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## Reaction of a diaryldigermynes with ethylene†

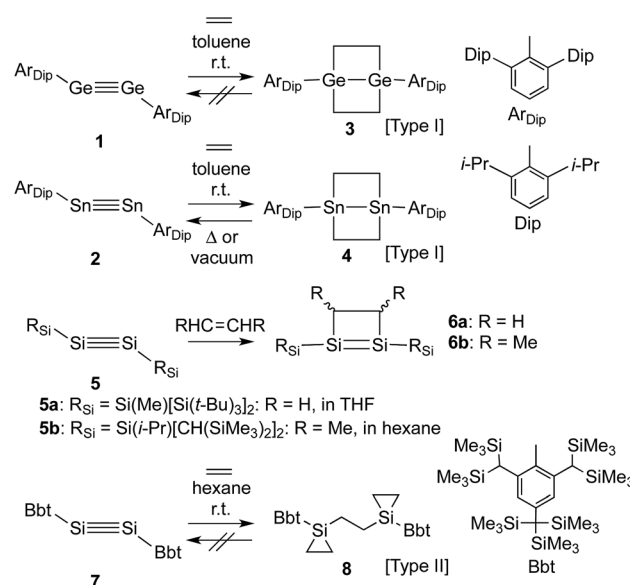
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Reaction of the stable digermynes BbtGe≡GeBbt (Bbt = 2,6-[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>-4-[C(SiMe<sub>3</sub>)<sub>3</sub>]-C<sub>6</sub>H<sub>2</sub>) with ethylene initially afforded the corresponding 1,2-digermacyclobutene. Depending on the reaction conditions applied, further reaction of this 1,2-digermacyclobutene with ethylene furnished two different reaction products: a 1,4-digermabicyclo[2.2.0]hexane or a bis(germiranyl)ethane. Combined experimental and theoretical results suggested that the 1,4-digermabicyclo[2.2.0]hexane and the bis(germiranyl)ethane are the thermodynamic and kinetic reaction products, respectively. A reaction mechanism in agreement with these results was proposed.

Control over the modification of olefin groups is important in organic synthesis, as a variety of preparative methods for the introduction of functional groups start from C–C multiple bonds. Even though several olefin addition reactions, such as hydrosilylation,<sup>1</sup> hydroboration<sup>2</sup> and olefin polymerisation,<sup>3</sup> are well established, the use of transition metal catalysts is required in many cases. However, divalent or multiple-bonded compounds of heavier group 14 elements have recently received much attention as potential transition metal-free catalysts.<sup>4</sup> These compounds generally react with olefins or other compounds that have carbon-containing multiple bonds to form the corresponding cycloadducts, tantamount to a strong propensity to activate small inert molecules. Unfortunately, low-coordinate species of heavier main group elements are usually difficult to isolate, mostly due to their inherently high reactivity towards addition reactions involving atmospheric moisture and/or aerobic oxygen and self-oligomerisation. Nevertheless, these compounds can be isolated while retaining their characteristic reactivity when sterically demanding substituents are used to provide kinetic stabilisation.<sup>5</sup> Power and co-workers have, for example, reported the isolation of the heavier acetylene analogues Ar<sub>Dip</sub>Ge≡GeAr<sub>Dip</sub> (**1**)<sup>6</sup> and Ar<sub>Dip</sub>Sn≡SnAr<sub>Dip</sub> (**2**)<sup>7</sup> as stable compounds. The reactions of **1** and **2** with ethylene proceed smoothly in the absence of any transition metal catalyst at room temperature to afford the corresponding 4-membered cycloadducts **3** and **4** (Type I; Scheme 1).<sup>8,9</sup> Subsequently, **4** is able to undergo a thermal retro-cycloaddition to generate **2**, concomitant with the release of two molecules of ethylene.

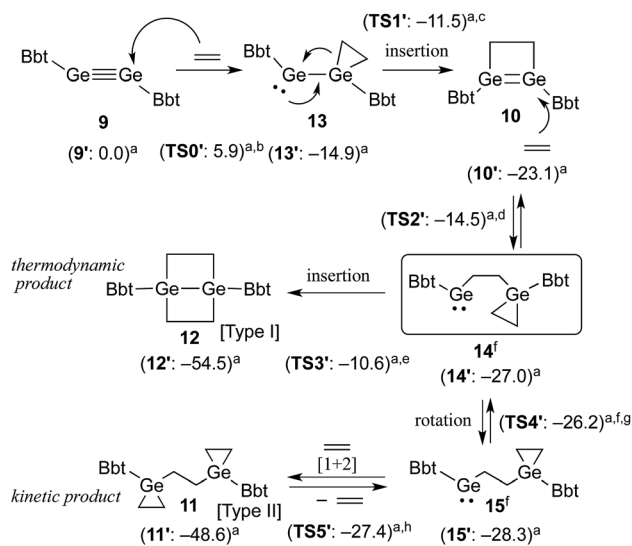
Accordingly, distannyne **2** can, in contrast to digermynes **1**, be considered as an ethylene-storage molecule. In this context, the reaction of a comparable disilyne with ethylene should also be of great interest. Independently, the groups of Wiberg and Sekiguchi have reported the stereoselective [2+2] cycloaddition of stable disilynes **5a,b** (R<sub>Si</sub>Si≡SiR<sub>Si</sub>; **5a**: R<sub>Si</sub> = Si(Me)[Si(*t*-Bu)<sub>3</sub>]<sub>2</sub>,<sup>10</sup> **5b**: R<sub>Si</sub> = Si[CH(SiMe<sub>3</sub>)<sub>2</sub>](*i*-Pr)<sup>11</sup>) with alkenes (RHC=CHR) to afford disilenes **6a,b** (**6a**: R = H, **6b**: R = Me).<sup>10,12</sup> However, neither the further reaction of **6a,b** with ethylene, nor any possible retro-reaction were reported.

Previously, we have reported the synthesis of the stable diaryldisilyne BbtSi≡SiBbt (**7**, Bbt = 2,6-[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>-4-[C(SiMe<sub>3</sub>)<sub>3</sub>]-C<sub>6</sub>H<sub>2</sub>).<sup>13</sup> The reaction of **7** with ethylene resulted in the unexpected formation of **8** (Type II; Scheme 1), containing

Scheme 1 Reactions of dimetallynes **1**, **2**, **5** and **7** with ethylene.<sup>a</sup>Institute for Chemical Research, Kyoto University, Gokasho Uji, Kyoto 611-0011, Japan. E-mail: sasamori@boc.kuicr.kyoto-u.ac.jp<sup>b</sup>Fukui Institute for Fundamental Chemistry, Kyoto University, Kyoto 606-8103, Japan† Electronic supplementary information (ESI) available: experimental and computational details, as well as X-ray crystallographic data for **10**–**12** are available. CCDC 1054594–1054596. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5sc01266j

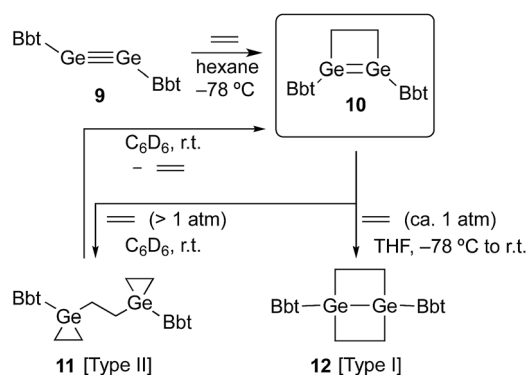
two silacyclopropane moieties. Compound **8** was found to be remarkably stable, as decomposition of these silacyclopropane moieties was not observed, even upon heating.<sup>14</sup> Subsequently, we began to investigate the reactivity difference between diaryldisilynes and diaryldigermynes. Herein, we report the reaction of the stable diaryldigermine  $\text{BbtGe}\equiv\text{GeBbt}$  (**9**)<sup>15</sup> with ethylene to afford the corresponding 1,2-digermacyclobutene (**10**), which is the formal [2+2] cycloadduct of **9**. Depending on the reaction conditions, further treatment of **10** with ethylene resulted in the formation of two products, specifically a four-membered cycloadduct (**12**, Type I; Scheme 2) and a three-membered cycloadduct (**11**, Type II; Scheme 2).

A hexane solution of digermine **9** was frozen ( $-196\text{ }^\circ\text{C}$ ) and degassed in a J-Young tube, before being charged with ethylene.<sup>16</sup> The colour of the solution changed from dark red to purple. Removal of the solvent from the reaction mixture afforded 1,2-digermacyclobutene **10**. The formation of **10** from the reaction of digermine **9** with ethylene can be explained by the same mechanism used to describe the reaction of disilynes with olefins:<sup>12</sup> initially, interaction between ethylene and one of the Ge atoms in the  $\text{Ge}\equiv\text{Ge}$  bond generates germirane-substituted germylene **13** as an intermediate,<sup>17</sup> which subsequently inserts intramolecularly into the Ge–C bond of the germirane moiety (Scheme 3). X-ray crystallographic analysis of **10** revealed a non-planar structure for the four-membered  $\text{Ge}=\text{Ge}-\text{C}-\text{C}$  ring (Fig. 1).<sup>18</sup> The two Bbt groups were found to be oriented in opposite directions, resulting in a *trans*-bent geometry for the  $\text{Ge}=\text{Ge}$  moiety with *trans*-bent angles of  $39.5^\circ$  (Ge1) and  $39.7^\circ$  (Ge2). A  $\text{Ge}=\text{Ge}$  bond length of  $2.4132(5)\text{ \AA}$  was observed, which is slightly shorter than a typical  $\text{Ge}-\text{Ge}$  single bond (*ca.*  $2.44\text{ \AA}$ ),<sup>19</sup> but consistent with previously reported  $\text{Ge}=\text{Ge}$  double bonds in digermenes (*ca.*  $2.2\text{--}2.5\text{ \AA}$ ).<sup>19</sup> These structural features suggested that the  $\text{Ge}=\text{Ge}$  double bond in **10** should be weakened by the severe intrinsic strain of the four-membered  $\text{Ge}=\text{Ge}-\text{C}-\text{C}$  ring and the highly *trans*-bent geometry. The  $^1\text{H}$  NMR spectrum of **10** exhibited signals commensurate with two identical Bbt groups, as well as signals consistent with two equivalent  $\text{SiMe}_3$  groups at the *ortho*-positions of the Bbt groups, thus confirming a fast inversion of the *trans*-bent geometry of the  $\text{Ge}=\text{Ge}$  bond in **10** in solution.



Scheme 3 Proposed mechanism for the reaction of **9** with ethylene. (a) Calculated relative energies ( $\text{kcal mol}^{-1}$ ) for model compounds bearing 2,6- $[\text{CH}(\text{SiMe}_3)_2]_2\text{-C}_6\text{H}_3$  (Bbp) groups instead of Bbt groups. (b)  $\Delta E^\ddagger$  ( $9\text{--}13'$ ) =  $5.9\text{ kcal mol}^{-1}$ . (c)  $\Delta E^\ddagger$  ( $13'\text{--}10'$ ) =  $3.4\text{ kcal mol}^{-1}$ . (d)  $\Delta E^\ddagger$  ( $10'\text{--}14'$ ) =  $8.6\text{ kcal mol}^{-1}$ . (e)  $\Delta E^\ddagger$  ( $14'\text{--}12'$ ) =  $16.4\text{ kcal mol}^{-1}$ . (f) **14** and **15** are rotational isomers with respect to a rotation around the central  $\text{GeH}_2\text{C}-\text{CH}_2\text{Ge}$  bond. (g)  $\Delta E^\ddagger$  ( $14'\text{--}15'$ ) =  $0.8\text{ kcal mol}^{-1}$ . (h)  $\Delta E^\ddagger$  ( $15'\text{--}11'$ ) =  $0.9\text{ kcal mol}^{-1}$ .

In order to induce a further reaction of **10** with a second molecule of the alkene, ethylene was condensed into a sealed vessel, which contained a frozen and degassed  $\text{C}_6\text{D}_6$  solution of **10** at  $-196\text{ }^\circ\text{C}$ . Subsequently, the reaction mixture was allowed to warm to r.t. in this sealed tube, and based on the volume of the tube, **10** was treated with an excess of ethylene (*ca.*  $5\text{ atm}$ ). The purple colour of **10** disappeared immediately,<sup>20</sup> and **11** (Type II; Scheme 2) was obtained as a colourless precipitate.<sup>21</sup> Upon opening the sealed tube in an argon-filled glove box, the colourless powder turned purple again, and on the basis of its  $^1\text{H}$  NMR spectrum it could be established that **11** retroconverted quantitatively to afford **10** within a few minutes at r.t. Accordingly, the reaction of **10** with ethylene to furnish **11** is, depending on the ethylene pressure, reversible. On the other hand, exposure of a degassed THF solution of **10**



Scheme 2 Reaction of diaryldigermine **9** with ethylene.

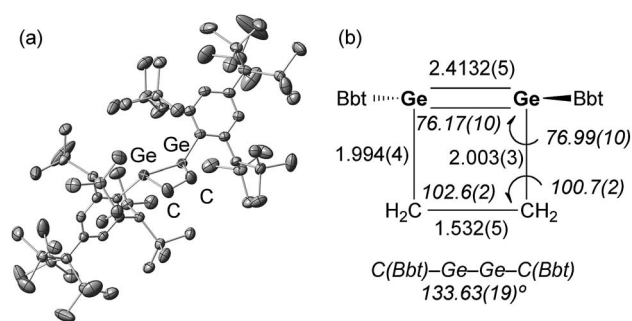


Fig. 1 (a) Molecular structure of **10** (thermal ellipsoids at 50% probability; hydrogen atoms omitted for clarity), and (b) selected metric parameters for the digermacyclobutene core in **10**.



to ethylene at ambient pressure (*ca.* 1 atm;  $-78\text{ }^{\circ}\text{C}$  to r.t.; 1 d) afforded stable colourless crystals of **12** (Type I; Scheme 2) in quantitative yield. Depending on the reaction conditions, the reaction of **10** with ethylene thus delivers different reaction products. The molecular structures of **11** and **12** were determined unambiguously by spectroscopic and X-ray crystallographic analyses.<sup>22</sup>

In order to elucidate the underlying reaction mechanism (Scheme 3), the reaction between digermynes **9** and ethylene was monitored by  $^1\text{H}$  NMR spectroscopy in THF-*d*<sub>8</sub>. After exposing a degassed THF-*d*<sub>8</sub> solution of **9** to ethylene (*ca.* 1 atm) at  $-78\text{ }^{\circ}\text{C}$  and then allowing it to warm to r.t., the colour of **9** disappeared and only signals associated with **10** were observed. After 10 min, the intensity of these signals decreased, and additional signals consistent with the formation of **11** were observed (**10** : **11** = *ca.* 1 : 1). After 20 min, signals in agreement with the formation of **12** appeared, and after 5 hours, the quantitative formation of **12** was observed. These experimental results suggested that the reaction of **10** with ethylene furnishes **11** and **12** as the kinetic and thermodynamic products, respectively.

Taking all the previously discussed results into consideration, the reaction mechanism for the reaction between digermynes **9** and ethylene can most likely be interpreted as follows: the reaction is initiated by a nucleophilic attack of ethylene towards the LUMO of **9** to afford **13**, which readily undergoes an intramolecular ring-expansion, affording **10** *via* a germylgermylene-digermene rearrangement.<sup>23</sup> Subsequently, nucleophilic attack of another molecule of ethylene towards the LUMO of **10** affords germylene **14**, which is expected to easily undergo a [1+2] cycloaddition reaction between a further molecule of ethylene and the second germylene moiety. While this [1+2] cycloaddition reaction should be reversible,<sup>24</sup> considering the results of the NMR monitoring reactions, the intramolecular C–Ge insertion of **14** is expected to proceed irreversibly to provide the thermodynamically stable product 1,4-digermabicyclo[2.2.0]hexane (**12**). The solubility of **11** in benzene was found to be limited, and the precipitation of **11** in the form of a colourless solid was observed when the reaction was conducted in this solvent. When the same reaction was carried out in THF, the kinetic product **11** was generated at an early stage in the reaction, and subsequently both **10** and **11** were converted to the thermodynamic product **12**. It can thus be concluded that the reactions of such digermynes are mostly initiated by nucleophilic attack of  $\pi$ -electrons towards the in-plane  $\pi^*$  orbital (LUMO) of the Ge–Ge triple bond, which is consistent with the previously reported reactivity of  $\pi$ -bond compounds containing heavier group 14 elements.

The proposed reaction pathways were also examined by density functional theory (DFT) calculations (see Fig. S11†), using appropriate model compounds (**9'**–**15'**) bearing Bbp (Bbp = 2,6-[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>) instead of Bbt groups (Scheme 3).<sup>25</sup> The results suggested that intermediate **13'** is formed with a small reaction barrier of 5.9 kcal mol<sup>-1</sup>, and is thermodynamically more stable than **9'** + ethylene by 14.9 kcal mol<sup>-1</sup>. Subsequently, **13'** can afford **10'** (8.2 kcal mol<sup>-1</sup> more stable) with a small reaction barrier of 3.4 kcal mol<sup>-1</sup>. Following that, the reaction of **10'** with ethylene can provide key intermediate

**14'** (3.9 kcal mol<sup>-1</sup> more stable) with a reaction barrier of 8.6 kcal mol<sup>-1</sup>. The second molecule of ethylene can then react smoothly with **14'** to give product **11'** *via* intermediate **15'**, which is a rotational isomer with a very low reaction barrier (<1.0 kcal mol<sup>-1</sup>), while product **12'** is produced with a large barrier of 16.4 kcal mol<sup>-1</sup>, which is 5.9 kcal mol<sup>-1</sup> more stable than product **11'**. The results of these DFT calculations corroborated the hypothesis that the reaction of **10** with ethylene should furnish **11** and **12** as the kinetic and thermodynamic products, respectively.<sup>26</sup>

Finally, the reactivity difference between the reaction of ethylene with digermynes (**1** and **9**) and that with disilyne (**7**) can be explained as follows: for the reaction with **1** (Ar<sub>Dip</sub>-Ge≡GeAr<sub>Dip</sub>), the calculations draw the conclusion that the corresponding Type II product with three-membered rings should be the kinetic product, while the Type I product **3**, *i.e.* 1,4-digermabicyclo[2.2.0]hexane, should be the thermodynamic product, indicating that the observation of the kinetic product under these reaction conditions is unlikely.<sup>27</sup> These conclusions are in agreement with our experimental observations. For the reaction of **7** with ethylene, theoretical calculations indicated that Type II product **8** should be both the kinetically and the thermodynamically favoured product.<sup>28</sup> These results could be interpreted in terms of the relative stability of the Ge- or Si-containing three-membered rings.

## Conclusions

In summary, we found that the reaction of digermynes **9** with ethylene affords two different reaction products (**11**, **12**), depending on the reaction conditions applied. The stable digermacyclobutene **10**, which is an intermediate in this reaction, could be isolated and subsequently treated under controlled reaction conditions with a second molecule of ethylene. A combined theoretical and experimental investigation of these reactions allowed the assignment of **11** and **12** as the kinetic and thermodynamic reaction products, respectively.

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- 16 Experimental details and chemical data for previously unreported compounds are given in the ESI.†
- 17 Given the structure and NBO charge (C<sub>2</sub>H<sub>4</sub> part, +0.045) of transition state **TS0'**, the initial interaction between ethylene and digermine **9** can be feasibly explained by an interaction between the HOMO of ethylene and the in-plane π\* orbital (LUMO) of **9**. Conversely, the geometry of intermediate **13'** should, considering its geometry and NBO charge (C<sub>2</sub>H<sub>4</sub> part, -0.586), be interpreted in terms of an orbital interaction between the π\* orbital of ethylene and the out-of-plane π orbital of **9**. For further details, see ref. 15 and the ESI.†
- 18 Torsion angle: 11.06(18)°.
- 19 For example, the Ge–Ge and Ge=Ge bond lengths in Ar<sub>Dip</sub>H<sub>2</sub>Ge–GeH<sub>2</sub>Ar<sub>Dip</sub> and Ar<sub>Dip</sub>HGe=GeHAr<sub>Dip</sub> are 2.4019(10) Å and 2.3026(3) Å, respectively; see: G. H. Spikes, J. C. Fettinger and P. P. Power, *J. Am. Chem. Soc.*, 2005, **127**, 12232.
- 20 **10**: λ<sub>max</sub> = 494 nm (ε 10 000).
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- 26 In general, [2+2] cycloaddition reactions between a C=C π-bond and a Ge=Ge π-bond (with out-of-plane π/π\* orbital) are symmetry forbidden according to the Woodward–Hoffmann rules. Thus, the concerted [2+2] cycloaddition pathway from **9** to **10** as well as from **10** to **12** can be excluded. In fact, a reaction barrier of ΔE<sup>‡</sup> = 25.4 kcal mol<sup>-1</sup> was calculated for the concerted [2+2] cycloaddition from **10'** to **12'**, which is substantially larger than the barrier in the pathway shown in Scheme 3 (ΔE<sup>‡</sup> = 16.4 kcal mol<sup>-1</sup>). Another possibility of a [2+2] cycloaddition via a biradical pathway was suggested in a previous paper (K. L. Hurni and K. M. Baines, *Chem. Commun.*, 2011, **47**, 8382), but could be excluded on the basis of the results of attempted calculations on these reaction pathways, which showed substantially larger barriers.
- 27 The Type I product **3**, *i.e.* 1,4-digerma-bicyclo[2.2.0]hexane, was calculated to be 1.3 kcal mol<sup>-1</sup> more stable than the Type II product, *i.e.* the bis(germiranyl)ethane. A reaction barrier of *ca.* 19 kcal mol<sup>-1</sup> was calculated for the retro-reaction from the Type II product to the Ar<sub>Dip</sub> analogue of intermediate **14'**, indicating a reversible reaction at r.t. Conversely, a barrier of *ca.* 40 kcal mol<sup>-1</sup> was obtained for the conversion of Type I product **3** to the intermediate, suggesting an irreversible reaction. Accordingly, **3** should be the final product under thermodynamically controlled conditions. In our case, the low solubility in non-polar



solvents such as benzene or hexane most probably enabled us to isolate the kinetic product **11**.

28 In the case of Si, the Type II product, *i.e.* **8**, was calculated to be 23.1 kcal mol<sup>-1</sup> more stable than the Type I product, *i.e.*

the 1,4-disila-bicyclo[2.2.0]hexane analogue. Levels of theory: 6-311+G(2df)[Si] and 6-31G(d,p)[C,H]//B3PW91/3-21G\*.

