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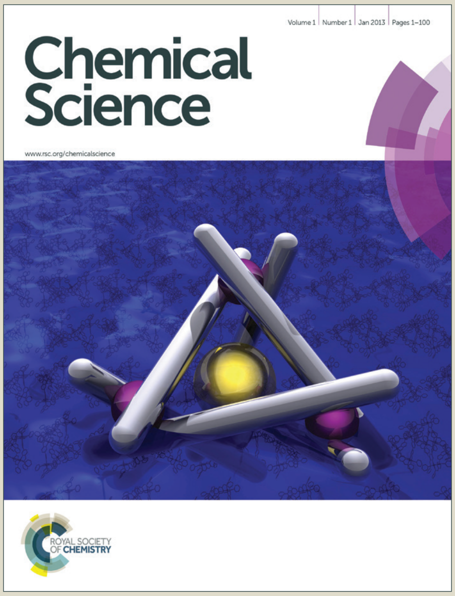

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COMMUNICATION

Reaction of a Diaryldigermyne with Ethylene

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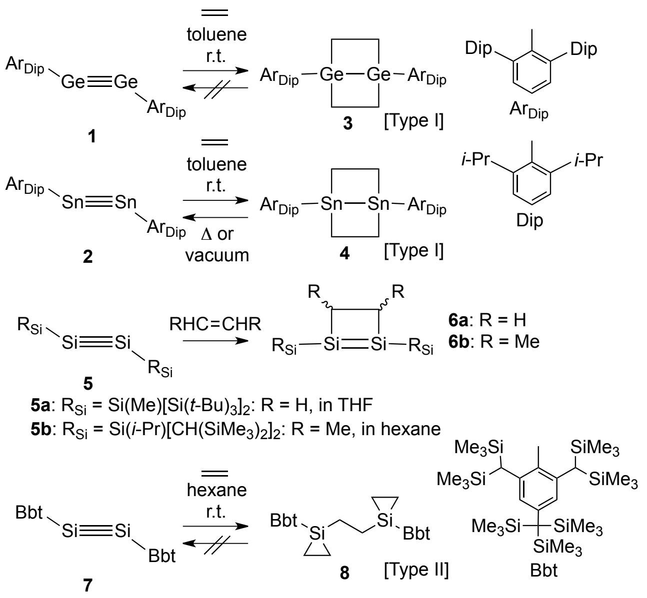
Reaction of the stable digermyne BbtGe≡GeBbt (Bbt = 2,6-[CH(SiMe$_3$)$_2$]$_2$-4-[C(SiMe$_3$)$_3$]-C$_6$H$_2$) with ethylene initially afforded the corresponding 1,2-digermacyclobutene. Depending on the reaction conditions applied, further reaction of this 1,2-digermacyclobutene with ethylene was able to furnish two different reaction products: a 1,4-digerma-bicyclo[2.2.0]hexane or a bis(germiranyl)ethane. Combined experimental and theoretical results suggested that the 1,4-digerma-bicyclo[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 of importance in organic synthesis, as a variety of preparative methods for the introduction of functional groups starts from C–C multiple bonds. Even though several olefin addition reactions, such as hydrosilylation,[1] hydroboration,[2] 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 contain carbon-containing multiple bonds to form the corresponding cycloadducts, tantamount to a strong propensity to activate small inert molecules. Unfortunately, low-coordinated 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 under retention of their characteristic reactivity, when sterically demanding substituents offer 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 reaction of **1** and **2** with ethylene proceeds 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 a release of two molecules of ethylene. Accordingly, distannyne **2** can, in contrast to digermyne **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**: Si[CH(SiMe$_3$)$_2$](i-Pr)[11]) with alkenes (RHC=CHR) to afford disilenes **6a,b** (**6a**: R = H, **6b**: R = Me).[10,12] However, neither further reactions of **6a,b** with ethylene, nor possible retro-reactions were reported.



Scheme 1. Reactions of dimetallynes **1**,**2**,**5**, and **7** with ethylene.

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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. See DOI: 10.1039/x0xx00000x

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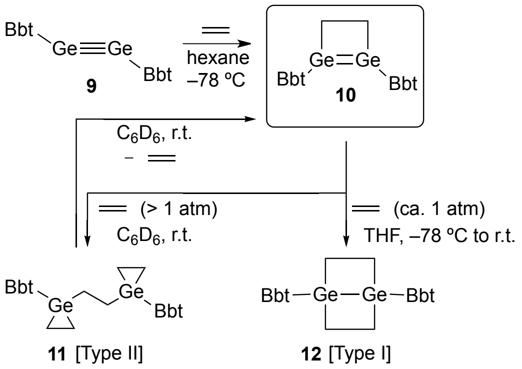
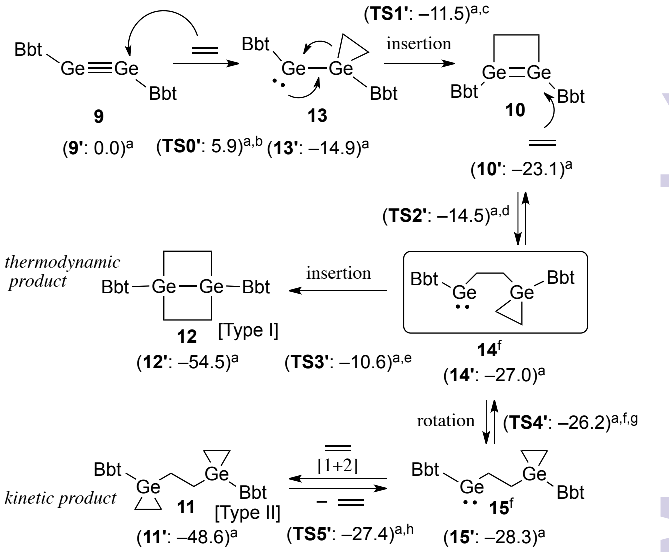


Scheme 2. Reactions of diaryldigermyne **9** with ethylene.

Previously, we have reported the synthesis of the stable diaryldisilyne BbtSi≡SiBbt (**7**, Bbt = 2,6-[CH(SiMe$_3$)$_2$]-4-[C(SiMe$_3$)$_3$]-C$_6$H$_2$).[13] The reaction of **7** with ethylene resulted in the unexpected formation of **8** (Type **II**; Scheme 1), containing 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 would like to report the reaction of the stable diaryldigermyne BbtGe≡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 (**12**, Type **I**; Scheme 2) and a three-membered (**11**, Type **II**; Scheme 2) cycloadduct.

A hexane solution of digermyne **9** was frozen (–196 ˚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 digermyne **9** with ethylene can be explained by the same mechanism used to describe the reaction between disilynes with olefins:[12] initially, interaction between ethylene and one of the Ge atoms in the Ge≡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). The X-ray crystallographic analysis of **10** revealed a non-planar structure for the four-membered Ge=Ge–C–C ring.[18] The two Bbt groups were found to be oriented in opposite direction, resulting in a *trans*-bent geometry for the Ge=Ge moiety with *trans*-bent angles of 39.5˚ (Ge1) and 39.7˚ (Ge2). A Ge=Ge bond length of 2.4132(5) Å was observed, which is slightly shorter than typical Ge–Ge single bonds (ca. 2.44 Å),[19] but consistent with previously reported Ge=Ge double bonds in digermenes (ca. 2.2-2.5 Å).[19] These structural features suggested that the Ge=Ge double bond in **10** should be weakened by the severe intrinsic strain of the four-membered Ge=Ge–C–C ring and the highly *trans*-bent geometry. The ^{1}H 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 Ge=Ge bond in **10** in solution.



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

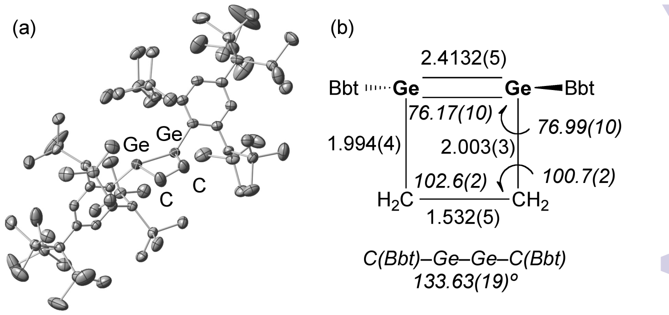


Fig. 1. (a) Molecular structure of **10** (thermal ellipsoids at 50% probability; hydrogen atoms omitted for clarity), and (b) selected metric parameters for the germacyclobutene core in **10**.

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$_6$D$_6$ solution of **10** at –196 ˚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 ^{1}H NMR spectra 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** to ethylene at ambient pressure (ca. 1 atm; –78 ˚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]

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In order to elucidate the underlying reaction mechanism (Scheme 3), the reaction between digermyne **9** and ethylene was monitored by ^{1}H NMR spectroscopy in THF-d_8. After exposing a degassed THF-d_8 solution of **9** to ethylene (ca. 1 atm) at –78 ˚C, and 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 digermyne **9** and ethylene should be most likely interpreted as follows: the reaction should be initiated by a nucleophilic attack of ethylene towards the LUMO of **9** to afford **13**, which should readily undergo an intramolecular ring-expansion, affording **10** via a germylgermylene-digermene rearrangement.[23] Subsequently, a nucleophilic attack of another molecule of ethylene towards the LUMO of **10** should afford germylene **14**, which would be 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,[24] considering the results of the NMR monitoring reactions, the intramolecular C–Ge insertion of **14** should be expected to proceed irreversibly to provide the thermodynamically stable product 1,4-digerma-bicyclo[2.2.0]hexane (**12**). As the solubility of **11** in benzene was found to be limited, 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 of the reaction, and subsequently both **10** and **11** were converted to afford the thermodynamic product **12**. It can be thus concluded that the reactions of such digermynes should be mostly initiated by a nucleophilic attack of π-electrons towards the in-plain 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 Figure S11), using appropriate model compounds (**9’**-**15’**) bearing Bbp (Bbp = 2,6-[CH(SiMe$_3$)$_2$]$_2$-C$_6$H$_3$) 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, and is thermodynamically more stable than **9’** + ethylene by 14.9 kcal/mol. Subsequently, **13’** can afford **10’** (8.2 kcal/mol more stable) with a small reaction barrier of 3.4 kcal/mol. Following that, the reaction of **10’** with ethylene can provide key intermediate **14’** (3.9 kcal/mol more stable) with a reaction barrier of 8.6 kcal/mol. 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), while product **12’** is produced with a large barrier of 16.4 kcal/mol, which is 5.2 kcal/mol 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 in the reaction of ethylene with digermynes (**1** and **9**) or disilyne (**7**) can be explained as follows: for the reaction with **1** (Ar$_{\mathrm{Dip}}$Ge≡GeAr$_{\mathrm{Dip}}$), 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-digerma-bicyclo[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 favourable product.[28] These results could be interpreted feasibly in terms of the relative stability of the Ge- or Si- containing three-membered rings.

Conclusions

In summary, we found that the reaction of digermyne **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.

Acknowledgements

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16 Experimental details and chemical data for previously unreported compounds are shown in the Supporting Information.

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18 Torsion angle: 11.06(18)˚.

19 For example, the Ge–Ge and Ge=Ge bond lengths in $Ar_{Dip}H_2Ge–GeH_2Ar_{Dip}$ and $Ar_{Dip}HGe=GeHAr_{Dip}$ are 2.4019(10) Å and 2.3026(3) Å, respectively; see: G. H. Spikes, J. C. Fettinger and Power, *J. Am. Chem. Soc.*, 2005, ***127***, 12232.

20 **10**: λ_{max} = 494 nm (ε 10,000).

21 Diaryldigermyne $Ar_{Tip}Ge{\equiv}GeAr_{Tip}$ [Ar_{Tip} = 2,6-bis(2,4,6-triisopropylphenyl)phenyl] was reported to undergo a similar reaction with three molecules of 2,3-dimethyl-1,3-butadiene; see: M. Stender, A. D. Phillips and P. P. Power, *Chem Commun*, 2002, 1312.

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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) should be 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 $\Delta E^{\ddagger}$ = 25.4 kcal/mol was calculated for the concerted [2+2] cycloaddition from **10’** to **12’**, which was substantially larger than the barrier in the pathway shown in Scheme 3 ($\Delta E^{\ddagger}$ = 16.4 kcal/mol). Another possibility for 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 of **3**, *i.e.* 1,4-digerma-bicyclo[2.2.0]hexane, was calculated to be 1.3 kcal/mol more stable than the type II product of the bis(germiranyl)ethane. A reaction barrier of ca. 19 kcal/mol 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 ca. 40 kcal/mol was obtained for 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 solvent such as benzene or hexane has most probably enabled us to isolate the kinetic product of **11**.

28 In the case of Si, the type II product, *i.e.* **8**, was calculated to be 23.1 kcal/mol 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*.

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