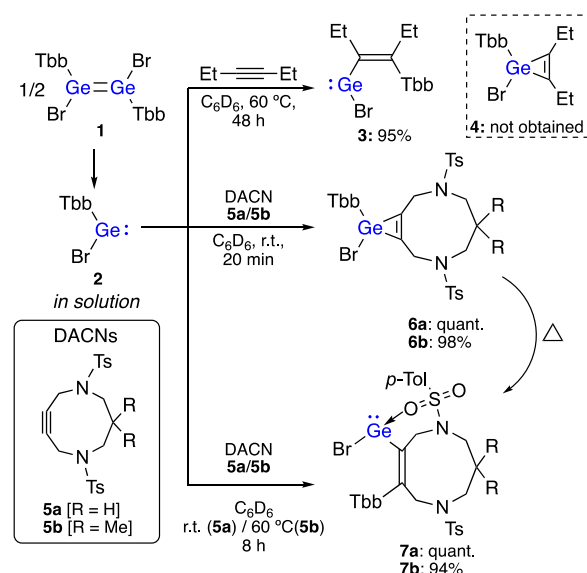
bond (E = heavier group-14 elements),<sup>14,15</sup> the 1,2-insertion of molecules with CC multiple bonds into E–C bonds remains rare,<sup>16</sup> even though 1,2-insertions of CC multiple bonds into a carbon-transition metal bond should be of great importance in synthetic organic and polymer chemistry. Although theoretical calculations have suggested that the 1,2-insertion reactions of alkynes into the Ge–C bond of Me<sub>2</sub>Ge: could preferably occur for vinylgermylenes,<sup>17</sup> several reactions of stable tetrylenes with alkynes have furnished the corresponding [1+2]-cycloadducts, *i.e.*, stable germirenes.<sup>9,18</sup> Herein, we report the reactions of alkynes with a stable bromogermylene, Tbb(Br)Ge: (**2**, Tbb = 2,6-bis[CH(SiMe<sub>3</sub>)<sub>2</sub>]-4-*t*-butylphenyl),<sup>19</sup> generated from the corresponding dibromodigermene **1** in solution (Scheme 1). These reactions afford the corresponding bromovinylgermylenes *via* an 1,2-insertion of alkynes into the Ge–C(aryl group) bond of an *in situ* generated bromogermylene **2**. Our experimental and theoretical investigations clearly demonstrate that in such reactions between a germylene with an alkyne, the corresponding vinylbromogermylene and germirene represent the thermodynamic and kinetic controlled product, respectively.



**Scheme 1.** A 1,2-Insertion reaction of alkynes into a Ge–C(aryl) bond of the *in situ*-generated bromogermylene.

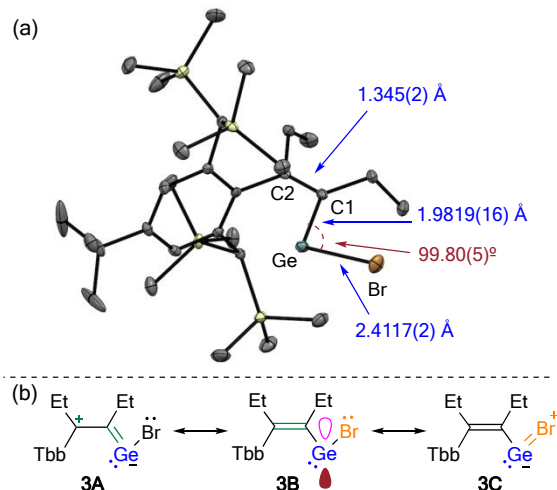
## Results and Discussion

The treatment of a C<sub>6</sub>D<sub>6</sub> solution of bromogermylene **2**,<sup>19</sup> which was generated from dibromodigermene **1** as an equilibrium state in solution, with 3-hexyne at 60 °C afforded the insertion product, *i.e.*, bromovinylgermylene **3** in 95% yield (Scheme 2). It should be noted that the expected product, germirene **4**, was not obtained under these conditions. Bromovinylgermylene **3** exhibits excellent thermal stability in the crystalline state (mp. 129.4 °C) as well as in benzene upon heating to 80 °C under an inert atmosphere.<sup>20–22</sup>



**Scheme 2.** Insertion reactions of alkynes with bromogermylene **2** (Tbb = 2,6-[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>-4-*t*-butyl-phenyl).

The C–C bond formation *via* the cleavage of the Ge–C(Tbb) bond in **2** should proceed in an analogous manner to that of transition-metal complexes, which engage in  $\sigma$ -bond metathesis that leads to the insertion products.<sup>5</sup> In contrast to Power's reports,<sup>16</sup> which demonstrated facile 1,1-insertion reactions at room temperature for CO and MeNC into the Ge–C bond of a stable diarylgermylene, the reaction of **2** with 3-hexyne required long reaction times and heating to elevated temperatures. In addition, **1/2** is inert toward CO at room temperature, probably due to the low electrophilicity of bromogermylene **2**, which may arise from the resonance effect of the lone pair at the bromine atom.

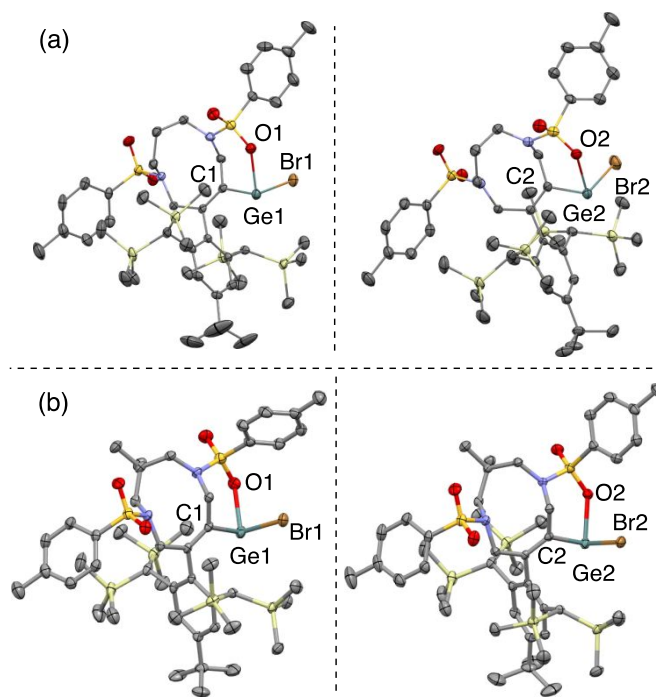


**Figure 1.** (a) Molecular structure of bromovinylgermylene **3** (ORTEP with thermal ellipsoids at 50% probability); hydrogen atoms and solvent molecules are omitted for clarity. (b) Resonance structures of **3**.

An X-ray crystallographic analysis of bromovinylgermylene **3** (Figure 1) revealed a monomeric structure in the crystalline state, evident from the long distance between the closest Ge

atoms ( $> 10 \text{ \AA}$ ).<sup>23</sup> The Ge–C bond in **3** [1.9819(16)  $\text{\AA}$ ] is shorter than those in previously reported diarylgermylenes [2.020(2)–2.053(4)  $\text{\AA}$ ],<sup>24</sup> and longer than that of the previously reported divinylgermylene<sup>22b</sup> [1.849(4)  $\text{\AA}$ ], while the C1–C2 bond in **3** [1.345(2)  $\text{\AA}$ ] falls within the range of typical C=C double bonds. Although sufficiently similar compounds for an appropriate comparison of the Ge–Br bond of **3** [2.4117(2)  $\text{\AA}$ ] remain elusive, it is slightly shorter than those of  $\text{GeBr}_2(\text{dioxane})$  [2.451(2)  $\text{\AA}$ ].<sup>25</sup> These structural features suggest a considerable  $\pi$ -type electron donation from the C=C  $\pi$ -electrons and the lone pair on the Br atom to the vacant 4p orbital on the Ge atom in **3**, *i.e.*, the contributions of resonance structures **3A**–**3C** are most likely non-negligible (Figure 1b). On the basis of the theoretical calculations, the second-order perturbation energies were estimated, which show a higher effective contribution from the lone pair of the Br atom [15.2 kcal/mol] relative to that from the C=C  $\pi$ -electrons [10.7 kcal/mol].<sup>26–28</sup> Thus, it can be concluded that the contribution from resonance structure **3C** should be expected to be more effective than that of **3A**, which is probably due to favourable size-matching [4p(Ge)–4p(Br) vs. 4p(Ge)– $\pi(\text{C}=\text{C})$ ].

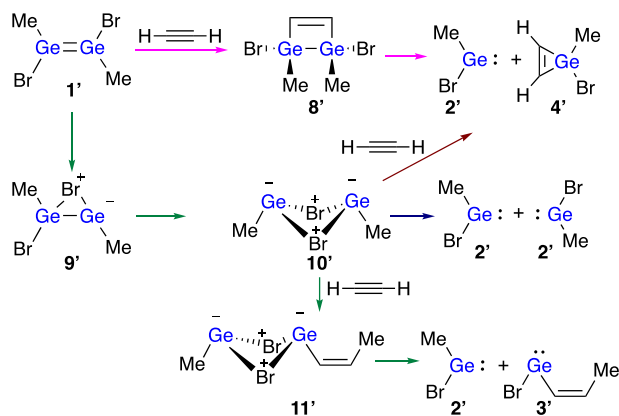
Although the addition reaction between 3-hexyne and dibromodigermene **1**, which resulted in the exclusive formation of **3**, was carefully monitored by  $^1\text{H}$  NMR spectroscopy, any intermediate such as [1+2]-cycloadduct intermediate **4** was not observed. We thought this would be because the high reaction temperature would make the reaction faster. Subsequently, we examined the reaction of **1** with highly reactive cycloalkynes, diazacyclononynes (DACNs) **5a/5b**,<sup>29</sup> with the hope of observing the possible intermediate. As expected, the reaction of **1** with DACNs **5a/5b** in  $\text{C}_6\text{D}_6$  at room temperature resulted in the smooth formation of [1+2]-cycloadducts **6a/6b** as evident from the  $^1\text{H}$  NMR spectra. While germirene **6a** underwent slow isomerization into the insertion product **7a** at room temperature, cycloadduct **6b** was stable at room temperature for at least 24 hours, and quantitatively converted into **7b** only upon heating to 60  $^\circ\text{C}$ . These experimental results suggested that **6a,b** should be considered as the kinetic products, while vinylgermylenes **7a,b** should be the thermodynamic products. The extremely high reactivity of DACNs would make the reaction barriers with germylene **2** lowered enough, resulting the formation of the kinetic products, *i. e.*, germiranes **6a,b**, as observable compounds.



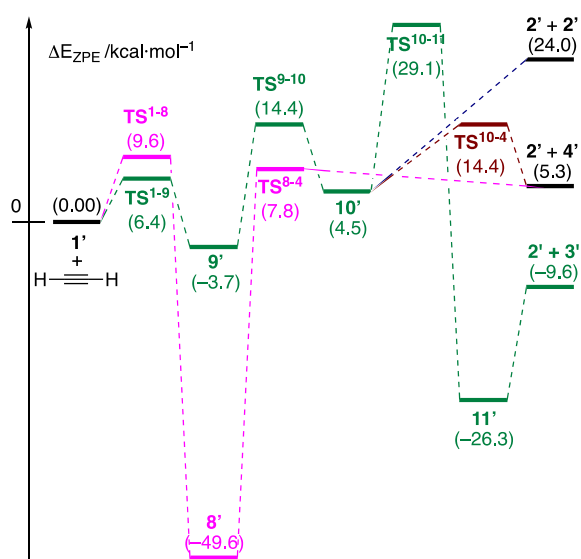
**Figure 2.** Molecular structures of the two independent molecules found in the unit cell of (a) bromovinylgermylene **7a** and (b) bromovinylgermylene **7b** (ORTEP with thermal ellipsoids at 50% probability); hydrogen atoms and solvent molecules are omitted for clarity. Selected structural parameters ( $\text{\AA}$ , deg) (a) **7a**: Ge1–Br1, 2.4285(5); Ge1–C1; 2.001(3); Ge1–O1, 2.203(2); C1–Ge1–Br1, 95.80(9); Ge2–Br2, 2.4316(5); Ge2–C2; 1.996(3); Ge2–O2, 2.231(2); C2–Ge2–Br2, 96.42(9). (b) **7b**: Ge1–Br1, 2.4331(4); Ge1–C1; 2.005(2); Ge1–O1, 2.2281(16); C1–Ge1–Br1, 96.96(6); Ge2–Br2, 2.4307(3); Ge2–C2; 1.9998(19); Ge2–O2, 2.2123(14); C2–Ge2–Br2, 95.43(5).

As in the case of **3**, XRD analysis of **7a,b** showed they exhibit monomeric structures similar to each other (Figure 2).<sup>23b</sup> Notably, in both cases of **7a** and **7b**, the short Ge–O distances (2.20–2.23  $\text{\AA}$ ) suggested the effective intramolecular coordination from the O atoms towards the central Ge atoms. The second-order perturbation energies of the lone pair orbital of the O atom towards the vacant p-orbital of the Ge atom were estimated as 77.6 (**7a**) and 75.9 kcal/mol (**7b**) based on the NBO calculations.<sup>26,27</sup>

In order to better understand the reaction mechanism, the potential energy surface (PES) was computed with the simplified models containing methyl groups instead of Tbb groups (Scheme 3 and Figure 3).<sup>26,30</sup> Although the Ge=Ge bond of 1,2-dibromodigermene **1** is known to be cleaved to give germylene **2** in solution,<sup>31,32</sup> the possibility that unexpected intermediates other than germirene **4** could be generated by direct reaction of digermene **1** with acetylene could not be fully excluded. Thus, the reaction starting from model dibromodigermene **1'** was explored computationally.



**Scheme 3.** Proposed mechanisms for the reaction of dibromodimethyldigermene **1'** with acetylene giving bromomethylgermylene **2'**, bromovinylgermylene **3'**, and bromomethylgermirene **4'**.

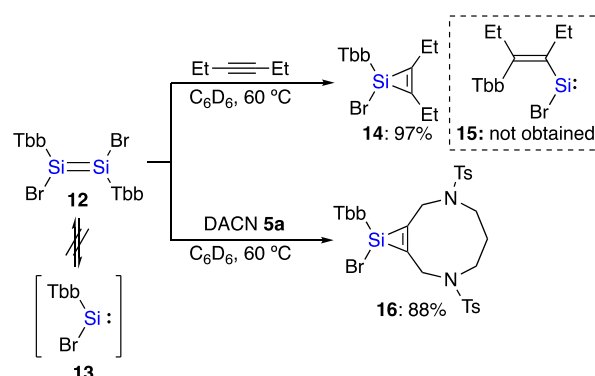


**Figure 3.** Calculated zero-point energy-corrected relative energies ( $\Delta E_{\text{ZPE}}$ ) for the reactions of **1'** with acetylene.<sup>30</sup>

As [2+2] cycloadditions of digermenes with alkynes is a general type of reactivity,<sup>33</sup> in this particular model cases, a low barrier ( $\Delta E_{\text{ZPE}}^{\ddagger} = 9.6$  kcal/mol) highly exothermic ( $\Delta E_{\text{ZPE}} = 49.6$  kcal/mol) access to 1,2-digermacyclobutene **8'** by direct reaction of **1'** with acetylene (pink lines in Figure 3) has been provided. The remarkable stability of intermediate **8'** prevents its reductive elimination of **2'** to afford bromomethylgermirene **4'**, which is a high barrier ( $\Delta E_{\text{ZPE}}^{\ddagger} = 57.4$  kcal/mol) and very endothermic ( $\Delta E_{\text{ZPE}}^{\ddagger} = 55.0$  kcal/mol) process, not sufficiently compensated even by the exothermicity of further reactions of **2'** (*vide infra*). Moreover, it should be noted that no pathway was found from **8'** to give bromovinylgermylene **3'**. An alternative to the dissociation pathway of dibromodigermene **1'** into two bromogermylene units (**2'**) prior to reaction with acetylene reagents entails the initial conversion into di( $\mu^2$ -bromo)digermylene **10'** (green lines in Figure 3). The transformation occurs by sequential approach of every bromine atom to the originally non-bonded

germanium centre in a two-step process through the bromine-bridged intermediate **9'**.<sup>34</sup> The first step is slightly exergonic and kinetically favoured compared to formation of digermacyclobutene **8'**, as it takes place through a low-lying transition state (TS) ( $\Delta E_{\text{ZPE}}^{\ddagger} = 6.4$  kcal/mol). Compound **10'** can split endergonically ( $\Delta E_{\text{ZPE}} = 19.5$  kcal/mol) affording two units of bromogermylene **2'** in a barrierless process (green and blue lines in Figure 3). From these results, it can be concluded that dibromodigermene **1'** should preferentially exist as the zwitterionic bromadigermirane **9'** that can, in turn, serve as source for bromogermylene **2'**. Alternatively, **10'** can react endothermically ( $\Delta E_{\text{ZPE}} = 0.8$  kcal/mol) with acetylene yielding the [1+2]cycloadduct **4'**, as kinetic control product along with loss of **2'**, with a barrier of 9.9 kcal/mol (green and red lines in Figure 3). Conversely, compound **10'** could also react exothermically with acetylene ( $\Delta E_{\text{ZPE}} = -21.8$  kcal/mol) to give the thermodynamic product **11'** *via* Ge-C insertion, which could undergo barrierless dissociation to give the final insertion product **3'** along with **2'** (green lines in Figure 3). Thus, theoretical calculations support the intermediacy of **10'**, generated *via* bromine-migrations from digermene **1'**, in the reaction with acetylene to give germirene **4'** or vinylgermylene **3'** with reasonable barriers as a kinetic or thermodynamic product, respectively. Both accesses to **4'** and **3'** are accompanied with generation of bromogermylene **2'**, which can also be formed directly from digermene **1'**. Thus, the reaction of **2'** with acetylene should be the key reaction.

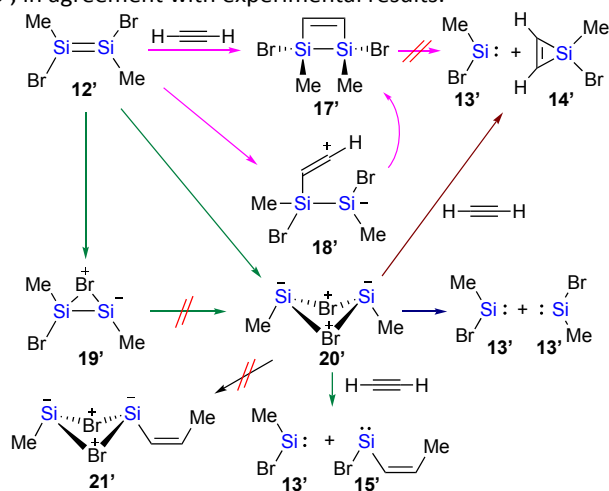
For a comparison with silicon-based analogues, we examined the reactions between dibromodisilene **12**<sup>35</sup> with dialkylalkynes. In contrast to the Ge cases, treatment of dibromodisilene **12** at 60 °C with alkynes resulted in the formation of 3-membered-ring products **14/16** in high yield *via* a [1+2]-cycloaddition without any isolation of vinylsilylene **15** (Scheme 4). This is consistent with previously reported reactions between stable dibromodisilenes and alkynes.<sup>35</sup> As there is no spectroscopic evidence for the cleavage of the Si=Si bond of **12** giving silylene **13**,<sup>32,36</sup> silirenes **14** and **16** could possibly be formed by the direct reaction of disilene **12** or a chemical equivalent of synthon **13** with alkynes.



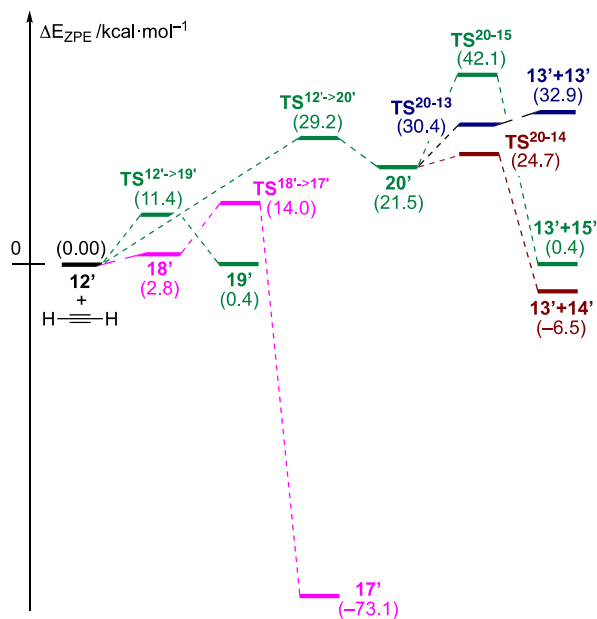
**Scheme 4.** Reactions of dibromodisilene **12** with dialkylalkynes.

As in the Ge-cases, the potential energy surface (PES) was computed with the simplified models containing methyl instead of Tbb groups (Scheme 5 and Figure 4).<sup>30</sup>

Contrary to the Ge-analogue, the [2+2]cycloaddition of model disilene **12'** with acetylene giving 1,2-disilacyclobutene **17'** is not a concerted but a stepwise process *via* an almost barrierless formed intermediate **18'**; cyclization to **17'** is a highly exothermic ( $\Delta E_{\text{ZPE}}^{\ddagger} = -73.1$  kcal/mol) process with an activation barrier of  $\Delta E_{\text{ZPE}}^{\ddagger} = 11.2$  kcal/mol (pink lines in Figure 4). Again, in contrast to the Ge-cases, bromosilylene **13'** and bromosilirene **14'** are not accessible from **17'** *via* reductive elimination, most likely due to its remarkably high stability (compared to **8'**). Dibromodisilene **12'** can undergo bromine-bridging transformation to give di( $\mu^2$ -bromo)disilylene **20'** (green lines in Figure 4), the rate-determining second step displaying larger barrier ( $\Delta E_{\text{ZPE}}^{\ddagger} = 29.2$  kcal/mol) than in the Ge-case (**1'** $\rightarrow$ **10'**). In contrast to Ge-case, di( $\mu^2$ -bromo)disilylene **20'** is not formed via mono-Br-bridging intermediate **19'** but directly from **12'**. In addition, the insertion product of acetylene into the Si-Me bond (**21'**) could not be reached from **20'**, which is different from the Ge-cases. Instead, bromovinylsilylene **15'** is exothermically formed ( $\Delta E_{\text{ZPE}} = -21.1$  kcal/mol) along with elimination of silylene **13'**, though the barrier is relatively high ( $\Delta E_{\text{ZPE}}^{\ddagger} = 20.6$  kcal/mol) (green lines in Figure 4). The endothermic ( $\Delta E_{\text{ZPE}} = 11.4$  kcal/mol) dissociation of **20'** giving two molecules of silylene **13'** is also possible (blue lines in Figure 4).<sup>26</sup> Conversely, the reaction of **20'** with acetylene exothermically affords bromosilirene **14'** and bromosilylene **13'** ( $\Delta E_{\text{ZPE}} = -28.0$  kcal/mol) as the lowest barrier and therefore kinetically favoured process ( $\Delta E_{\text{ZPE}}^{\ddagger} = 3.2$  kcal/mol), (red lines in Figure 4). Thus, it can be concluded that in the reaction of dibromodisilene **12'** with acetylene bromosilirene **14'** is expected to be preferentially formed *via* di( $\mu^2$ -bromo)disilylene **20'**, compared to bromovinylsilylene **15'**, in agreement with experimental results.



**Scheme 5.** Proposed mechanistic pathways for the reaction of dibromodimethyldisilene **12'** with acetylene giving bromomethylgermylene **13'**, bromovinylgermylene **15'**, and bromomethylgermyrene **14'**.

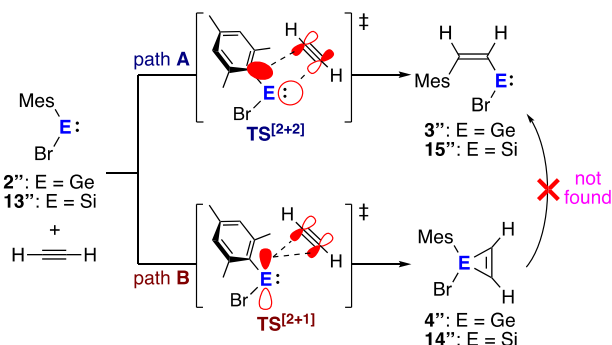


**Figure 4.** Calculated zero-point energy-corrected relative energies ( $\Delta E_{\text{ZPE}}$ ) for the reactions of **12'** with acetylene.<sup>30</sup>

It is worth mentioning that despite [2+2]cycloadducts of dibromodigermenes **1'** and dibromodisilenes **12'** with alkynes (**8'** and **17'**) turned out to be the thermodynamically most stable products in case of Me-substituted model compounds, such [2+2]cycloadduct-products were never experimentally obtained, probably owing to steric reasons, especially in case of the more congested disilacyclobutene **17**, due to the shorter Si-Si bond distance. The lower steric crowding in digermacyclobutene **8** would be supplemented by its kinetically unfavoured formation compared to the competitive bromine atoms migration in less bulky model compounds.

As described above, access to metallirenes **2'/14'** and vinylmetallylenes **3'/15'** are accompanied with generation of bromometallylenes **2'/13'**, the latter being also directly accessible from dimetallenes **1'/12'** by dissociation of the corresponding di( $\mu^2$ -bromo)dimetallylene isomers **10'/20'**. Therefore, the reaction of acetylenes with highly reactive bromometallylenes **2'/13'** should be a key reaction pathway and it is worth investigating these reactions in detail. Further calculations were performed using more crowded Mes-substituted model compounds, which are much closer to the real systems (Scheme 6 and Figure 5). Two pathways were found in the PES for the reaction of mesityl-bromometallylenes **2''/13''** with acetylene<sup>26,30</sup> (Scheme 6, both starting by formation of a van der Waals complex (**2''**·HCCH, **13''**·HCCH) between the basic C≡C  $\pi$ -bond and the acidic vacant p orbital of the metallylene moieties. In the Ge-case, the fastest path turned out to be the chelotropic [2+1] cycloaddition (path **B**,  $\Delta E_{\text{ZPE}}^{\ddagger} = 6.7$  kcal/mol) leading to the exothermic formation of germirene **4''** ( $\Delta E_{\text{ZPE}} = -10.2$  kcal/mol). This reaction arises from the nucleophilic interaction between the alkyne and the predominantly Ge atom-located LUMO of **2''**. In contrast, path **A** corresponds to an alkyne insertion into the Ge-C bond, resulting from the interaction between the  $\pi^*(\text{C}\equiv\text{C})$ -type LUMO of acetylene and the HOMO of germylene. The later

consists of a combination of a tilted *p*-type AO at the ipso-C atom of the Mes group with the *sp*-type AO at the Ge atom (Scheme 6). According to our calculations, this is a concerted reaction occurring through a slightly higher, yet low-lying transition state ( $\Delta E_{\text{ZPE}}^{\ddagger} = 10.3$  kcal/mol), affording the insertion product, *i.e.*, vinylgermylene **3''**, in a highly exothermic process ( $\Delta E_{\text{ZPE}}^{\ddagger} = -35.6$  kcal/mol). Thus, the alkyne insertion constitutes a one-step, thermodynamically controlled pathway (path **B**), whereas the competing chelotropic reaction gives rise to the kinetically controlled 1,2-insertion product **4''**. The estimated reaction barriers ( $\Delta E_{\text{ZPE}}^{\ddagger}$ ) for the formation of **4''** (forward: 6.7 kcal/mol; reverse: 16.9 kcal/mol) suggest a reversible reaction between **2''** and acetylene at room temperature.<sup>37</sup> This is partly due to the high ring-strain energy (RSE) of the germirene [GeC<sub>2</sub>] ring in **4''**, according to the value of 44.4 kcal/mol for the H-substituted compound,<sup>38</sup> obtained from evaluation of accurate homodesmotic reactions.<sup>39</sup> The barrier ( $\Delta E_{\text{ZPE}}^{\ddagger}$ ) for the formation of the thermodynamic product **3''** is larger (10.3 kcal/mol) than that for kinetic product **4''**, and the extremely high barrier (45.9 kcal/mol) from **3''** to **2''** prevents the backward reaction.



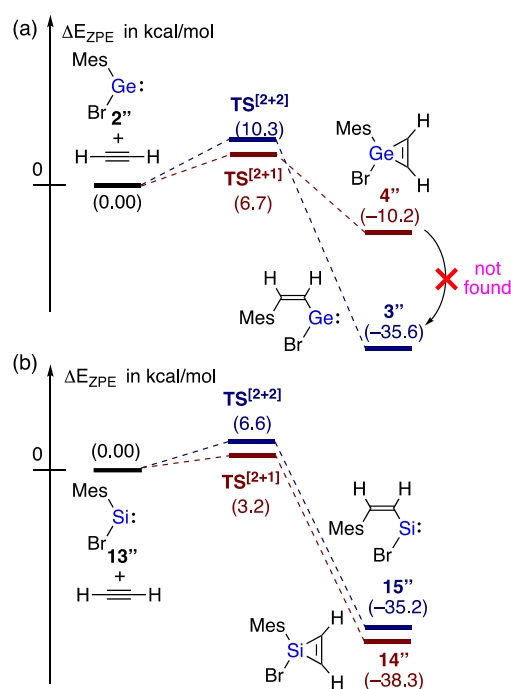
**Scheme 6.** Proposed mechanism for the reaction of mesitylbromometallylenes **2''** (E = Ge) and **13''** (E = Si) with acetylene.

Conversely, Mes-substituted bromosilylene **13''** reacts with acetylene preferentially furnishing silirene **14'** both kinetically ( $\Delta E_{\text{ZPE}}^{\ddagger} = 3.2$  kcal/mol) and thermodynamically ( $\Delta E_{\text{ZPE}} = -38.3$  kcal/mol) compared to vinylsilylene **15''** ( $\Delta E_{\text{ZPE}}^{\ddagger} = 6.6$  kcal/mol;  $\Delta E_{\text{ZPE}} = -35.2$  kcal/mol). The significantly smaller RSE of H-substituted 1*H*-silirene (40.6 kcal/mol) relative to that of 1*H*-germirene (*vide supra*)<sup>37</sup> could explain the most favoured formation of the former compared to the later.

In addition, further DFT calculations for the reaction of a bromogermylene with acetylene were carried in order to locate both pathways with real molecules.<sup>40</sup> Paralleling the above mentioned results for model compounds, the formation of **3** from the reaction between **2** and 3-hexyne is highly exergonic ( $\Delta E_{\text{ZPE}}^{\ddagger} = -22.6$  kcal/mol) with a slightly higher activation barrier ( $\Delta E_{\text{ZPE}}^{\ddagger} = 8.0$  kcal/mol), while germirene **4** would be formed less exergonically ( $\Delta E_{\text{ZPE}}^{\ddagger} = -6.9$  kcal/mol) with a lower barrier ( $\Delta E_{\text{ZPE}}^{\ddagger} = 6.8$  kcal/mol). These theoretical results are consistent with previously reported results on the reaction between a H-substituted germylene and acetylene,<sup>17</sup> thus reasonably explaining the experimentally observed results

of the formation of **3**, **6** and **7** (Scheme 2). It is worth mentioning that for both models (methyl- or mesityl-substituted) and real systems the direct transformation pathway from germirene **4/4'/4''** to vinylgermylene **3/3'/3''** was not found in the PESs.

Based on these theoretical results, it can be concluded that bromovinylgermylene **3/3'/3''** is a thermodynamic product, while germirene **4/4'/4''** is a kinetic product in the reaction of bromogermylene **2/2'/2''** with acetylene. Opposite to the bromogermylene reactivity, silirene **14''** were found to be the most favourable products both kinetically and thermodynamically in the reaction of bromosilylene **12''** with acetylene.



**Figure 5.** Calculated zero-point energy-corrected relative energies ( $\Delta E_{\text{ZPE}}$ ) for the reaction of (a) **2''** and (b) **13''** with acetylene.<sup>30</sup>

## Conclusions

We have presented the synthesis of monomeric bromovinylgermylenes **3** and **7** *via* the 1,2-insertion of alkynes into the Ge–C bond of dibromodigermene **1** or bromogermylene **2**, which proceeds in an analogous manner to those of transition-metal complexes including *e.g.* Pd or Rh. Our theoretical calculations and experimental results indicate that bromovinylgermylenes **3/3'/3''** are thermodynamic control products, while germirenes **4/4'/4''** are the kinetic control products in all cases, irrespective of starting from a dibromodigermene (*via* di( $\mu^2$ -bromo)digermylene intermediate) or a bromogermylene. In contrast, silirenes **14/14'/14''** were found to be the most favourable products both kinetically and thermodynamically in the reaction of the dibromodisilene **12/12'/12''** with alkynes.

## Conflicts of interest

There are no conflicts to declare.

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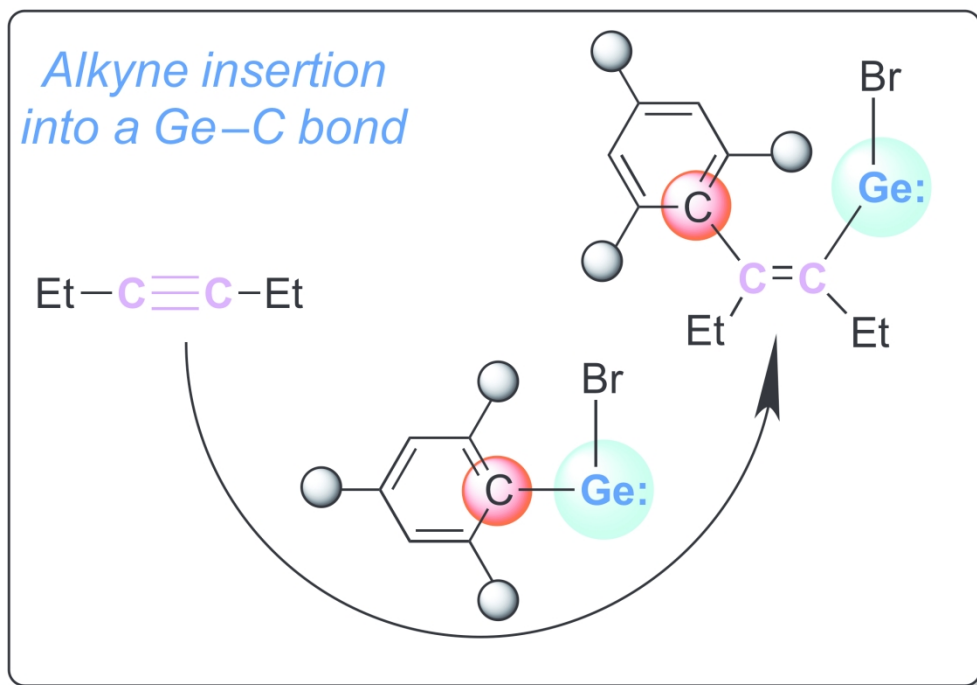
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100x70mm (602 x 600 DPI)