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Reaction of a diaryldigermynes with ethylene†

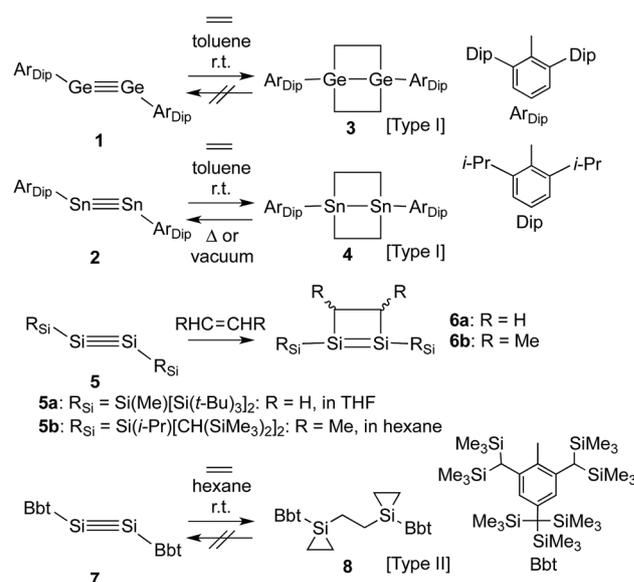
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Reaction of the stable digermynes BbtGe≡GeBbt (Bbt = 2,6-[CH(SiMe₃)₂]-4-[C(SiMe₃)₃]-C₆H₂) with ethylene initially afforded the corresponding 1,2-digermacyclobutene. Depending on the reaction conditions applied, further reaction of this 1,2-digermacyclobutene 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,¹ hydroboration² and olefin polymerisation,³ 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.⁴ 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.⁵ Power and co-workers have, for example, reported the isolation of the heavier acetylene analogues Ar_{Dip}Ge≡GeAr_{Dip} (**1**)⁶ and Ar_{Dip}Sn≡SnAr_{Dip} (**2**)⁷ 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).^{8,9} 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_{Si}Si≡SiR_{Si}; **5a**: R_{Si} = Si(Me)[Si(*t*-Bu)₃]₂,¹⁰ **5b**: R_{Si} = Si[CH(SiMe₃)₂](*i*-Pr)¹¹) with alkenes (RHC=CHR) to afford disilenes **6a,b** (**6a**: R = H, **6b**: R = Me).^{10,12} 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(SiMe₃)₂]-4-[C(SiMe₃)₃]-C₆H₂).¹³ 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.

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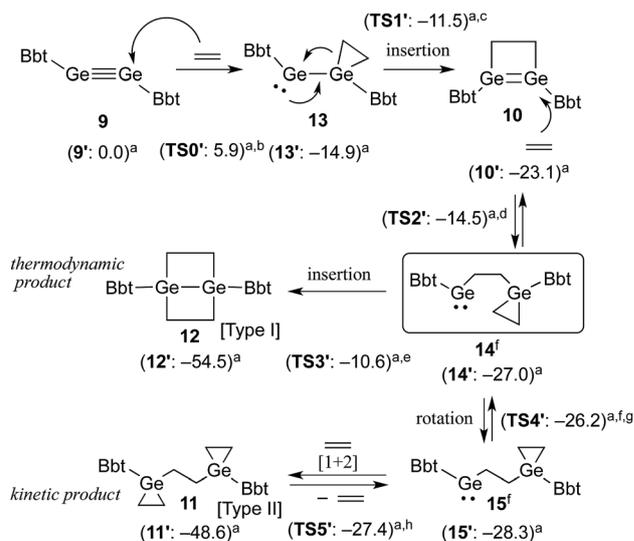
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† Electronic supplementary information (ESI) available: experimental and computational details, as well as X-ray crystallographic data for **10–12** are available. CCDC 1054594–1054596. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5sc01266j



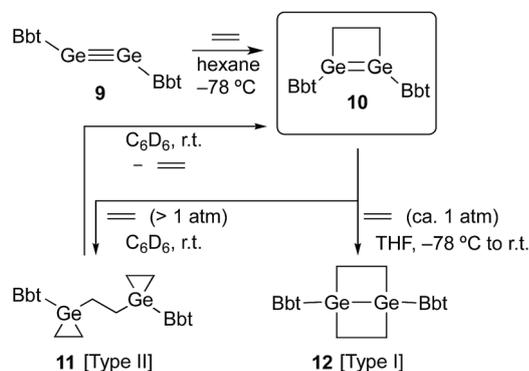
two silacyclopropane moieties. Compound **8** was found to be remarkably stable, as decomposition of these silacyclopropane moieties was not observed, even upon heating.¹⁴ Subsequently, we began to investigate the reactivity difference between diaryldisilynes and diaryldigermynes. Herein, we report the reaction of the stable diaryldigermine $\text{BbtGe}\equiv\text{GeBbt}$ (**9**)¹⁵ 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.¹⁶ 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:¹² 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,¹⁷ 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).¹⁸ 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° (Ge1) and 39.7° (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 \AA),¹⁹ but consistent with previously reported $\text{Ge}=\text{Ge}$ double bonds in digermenes (*ca.* $2.2\text{--}2.5\text{ \AA}$).¹⁹ 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 ^1H NMR spectrum of **10** exhibited signals commensurate with two identical Bbt groups, as well as signals consistent with two equivalent 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 (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) ΔE^\ddagger ($9\text{--}13'$) = 5.9 kcal mol^{-1} . (c) ΔE^\ddagger ($13'\text{--}10'$) = 3.4 kcal mol^{-1} . (d) ΔE^\ddagger ($10'\text{--}14'$) = 8.6 kcal mol^{-1} . (e) ΔE^\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) ΔE^\ddagger ($14'\text{--}15'$) = 0.8 kcal mol^{-1} . (h) ΔE^\ddagger ($15'\text{--}11'$) = 0.9 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 C_6D_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 atm). The purple colour of **10** disappeared immediately,²⁰ and **11** (Type II; Scheme 2) was obtained as a colourless precipitate.²¹ Upon opening the sealed tube in an argon-filled glove box, the colourless powder turned purple again, and on the basis of its ^1H 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.

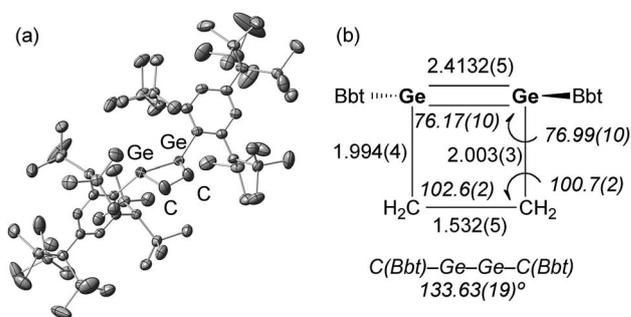


Fig. 1 (a) Molecular structure of **10** (thermal ellipsoids at 50% probability; hydrogen atoms omitted for clarity), and (b) selected metric parameters for the digermacyclobutene core in **10**.



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.²²

In order to elucidate the underlying reaction mechanism (Scheme 3), the reaction between digermynes **9** and ethylene was monitored by ^1H NMR spectroscopy in THF-*d*₈. After exposing a degassed THF-*d*₈ 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 gerymylene-digermene rearrangement.²³ Subsequently, nucleophilic attack of another molecule of ethylene towards the LUMO of **10** affords gerymylene **14**, which is expected to easily undergo a [1+2] cycloaddition reaction between a further molecule of ethylene and the second gerymylene moiety. While this [1+2] cycloaddition reaction should be reversible,²⁴ 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 π -electrons towards the in-plane π^* orbital (LUMO) of the Ge–Ge triple bond, which is consistent with the previously reported reactivity of π -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(SiMe₃)₂]₂-C₆H₃) instead of Bbt groups (Scheme 3).²⁵ The results suggested that intermediate **13'** is formed with a small reaction barrier of 5.9 kcal mol⁻¹, and is thermodynamically more stable than **9'** + ethylene by 14.9 kcal mol⁻¹. Subsequently, **13'** can afford **10'** (8.2 kcal mol⁻¹ more stable) with a small reaction barrier of 3.4 kcal mol⁻¹. Following that, the reaction of **10'** with ethylene can provide key intermediate

14' (3.9 kcal mol⁻¹ more stable) with a reaction barrier of 8.6 kcal mol⁻¹. 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⁻¹), while product **12'** is produced with a large barrier of 16.4 kcal mol⁻¹, which is 5.9 kcal mol⁻¹ 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.²⁶

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_{Dip}-Ge≡GeAr_{Dip}), 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.²⁷ 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.²⁸ 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 digermabicyclobutene **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.

Acknowledgements

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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 (C₂H₄ 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 (C₂H₄ 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)°.
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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[‡] = 25.4 kcal mol⁻¹ 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[‡] = 16.4 kcal mol⁻¹). 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⁻¹ more stable than the Type II product, *i.e.* the bis(germiranyl)ethane. A reaction barrier of *ca.* 19 kcal mol⁻¹ was calculated for the retro-reaction from the Type II product to the Ar_{Dip} analogue of intermediate **14'**, indicating a reversible reaction at r.t. Conversely, a barrier of *ca.* 40 kcal mol⁻¹ 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⁻¹ 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*.

