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Tomohiro Sugahara, Jing-Dong Guo, Takahiro Sasamori,* Yusaku Karatsu, Yukio Furukawa,
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Reaction of a Stable Digermyne with Acetylenes: Synthesis of a 1,2-Digermabenzene and a 1,4-Digermabarrelene[#]

Tomohiro Sugahara,[1] Jing-Dong Guo,[1, 2] Takahiro Sasamori,[1]* Yusaku Karatsu,[3] Yukio Furukawa,[3] Arturo Espinosa Ferao,[4] Shigeru Nagase,[2] and Norihiro Tokitoh[1]

[1] Institute for Chemical Research, Kyoto University, Gokasho Uji, Kyoto 611-0011, Japan

[2] Fukui Institute for Fundamental Chemistry, Kyoto University, Kyoto, Kyoto 606-8103, Japan

[3] Department of Chemistry and Biochemistry, School of Advanced Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan

[4] Departmento de Química Orgánica, Universidad de Murcia, Campus de Espinardo, 30100 Murcia, Spain

E-mail: sasamori@boc.kuicr.kyoto-u.ac.jp
Takahiro Sasamori
Takahiro Sasamori received Ph.D. Degree from Kyushu University in 2002. He got a position as Assistant Professor in 2003 and as Associate Professor in 2009 at Institute for Chemical Research, Kyoto University. His main research fields are organometallic and main group element chemistry.

Abstract

Reactions between acetylenes and a stable digermyne bearing $\text{4-}t\text{-Bu-2,6-[CH(SiMe}_3)_2]_2\text{-C}_6\text{H}_2$ (Tbb) groups afforded the corresponding stable 1,2-digermabenzenes together with the respective 1,4-digermabarrelenes. The properties of the obtained products and the reaction mechanism are discussed on the basis of experimental and theoretical results.

1. Introduction

Multiple-bond compounds of heavier group 14 elements represent the heavier homologues of unsaturated organic compounds. For a long time, these compounds were considered hardly isolable as stable, monomeric compounds under ambient conditions, on account of their inherently high propensity towards auto-oligomerization and their high reactivity towards addition reactions with moisture and/or aerobic oxygen.[1] However, this is only correct in the absence of appropriate stabilization methods, as the introduction of bulky substituents on the heavier group 14 elements offers kinetic protection, and their presence renders such multiple-bond compounds isolable and stable under ambient conditions. Especially homonuclear triple-bond compounds of heavier group 14 elements, *i.e.*, the heavier analogues of acetylene, have attracted much attention on account of their unique chemical and physical properties that arise from their *trans*-bent structures, which stand in strong contrast to the linear structures of carbon-based alkynes.[1,2] Power and coworkers have achieved the synthesis and isolation of stable digermynes (ArGe≡GeAr), distannynes (ArSn≡SnAr), and diplumbynes (ArPb≡PbAr) using bulky *m*-terphenyl ligands.[2,3] In 2004, Sekiguchi and Wiberg independently reported the synthesis of stable disilynes bearing bulky silyl groups.[4] Later on, we reported the synthesis of the stable diaryldisilyne **1**[5] and the diaryldigermynes **2**,[6] which bear the bulky aryl substituents Bbt or Tbb [Bbt = $\text{2,4-[CH(SiMe}_3)_2]_2\text{-4-[C(SiMe}_3)_3]\text{-C}_6\text{H}_2$; Tbb = $\text{4-}t\text{-Bu-2,6-[CH(SiMe}_3)_2]_2\text{-C}_6\text{H}_2$] (Chart 1). So far, several stable examples of compounds with triple bonds between heavier group 14 elements have been synthesized and these have allowed us study their intrinsic nature and properties.[3-7] Accordingly, these species are no longer laboratory curiosities, but key components for advanced synthetic projects.

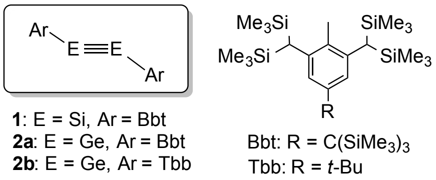
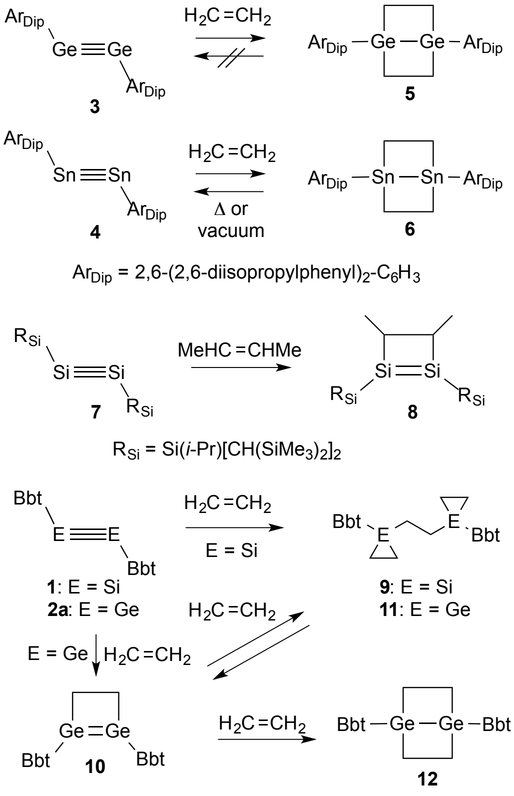


Chart 1. Stable disilyne and digermynes

Modifications of unsaturated hydrocarbons such as alkenes and alkynes are of great importance in organic synthesis, as most methods for the introduction of functional groups start with modifications of a C–C multiple bond. Most modifications of unsaturated hydrocarbons thereby require transition metal catalysts to activate the C–C π-bonds.[8] Moreover, low-coordinated species of heavier group 14 elements (divalent species or multiple-bonded compounds) have recently attracted considerable attention as potential transition-metal-free reaction initiators for unsaturated hydrocarbons. Such low-coordinated species of heavier group 14 elements have already shown high electrophilic reactivity toward small unsaturated organic molecules such as ketones, alkenes, or alkynes.[9] For example, Power *et al.* reported that the stable digermyne **3** as well as the distannyne **4** smoothly react in the absence of any transition metal catalyst with two molecules of ethylene at room temperature to afford the corresponding 4-membered-ring cycloadducts **5** and **6**, respectively (Scheme 1).[10] The cycloaddition of Sn-analogue **6** was found to be thermally reversible to release **4** together with two molecules of ethylene. The stereoselective [2+2] cycloaddition of the stable disilyne $\text{R}_{\text{Si}}\text{Si}{\equiv}\text{SiR}_{\text{Si}}$ (**7**; R_{Si} = $\text{Si[CH(SiMe}_3)_2](i\text{-Pr})$) with *cis*- and *trans*-2-butens to generate disilenes **8** was reported by Sekiguchi and coworkers.[11] Recently, we reported the reaction of stable disilyne **1** and digermyne **2a** with ethylene to furnish cyclic products **9** and **10**.[12,13] Interestingly, **10** was converted into **11** at high ethylene pressures, while **11** underwent a retro-cycloaddition to release **10** and ethylene under ambient conditions.[13] Furthermore, upon treatment with ethylene at low temperature in THF, **10** furnished four-membered ring species **12**, which is an analogue of **5**. It can thus be concluded that **11** and **12** should be the kinetic and thermodynamic products for the reaction between

2a and ethylene, respectively. In order to validate this hypothesis, we conducted systematic investigations on the reactivity of a disilyne and a digermyne with ethylene.

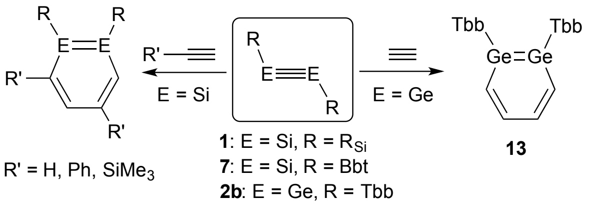
The reaction of disilynes (*e.g.* **1** and **7**) and digermynes (*e.g.* **2**) with acetylene are of great interest, as have been reported to afford the corresponding stable 1,2-disila- and 1,2-digermabenzenes.[11,14,15] In the case of the carbon analogues, the trimerization of acetylene to afford a six-membered cyclic π-conjugated system (*i.e.* an aromatic ring system) usually requires an appropriate transition metal catalyst and severe conditions, as for example in the well-known Reppe reaction. In contrast, a cyclic six-membered π-conjugated aromatic ring system containing two heavier group 14 elements can be generated under ambient conditions in the absence of any transition metal catalysts from the reaction of two molecules of acetylene and one heavier dimetallyne (*vide supra*).



Scheme 1. Reactions of dimetallynes with alkenes

Among the abundance of unsaturated organic compounds, benzene occupies a truly outstanding position. The replacement of carbon atoms in the benzene ring with heavier group 14 elements, generating so-called heavy aromatics,[15] has generated much interest, even though this class of compounds is known to be highly susceptible towards auto-oligo- and polymerizations. So far, treatment of disilynes or digermynes with acetylene remains the only synthetic method to generate 1,2-disila- or 1,2-digermabenzenes.[11,14,15] Such transformations are not only of great interest due to their unique reactivity, but the resulting heavy aromatic systems that include two heavy atoms are also highly interesting with respect to structural aspects, such as bond-alternation, planarity of the aromatic ring, and other features that may be affected by the double bond character of the E=E bonds.

In a preliminary report, we described that the reaction of **2b** with acetylene furnished the corresponding 1,2-digermabenzene (**13**) as the main product.[15] However, this reaction also generated another unprecedented product, 1,4-digermabarrelene **14**, which could be isolated and fully characterized. Herein, we report the reaction of the digermyne TbbGe≡GeTbb (**2b**) with acetylene in detail and we discuss the reaction mechanism on the basis of experimental and theoretical results.

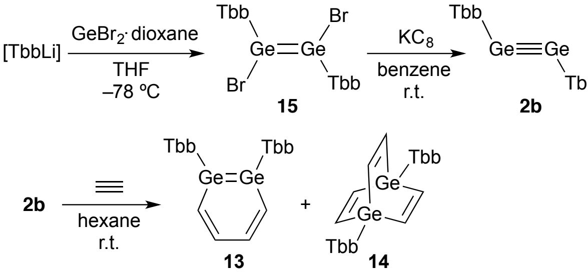


Scheme 2. 1,2-dimetallabenzenes from the reaction between dimetallynes and alkynes

2. Results and Discussion

Reaction of digermyne 2b with acetylene.

The synthesis of TbbBr and its subsequent application to the stabilization of other reactive main group element species is reported elsewhere.[16] Digermyne **2b** was prepared by a synthesis similar to that of BbtGe≡GeBbt.[6] Dibromodigermene Tbb(Br)Ge=Ge(Br)Tbb (**15**) was obtained from the reaction of TbbLi with $GeBr_2$·dioxane, followed by a subsequent reduction with KC_8 in benzene at room temperature to furnish digermyne **2b** in 99% yield as stable red crystals (Scheme 3).



Scheme 3. Synthesis of digermyne **2b** and its subsequent reaction with acetylene to afford 1,2-digermabenzene **13** and 1,4-digermabarrelene **14**.

The structural parameters of digermene **15** and digermyne **2b** were unambiguously determined by single-crystal X-ray diffraction analysis (Figure 1).[17] In both cases, two independent molecules were found in the unit cell, and each independent molecule contained a crystallographic center of symmetry. The Ge–Ge bonds in digermene **15** [2.4064(8) and 2.3969(8) Å] are slightly longer than those in carbon-substituted digermenes, indicating a weakened Ge=Ge bond.[6] Conversely, digermyne **2b** exhibits a *trans*-bent structure with Ge–Ge–C bond angles of ~130°, which is comparable to previously reported stable digermynes.[3a,6] The observed Ge≡Ge bonds in **2b** [2.2410(9) and 2.2221(9) Å] are comparable to those of previously reported stable digermynes [*e.g.*, 2.2060(7) Å for BbtGe≡GeBbt (**2a**) or 2.2850(6) Å for Ar_{Dip}Ge≡GeAr_{Dip} (**3**)].[3a,6] The Raman spectrum of **2b** revealed a strong Raman shift at 408 cm^{-1}, which is comparable to that of **2a** (398 cm^{-1}).[6b] At the B3PW91/6-311G(3d,p) level of theory, a Ge–Ge vibrational frequency of 406 cm^{-1} was calculated for **2b**. The spectral and structural features observed for **2b** suggest a considerable triple-bond character for the Ge≡Ge bond in **2b**, similar to those in **2a** and **3**.[18]

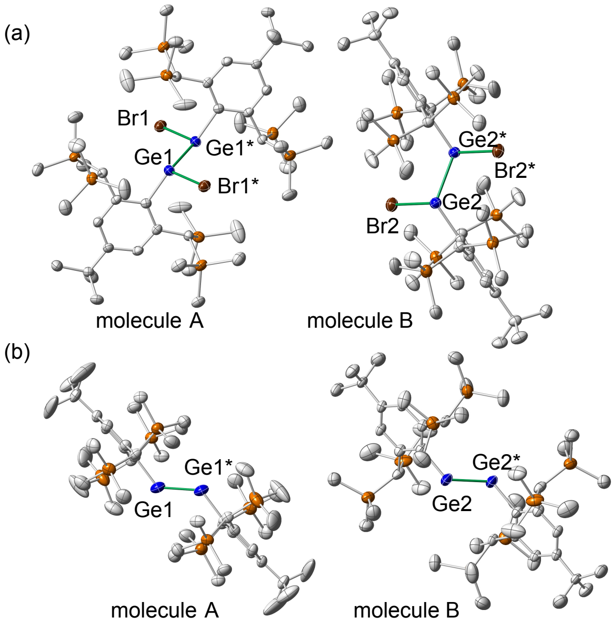
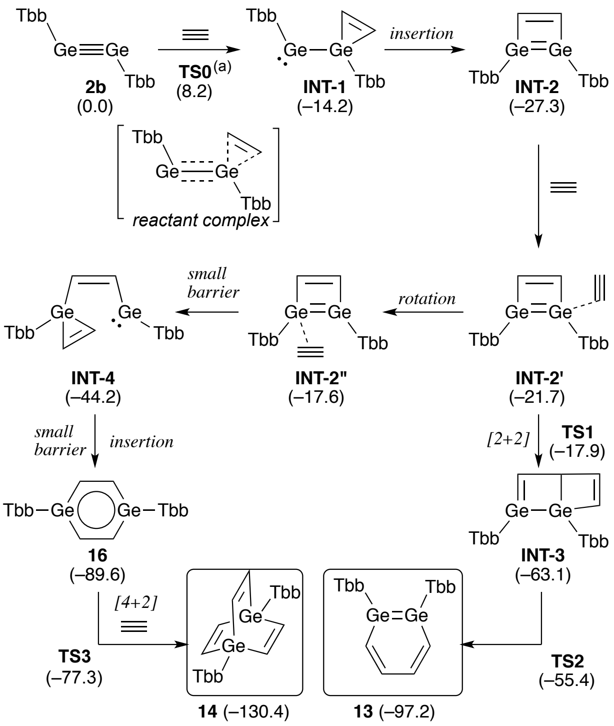


Figure 1. Molecular structure of (a) dibromodigermene **15** and (b) digermyne **2b** (atomic displacement parameters set at 50% probability; hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (º) for (a): Ge1–Ge1*, 2.4064(8); Ge1–Br1, 2.3655(6); Ge2–Ge2*, 2.3969(8); Ge2–Br2, 2.3636(6). Selected bond lengths (Å) and angles (º) for (b): Ge1–Ge1*, 2.2410(9); Ge2–Ge2*, 2.2221(9); C–Ge1–Ge1*, 130.46(11); C–Ge2–Ge2*, 130.69(11).

When a hexane solution of **2b** was exposed to 1 atm of acetylene at room temperature, its deep red color changed immediately to pale yellow. After removing the solvent, signals for both 1,2-digermabenzene **13** and 1,4-digermabarrelene **14** were observed in the NMR spectra of the crude mixture,[15] and judging from their ^{1}H NMR spectra, yields of 61% (**13**) and 22% (**14**) were estimated (Scheme 3). Recrystallization of the crude mixture from benzene at room temperature afforded yellow crystals of **13** in 25% yield. Subsequently, the filtrate was exposed to air, and recrystallization of the thus obtained residue from hexane at room temperature afforded **14** as colorless crystals in 20% yield. Both **13** and **14** were fully characterized by spectroscopic and single-crystal X-ray diffraction techniques.[19]

Reaction mechanism.

It seems feasible to conclude that 1,2-digermabenzene **13** should be the major product from the reaction of digermyne **2b** with acetylene, whereas 1,4-digemabarrelene **14** should be a by-product. The formation of **14** should probably be interpreted as a result of the presence of the intermediate 1,4-digermabenzene **16**, which could readily undergo a [4+2] cycloaddition with one molecule of acetylene to give **14**. In order to elucidate the underlying reaction mechanism, detailed theoretical calculations for the reaction of **2b** with acetylene to generate **13** and **14** were carried out at the B3PW91/6-311G(3d,p)//B3PW91/3-21G(d) level of theory (Scheme 4). The key intermediate in this reaction is digermacyclobutadiene **INT-2**, which is the common intermediate for both **13** and **14**. The pathway from **2b** to **INT-2** proceeds via the formation of a reactant complex (a van der Waals complex), which is formed by the interaction of the out-of-plane π*-orbital of **2b** with the π-orbital of acetylene.[20] Subsequently, both the [2+1] cycloaddition affording intermediate **INT-1**, and the isomerization of **INT-1** to **INT-2** by migration of a carbon atom would occur as low-barrier or barrierless processes, respectively.



Scheme 4. Calculated reaction mechanism for the reaction of **2b** with acetylene. Relative ZPE-corrected energies (kcal/mol) were calculated at the B3PW91/6-311G(3d,p)//B3PW91/3-21G(d) level of theory, and are shown in parentheses. (a) We could not locate TS0, but instead, we obtained a reactant complex (re-complex with 8.2 kcal/mol higher in energy than reactants), which is very close to TS0. That means the barrier from re-complex to TS0 is almost zero.

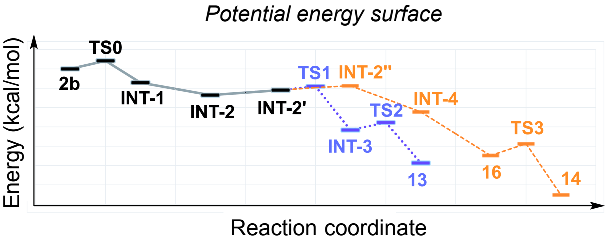
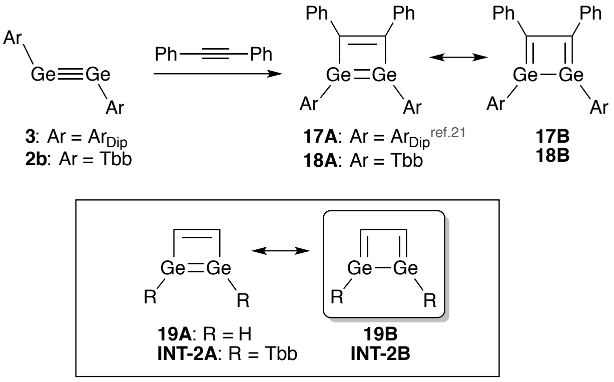


Figure 2. Energy profile for the reaction of **2b** with acetylene.



Scheme 5. Reaction of digermynes with tolan and the canonical structures for the resulting 1,2-digermacyclobutadienes.

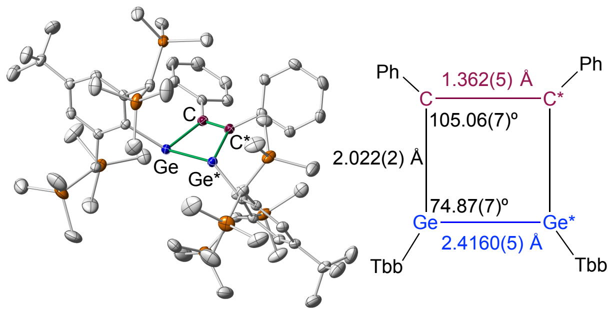
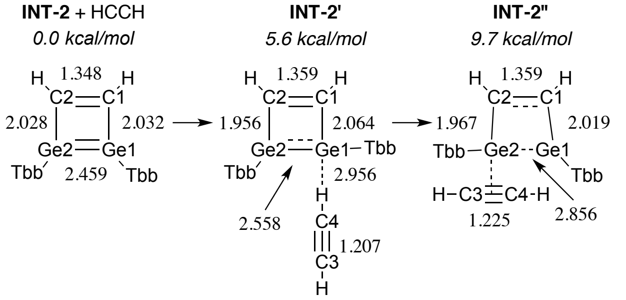


Figure 3. Molecular structure of 1,2-digermacyclobutadiene **18** (left; atomic displacement parameters set at 50% probability), and selected structural parameters for the [Ge_2C_2] ring (right).

The formation of 1,2-digermacyclobutadiene (**17**) from the reaction of digermyne **3** with tolan (PhC≡CPh) via formal [2+2]cycloaddition has previously been reported (Scheme 5).[11,21] Similarly, the reaction of **2b** with tolan in C_6D_6 at room temperature resulted in the formation of 1,2-digerma-3,4-diphenylcyclobutadiene **18** as a stable, red, crystalline compound. The structural parameters of **18**, determined by single-crystal X-ray diffraction, are similar to those of **17**,[22] exhibiting an almost planar [Ge_2C_2] ring (Figure 3). Moreover, **18** contains an intramolecular crystallographic C_2 axis through the center of the Ge–Ge and C–C bonds. Considering the lengths of the Ge–Ge [2.4160(5) Å], Ge–C [2.022(2) Å], and C–C [1.362(5) Å] bonds, it seems feasible to assume that the predominant contribution to the observed structure arises from canonical structure **18A**, which exhibits a Ge=Ge double bond character (Scheme 5). However, the results of detailed theoretical calculations on the parent 1,2-digermacyclobutadiene (**19**), including WBI, AIM, and NBO analyses, suggested a dominant contribution from canonical structure **19B**.[23] The long Ge–Ge bond (2.600 Å; WBI 1.086), the relatively short C–C bond (1.426 Å; WBI 1.349), in combination with the elongated Ge=C bond (1.854 Å; WBI 1.419) clearly support this notion and the corresponding description as a 1,4-digerma-1,3-cyclobutadiene with a loose Ge-Ge bond. Especially the NBO calculations showed only one σ-bond between the Ge atoms, as well as σ- and π-bonds between the Ge and carbon atoms.[24] Conversely, NBO and AIM calculations on **18** and **INT-2** suggested the presence of Ge=Ge and C=C double bonds, as well as of Ge–C single bonds.[24,25] In their entirety, these theoretical results indicate that, on account of the steric and/or electronic effect of the bulky Tbb groups, **INT-2** should consist mainly of **INT-2A** with a –Ge=Ge–C=C– character. The parent 1,2-digermacyclobutadiene (**19**) exhibits a different electronic distribution, mostly based on **19B** with a –Ge=C–C=Ge– character. The combined consideration of these theoretical results on **18** and **19** point to an increased C=C bond character in the case of the bis-C-phenyl substituted **18**, in order to allow for a dominant stabilization effect from the conjugation between these aromatic rings, which in turn favors structure type **A**. Therefore, **INT-2** should exhibit a Ge=C bond character (as in **INT-2B**), which is to some extent similar to **19B**.

Once **INT-2** is formed via an exothermic step (27.3 kcal/mol) from **2b**, the second molecule of acetylene should approach giving rise to the intermediate complex **INT-2'** due to charge transfer, which is energetically more unfavorable (5.6 kcal/mol) than **INT-2** (Scheme 6). The calculated Ge1···HC4 (2.956 Å) and Ge1···C4 (4.020 Å) distances in **INT-2'** are relatively long, probably due to the steric repulsion that also leads to the energy increase. Nevertheless, this intermediate should be formed due to the existence of stabilizing Ge···HC interactions. This interaction seems to be a requisite for the reaction to occur and accordingly the reason why no further reaction proceeded in the reaction of **2b** with tolan, which does not contain HC≡ bonds. Subsequently, Dewar-1,2-digermabenzene **INT-3** would be generated from **INT-2'** through a [2+2] cycloaddition of **INT-2'** with acetylene via **TS1**, which includes an activation barrier of 3.8 kcal/mol.[26] The last step, *i.e.* the dissociation of a Ge–C bond in **INT-3** to form 1,2-digermabenzene **13**, involves an activation barrier of 7.7 kcal/mol.



Scheme 6. Optimized structures for **INT-2**, **INT-2'**, and **INT-2"** (bond distances in Å).

Starting from **INT-2'**, the reaction pathway to 1,4-digermabarrelene **14** contains **INT-2"** as another important intermediate (Scheme 6). While the Ge–Ge bond length increases significantly from **INT-2'** (2.558 Å) to **INT-2''** (2.856 Å), the C–C bond length in the coordinated acetylene (1.225 Å) is just slightly longer than that calculated for free C_2H_2 (1.205 Å). These conformational changes are probably due to a strong charge transfer (CT) between the Ge atom and the second C_2H_2 moiety.[27] The main contribution to this CT should arise from the overlapping of the π-orbitals of the C3-C4 bond with the unoccupied π*-orbital located at the Ge2 atom. On the basis of NBO calculations (second order perturbation theory), a stabilization energy of 2.4 kcal/mol was calculated for the CT.[24] However, **INT-2''** is still 4.1 kcal/mol less stable than **INT-2'** and 9.7 kcal/mol less stable than **INT-2**. This may be attributed to the energetically demanding conformational changes, even after considering the CT effect.

Accordingly, the Ge–Ge bond weakens substantially upon coordination of the second molecule of acetylene in **INT-2"**, and **INT-4** containing a three-membered [C_2Ge] ring is readily formed given its very small activation barrier. Subsequently, **INT-4** can readily undergo isomerization to afford 1,4-digermabenzene **16**, which exhibits a planar geometry at a singlet closed-shell state confirmed by stable wave functions.[28] The other product, 1,4-digermabarrelene **14**, can be formed via a [4+2] cycloaddition between **16** and a third molecule of acetylene, which includes an activation barrier of 12.3 kcal/mol. Overall, both pathways in Scheme 4 show highly exothermic processes. Although the pathway toward **14** is by 33.2 kcal/mol more exothermic than that furnishing **13**, the main product was **13** and not **14**. The theoretically calculated pathways showed that the activation energy from key intermediate **INT-2'** to **INT-3** (3.8 kcal/mol), which is involved in the formation of **13**, should be slightly smaller (0.3 kcal/mol) relative to that from **INT-2'** to **INT-2''**. As a result of these theoretical insights, we examined the product ratios obtained at higher and lower reaction temperature. A **13**:**14** product ratio of 2:1 and 7:1 was observed at 50 ºC and –78 ºC, respectively, thus supporting the calculated reaction mechanism.

Molecular Structures of 1,2-digermabenzene 13 and 1,4-digermabarrelene 14.

The structural parameters of 1,2-digermabenzene **13** and 1,4-digermabarrelene **14** were determined unambiguously by single-crystal X-ray diffraction analysis.[19] Single crystals of **13** were obtained by recrystallization from benzene. The structure of **13** (Figure 4) exhibits a crystallographic C_2 axis that bisects the Ge–Ge* and C–C* bonds.[29] The Ge=Ge distance in **13** is 2.3117(6) Å, which is slightly longer than those in previously reported digermenes (*e.g.*, 2.2856(8) Å for $Mes_2Ge{=}GeMes_2$; Mes = mesityl[30]), showing a distinct, albeit weakened, Ge=Ge π-bond character. Within the central $[Ge_2C_4]$ ring, a Ge–C bond length of 1.897(3) Å was observed, which falls between previously reported average values for Ge–C (~ 1.95 Å) and Ge=C bonds (~ 1.83 Å).[31] In the central $[Ge_2C_4]$ ring, C–C bond lengths of 1.359(5) Å (C1–C2) and 1.417(7) Å (C2–C2*) were observed, which are similar to those in benzene (1.39-1.40 Å), suggesting a delocalization of π-electron density over the $[Ge_2C_4]$ moiety. It should also be noted that the central $[Ge_2C_4]$ ring in 1,2-digermabenzene **13** exhibits a non-planar geometry, wherein the Ge–Ge axis comprises an angle of 8.6° relative to the $[C_4]$ plane (Figure 4). This result stands in sharp contrast to stable 1,2-disilabenzenes,[14] which contain a virtually planar $[Si_2C_4]$ ring.

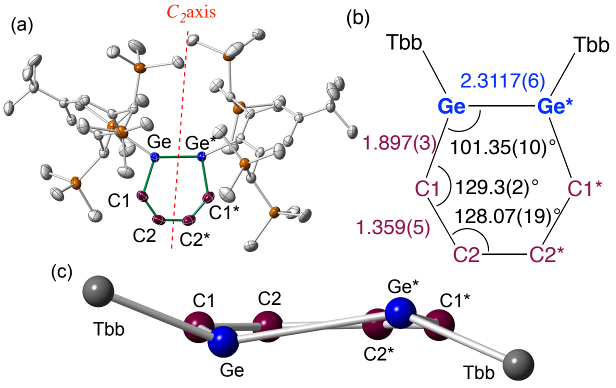


Figure 4. (a) Molecular structure of **13** (atomic displacement parameters set at 50% probability; hydrogen atoms omitted for clarity); (b) selected metric parameters for the $[Ge_2C_4]$ core in **13**; (c) side view of the $[Ge_2C_4]$ core in **13**.

The ^1H NMR spectrum of **13** in C_6D_6 suggested a C_2-symmetric structure in solution on the basis of the diastereomeric non-equivalency of the $SiMe_3$ groups, which is consistent with the C_2-structure with a non-planar geometry at Ge atoms as observed in the solid state.[29,32] For the parent 1,2-digermabenzene $C_4Ge_2H_6$ (**20**), theoretical calculations at the B3PW91/6-311G(3d,p)//B3PW91/6-311G(3d,p) level of theory suggested a planar geometry (C_{2v}) for the transition state, which was *ca.* 0.36 kcal/mol more unstable relative to the non-planar structure (C_2) at the minimum. Conversely, disilabenzene $C_4Si_2H_6$, exhibited a C_{2v} symmetric structure at the energetic minimum. Thus, it can be concluded that the non-planar structure of **13** should not be due to steric reasons and/or crystal packing, but arises from the intrinsic nature of the 1,2-digermabenzene ring system. The considerable aromaticity of the $[Ge_2C_4]$ ring in **13** is reflected experimentally in its characteristic NMR spectral features, *i.e.* low-field-shifted ^1H NMR chemical shifts (δ_H = 7.89 and 8.41) of the protons in the $[Ge_2C_4]$ ring, which arise from the ring current effect of the 6π-electrons. It is moreover reflected theoretically in the calculated NICS values and the ideal hydrogenation heat.[29] In order to compare their aromaticity, calculated NICS(r) and $NICS_{zz}(r)$ values[33] were plotted for parent models of a 1,2-digermabenzene (**20**; non-planar C_2 symmetry), a 1,2-disilabenzene (**21**; planar C_{2v} symmetry), and for benzene [GIAO-B3PW91/6-311G(3d,p)// B3PW91/6-311G(3d,p)] (Figure 5).[34] The NICS(r) and NICSzz(r) profiles for benzene were almost identical to those previously reported.[34] The $NICS_{zz}(r)$ profile for benzene exhibits the highest absolute value (–30.0) at r = 1 Å above the center of the C_6 plane, while the highest absolute value (–10.8) for the corresponding NICS(r) profile is observed at r = 0.8 Å. The profiles of 1,2-digermabenzene **20** are similar, albeit that the absolute values are slightly smaller relative to those of 1,2-disilabenzene **21**. The NICSzz(r) profiles for **20** and **21** exhibit highest values at r = 1.3 and 1.1 Å, respectively, which is slightly further away from the central ring than in the case of benzene, reflecting the larger π-orbitals of Si and Ge relative to C. Even though the highest absolute NICS(r) and NICSzz(r) values for **20** and **21** are smaller than those of benzene, they still suggest considerable aromaticity for 1,2-disilabenzene and 1,2-digermabenzene. Moreover, the NICS(r) values of **20** and **21** are comparable and slightly higher than that of benzene. The most negative NICS values for **20** and **21** were found at r = 0.8 and 0.7 Å, which is similar to that of benzene (r = 0.8 Å). On the basis of the highest absolute NICS(r) and NICSzz(r) values, it can be concluded that the aromaticity in the 1,2-digermabenzene and the 1,2-disilabenzene is considerable, albeit lower relative to benzene.

Solid-state Raman spectra of **13** were recorded under excitation from a He/Ne laser at 633 nm. The broadened Raman shift observed at ~ 320-340 cm^{-1} should be assigned to Ge–Ge vibrational frequencies, given that it is comparable to those of previously reported digermenes (*e.g.*, 404 cm^{-1} for $Me_2Ge{=}GeMe_2$).[35] Moreover, the results of calculations for **13** at the B3PW91/6-311G(3d,p)//B3PW91/6-311G(3d,p) level of theory predict Raman shifts at 304 and 324 cm^{-1} (Figure 6). The Raman shifts observed at 598 and 1469 cm^{-1} were assigned to the skeletal vibrations that are predominantly due to the $[C_4]$ moiety in the 1,2-digermabenzene, and for which values of 602 and 1503 cm^{-1} were calculated.

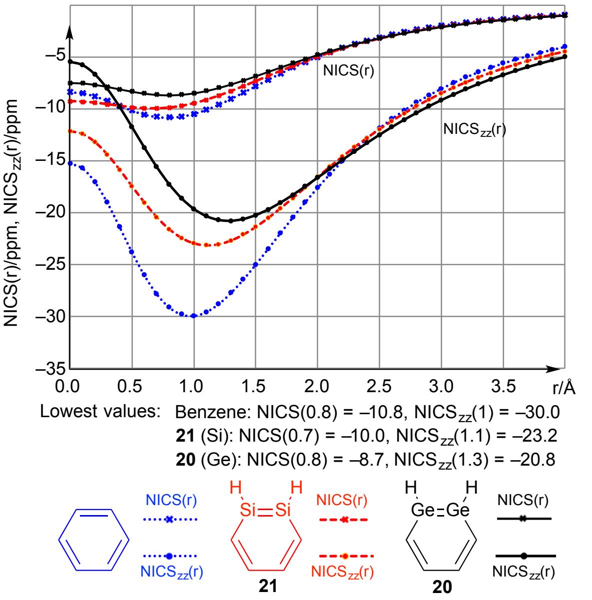


Figure 5. NICS(r) and $NICS_{zz}(r)$ values for 1,2-digermabenzene (**20**), 1,2-disilabenzene (**21**), and benzene calculated at the GIAO-B3PW91/6-311G(3d,p)// B3PW91/6-311G(3d,p) level of theory.

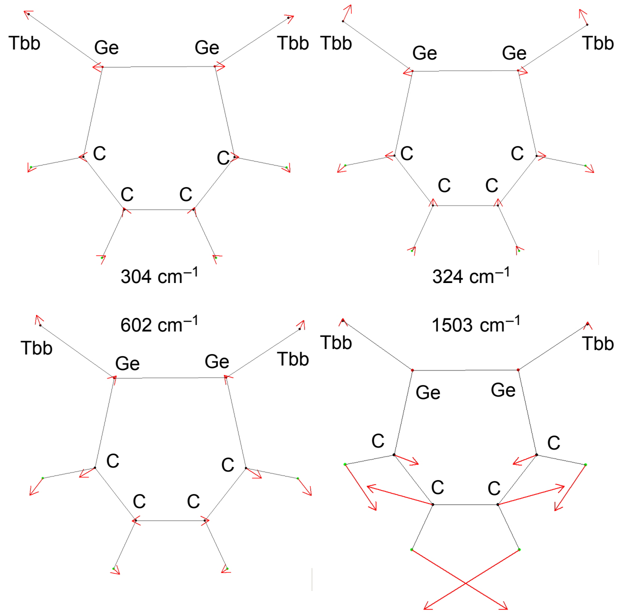


Figure 6. Vibrational modes for the 1,2-digermabenzene skeleton in **13** calculated at the B3PW91/6-311G(3d,p) level of theory.

So far, examples and structural analyses of isolable 1,4-digermabarrelenes still remain elusive. Conversely, the benzo-fused analogs, 1,4-dimetallatriptycenes, have already been structurally characterized.[36] Single crystals of 1,4-digermabarrelene **14**, suitable for single-crystal X-ray diffraction, were obtained by recrystallization from benzene, and its molecular structure, as well as selected structural parameters are shown in Figure 7. The [Ge_2C_6] core in **14** exhibits the characteristic structure of a 9,10-dimetallatriptycene containing heavier group 14 elements.[36] For example, the average internal angles at the bridging parts β(Ge–C–C; see Fig. 7) are slightly smaller than 120°, while the average angles α(C–Ge–C) are substantially smaller than 109.5°. The averages lengths of the Ge–C (~1.97 Å) and C–C bonds (~1.33 Å) are consistent with typical single Ge–C and double C=C bond values. Although the two germanium atoms were observed to be relatively close [Ge1···Ge2 = 3.1589(5) Å] compared to the sum of their van der Waals radii (~4.5 Å),[37] the theoretical calculations on the H-substituted parent model for the 1,4-digermabarrelene (**22**) did not indicate any favorable electronic interactions.

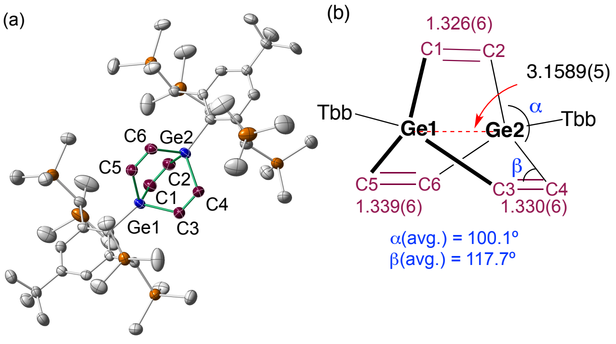


Figure 7. (a) Molecular structure of **14** (atomic displacement parameters set at 50% probability; hydrogen atoms and one molecule of benzene omitted for clarity); (b) selected metric parameters for the digermabarrelene core in **14**. Selected bond angles (°): α(C1–Ge1–C3), 96.65(18); α(C1–Ge1–C5), 102.28(18); α(C3–Ge1–C5), 101.13(18); α(C2–Ge2–C4), 96.75(18); α(C2–Ge2–C6), 102.73(18); α(C4–Ge2–C6), 100.93(17); β(Ge1–C1–C2), 117.1(3); β(Ge1–C3–C4), 117.7(3); β(Ge1–C5–C6), 118.1(3); β(Ge2–C2–C1), 118.4(3); β(Ge2–C4–C3), 117.4(3); β(Ge2–C6–C5), 117.6(3).

One of the most intriguing intrinsic properties of the 1,4-digermabarrelene is its low-lying degenerated LUMOs. Their energy levels are much lower than those of the parent carbon analog, *i.e.*, barrelene **23**,[38] and comparable to those of silicon analogue **24**[39] (Figure 8). One of the LUMOs is composed of π*-orbitals of the C=C moieties, while the other includes the two C=C π*-orbitals and the Ge–C σ*-orbitals. Moreover, the HOMO of **22**, which comprises the three π-orbitals of the C=C bonds, lies also below that of **23**. Currently, investigations into the redox properties of **14** are in progress in our laboratories.

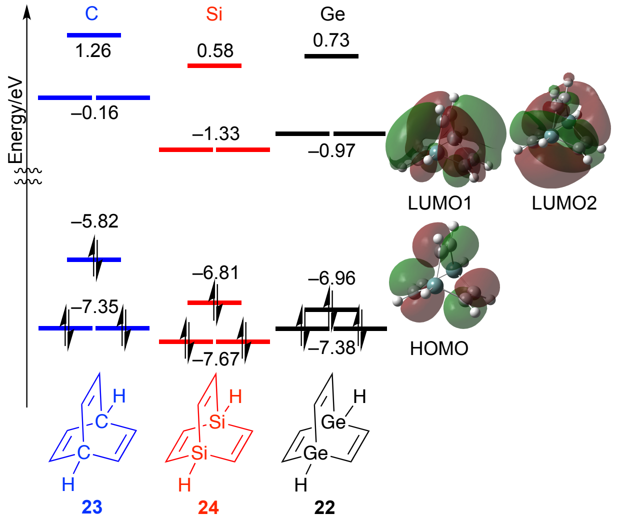


Figure 8. Frontier orbital diagrams for barrelene **23**, 1,4-disilabarrelene **24**, and 1,4-digermabarrelene **22**, calculated at the B3PW91/6-311G(3d,p)//B3PW91/6-311G(3d,p) level of theory (left), together with depictions of the HOMO and LUMOs of **22** (right).

3. Conclusion

The reaction of digermyne **2b** with acetylene afforded stable 1,2-digermabenzene **13** together with 1,4-digermabarrelene **14**. The reaction mechanism for the formation of **13** and **14** was investigated by detailed theoretical calculations. The results allow drawing the conclusion that 1,2-digermacyclobutadiene **INT-2** is the key intermediate for both **13** and **14**, whereby **13** represents the kinetically slightly favored product. Both **13** and **14** were structurally characterized and the aromaticity of the 1,2-digermabenzene was evaluated by theoretical calculations.

4. Experimental

General Remarks.

All manipulations were carried out under an argon atmosphere using either Schlenk line techniques or glove boxes. All solvents were purified by standard methods and/or the Ultimate Solvent System, Glass Contour Company. Remaining trace amounts of water and oxygen in the solvents were thoroughly removed by bulb-to-bulb distillation from a potassium mirror prior to use. ^{1}H (300 MHz) and ^{13}C (75 MHz)

NMR spectra were recorded on a JEOL JNM AL-300 spectrometer. High-resolution mass spectra (HRMS) were obtained on a Bruker micrOTOF focus-Kci mass spectrometer (DART) or a JEOL JMS-700 MStation (FAB). Raman spectra were measured on a Raman spectrometer consisting of a Spex 1877 Triplemate and an EG&G PARC 1421 intensified photodiode array detector. An NEC GLG 108 He/Ne laser (633 nm) was used for Raman excitation. All melting points were determined on a Büchi Melting Point Apparatus M-565 and are uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory (Institute for Chemical Research) of Kyoto University. Digermyne **2b** was prepared according to literature procedures.[15]

Reaction of 1,2-Tbb$_2$-digermyne 2b with an excess of acetylene in hexane.

In a Schlenk tube with a *J*-Young tap, degassed water was added to CaC_2 at r.t. under an argon atmosphere to generate acetylene, which was dried by passing through a column of P_2O_5. In an NMR tube with a *J*-Young tap, an *n*-hexane solution (0.3 mL) of **2b** (19.6 mg, 18.8μmol) was degassed *via* freeze-pump-thaw cycles. Then, the solution was exposed to acetylene gas (1 atm), generated as described above, and the tube was shaken at room temperature. The color of the solution changed from dark red to pale yellow after 10 min of shaking. All volatiles were removed under reduced pressure, and the pale yellow residue was recrystallized from benzene to afford 1,2-digermabenzene **13** (5.2 mg, 4.7 μmol, 25%, NMR yield 61%) and 1,4-digermabarrelene **14** (4.2 mg, 3.8 μmol, 20%, NMR yield 22%). **13**: yellow crystals, mp 198.1-199.0 °C (dec); ^{1}H NMR (300 MHz, C_6D_6, 298 K) δ 0.204 (s, 36H), 0.215 (s, 36H), 1.34 (s, 18 H), 2.58 (s, 4H), 7.04 (s, 4H), 7.89 (AA'BB', *J* = 3.9, 13.5 Hz, 2H), 8.41 (AA'BB', *J* = 3.9, 13.5, Hz, 2H); ^{13}C NMR (75 MHz, C_6D_6, 298 K) δ 1.37(q), 1.89 (q), 31.33 (q), 34.57 (d), 34.81 (s), 122.10 (d), 137.04 (d), 144.24 (s), 149.54 (s), 151.29 (s), 157.40 (d). UV/vis (hexane) λ_{max} (nm, ε) = 383 (9,600). Anal. Calcd for $C_{52}H_{102}Ge_2Si_8$: C, 56.92; H, 9.37. Found: C, 56.97; H, 9.36. Anal. MS (DART-TOF, positive mode): m/z calcd for $C_{52}H_{102}\,{}^{74}Ge_2Si_8$ 1098.4559 ($[M]^+$), found 1098.4599 ($[M]^+$). **14**: colorless crystals; m.p. 79.7-81.3 °C; ^{1}H NMR (300 MHz, C_6D_6, 298 K) δ 0.194 (s, 72H), 1.34 (s, 18 H), 2.54 (s, 4H), 7.01 (s, 4H), 7.96 (s, 6H); ^{13}C NMR (75 MHz, C_6D_6, 298 K) δ 0.838 (q), 29.89 (q), 31.26 (d), 34.40 (s), 121.80 (d), 129.01 (d), 149.56 (d), 150.80 (s), 151.43 (s). UV/vis (hexane) λ_{max} (nm, ε) = 287 (4,100), 296 (4,600). MS (DART-TOF, positive mode): m/z calcd for $C_{54}H_{105}\,{}^{74}Ge_2Si_8$ 1125.4794 ($[M+H]^+$), found 1125.4810 ($[M+H]^+$).

Reaction of digermyne 2b with diphenylacetylene.

In a *J*-Young NMR tube, a solution of **2b** (30.3 mg, 29.2 μmol) in C_6D_6 (0.5 mL) was treated with diphenylacetylene (6.0 mg, 0.034 mmol, 1.1 equiv.). After 10 min, the quantitative formation of 1,2-digermacyclobutadiene **18** was confirmed by ^{1}H NMR spectroscopy. The mixture was recrystallized from hexane to afford **18** as stable dark red crystals (13.0 mg, 10.7 μmol, 37%). **18**: dark red crystals, mp 68.6-68.7 °C; ^{1}H NMR (300 MHz, C_6D_6, r.t.): δ 0.23 (s, 72H), 1.37 (s, 9H), 2.86 (s, 4H), 6.85-7.02 (m, 10H), 7.18-7.21 (m, 4H); ^{13}C NMR (75 MHz, C_6D_6): δ 1.65 (q), 31.32 (q), 32.76 (d), 34.47 (s), 122.67 (d), 128.68 (d), 129.12 (d), 129.90 (d), 139.93 (s), 146.92 (s), 149.12 (s), 151.52 (s), 184.18 (s). UV/vis (hexane) λ_{max} (nm, ε) = 369 (sh, 12,000). Anal. MS (DART-TOF, positive mode): *m/z* calcd. for $C_{62}H_{108}\,{}^{74}Ge_2Si_8$: 1224.5029 ($[M+H]^+$); found: 1224.5045 ($[M+H]^+$).

Monitoring of the reaction of 1,2-Tbb$_2$-digermyne 2b with an excess of acetylene at –78 ºC.

A solution of **2b** (31.6 mg, 28.8 μmol) in *n*-hexane (0.5 mL) was degassed in a *J*-Young NMR tube, before being exposed to an excess of acetylene (*ca*. 1 atm.) at –78ºC for 3 min. Subsequently, the solution was warmed to room temperature and all volatiles were removed under reduced pressure. The yield of **13** and **14** was estimated by ^{1}H NMR spectroscopy (**13**:**14** = 7:1).

Monitoring of the reaction of 1,2-Tbb$_2$-digermyne 2b with an excess of acetylene at 50 ºC.

A solution of **2b** (31.6 mg, 28.8 μmol) in toluene (0.5 mL) was degassed in a *J*-Young NMR tube, before being exposed to acetylene. The solution was treated with an excess of acetylene (*ca*. 1 atm.) at 50 ºC for 10 min. Subsequently, the solution was warmed to room temperature, before all volatiles were removed under reduced pressure. The yield of **13** and **14** was estimated by ^{1}H NMR spectroscopy (**13**:**14** = 2:1).

Computational calculations.

The level of theory and the basis sets used for the structural optimization are contained within the references of the main text. Frequency calculations confirmed minimum energies for all optimized structures. All calculations were carried out using the *Gaussian 09* program package[40] except the structural and electronic analysis of the parent 1,2-digermacyclobutadiene (**19**) that was conducted with *ORCA*.[41]

X-ray crystallographic analysis.

Single crystals of [**2b**·C_6H_6], [**13**·C_6H_6], [**14**·C_6H_6], [**15**·C_6H_6], and **18** were obtained from recrystallization from benzene. Intensity data were collected on a RIGAKU Saturn70 CCD system with VariMax Mo Optics using MoKα radiation (λ = 0.71075 Å). Crystal data are shown in the references. The structures were solved by a direct method (SIR2004[42]) and refined by a full-matrix least square method on F^2 for all reflections (SHELXL-97[43]). All hydrogen atoms were placed using AFIX instructions, while all other atoms were refined anisotropically. Supplementary crystallographic data were deposited at the Cambridge Crystallographic Data Centre (CCDC; under reference numbers: CCDC1035078, 1035079, 1485559, 1035077, 1485558 for [**2b**·C_6H_6], [**13**·C_6H_6], [**14**·C_6H_6], [**15**·C_6H_6], and **18**, respectively) and can be obtained free of charge via www.ccdc.cam.ac.uk/data_request.cif.

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[#]Dedicated to Emeritus Professor Takayuki Kawashima on the occasion of his 70th birthday.

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17. X-ray crystallographic data for [$\mathbf{15}\cdot C_6H_6$]:[15] $C_{54}H_{104}Br_2Ge_2Si_8$, FW = 1283.09, T = −170 °C, triclinic, P–1 (no. 2), a = 9.5903(2) Å, b = 12.1744(3) Å, c = 30.5707(9) Å, α = 82.3768(19)°, β = 86.935(2)°, γ = 75.4857(13)°, V = 3424.10(15) Å^3, Z = 2, D_{calcd} = 1.224 g/cm^3, μ = 2.215 mm^{-1}, λ = 0.71075 Å, 2 $\theta_{\max}$ = 50.0°, 27891/11871 measured/independent reflections (R_{int} = 0.0498), 625 refined parameters, GOF = 1.021, R_1 = 0.0449 ($I > 2\ \sigma(I)$), wR_2 = 0.1256 (all data), largest difference peak and hole 1.841 and −1.098 e Å^{-3}. X-ray crystallographic data for [$\mathbf{2b}\cdot C_6H_6$]:[15] $C_{54}H_{104}Ge_2Si_8$, FW = 1123.27, T = −170 °C, triclinic, P–1 (no. 2), a = 13.2964(4) Å, b = 16.4120(10) Å, c = 17.2864(8) Å, α = 87.040(2)°, β = 73.057(2)°, γ = 69.160(3)°, V = 3366.7(3) Å^3, Z = 2, D_{calcd} = 1.108 g/cm^3, μ = 1.065 mm^{-1}, λ = 0.71075 Å, 2$\theta_{\max}$ = 51.0°, 29799/12418 measured/independent reflections (R_{int} = 0.0501), 602 refined parameters, GOF = 1.016, R_1 = 0.0604 ($I > 2\ \sigma(I)$), wR_2 = 0.1718 (all data), largest difference peak and hole 1.255 and −0.505 e Å^{-3}.
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19. X-ray crystallographic data for [$\mathbf{13}\cdot C_6H_6$]: $C_{58}H_{108}Ge_2Si_8$, FW = 1175.34, T = −170 °C, orthorhombic, $Pnna$ (no. 52), a = 18.2435(3) Å, b = 30.6273(4) Å, c = 12.6638(2) Å, V = 7075.89(19) Å^3, Z = 4, D_{calcd} = 1.103 g/cm^3, μ = 1.016 mm^{-1}, λ = 0.71075 Å, 2 $\theta_{\max}$ = 51.0°, 59699/6580 measured/independent reflections (R_{int} = 0.0791), 323 refined parameters, GOF = 1.034, R_1 = 0.0405 ($I > 2\ \sigma(I)$), wR_2 = 0.1128 (all data), largest difference peak and hole 1.145 and −0.523 e Å^{-3}. X-ray crystallographic data for [$\mathbf{14}\cdot C_6H_6$]: $C_{60}H_{110}Ge_2Si_8$, FW = 1201.38, T = −170 °C, triclinic, P–1 (no. 2), a = 12.2815(2) Å, b = 17.1720(5) Å, c = 18.6944(3) Å, α = 93.8158(13)°, β = 106.5432(10)°, γ = 105.0468(10)°, V = 3607.56(13) Å^3, Z = 2, D_{calcd} = 1.106 g/cm^3, μ = 0.998 mm^{-1}, λ = 0.71075 Å, 2 $\theta_{\max}$ = 52.0°, 43493/13645 measured/independent reflections (R_{int} = 0.0611), 683 refined parameters, GOF = 1.162, R_1 = 0.0839 ($I > 2\ \sigma(I)$), wR_2 = 0.1952 (all data), largest difference peak and hole 3.018 and −0.667 e Å^{-3}.

20. The geometry of the re-complex revealed that the Ge1-C1 distance (2.788 Å) is much longer than the Ge1-C2 distance (2.385 Å). This may be explained by a canonical molecular orbital analysis (for details, see SI). The HOMO and HOMO-1 of the re-complex exhibited interactions between both of the in-plane π-orbitals and the out-of-plane π-orbital of **2b** and the π*-orbitals of acetylene.
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22. X-ray crystallographic data for **18**: $C_{62}H_{108}Ge_2Si_8$: FW = 1223.38, $T = -170$ °C, orthorhombic, $P4_1/a$ (no. 88), a = 22.7759(2) Å, b = 22.7759(2) Å, c = 28.2418(3) Å, V = 14650.2(2) Å^3, Z = 8, D_{calcd} = 1.109 g/cm^3, μ = 0.984 mm^{-1}, λ = 0.71075 Å, 2 $\theta_{\max}$ = 54.0°, 128111/7997 measured/independent reflections (R_{int} = 0.0620), 341 refined parameters, GOF = 1.012, R_1 = 0.0442 ($I > 2\sigma(I)$), wR_2 = 0.1295 (all data), largest difference peak and hole 0.749 and −0.649 e Å^{-3}.
23. The results for the detailed theoretical calculations on **19** are shown in the Supporting Information.
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26. The related transition state (**TS1**) shows that the π-orbital of the second molecule of acetylene acts as an electron donor, which is consistent with its charge distribution: +0.02 (Mulliken) / +0.04 (NBO).
27. Total charge (NBO charge) of the HCCH part in **INT-2'** is –0.012 and that in **INT-2''** is +0.016.
28. The assigned aromaticity of **16** is supported by the geometry parameters (C=C: 1.392 Å and Ge–C: 1.869 Å) and the NICS values [NICS(0): –5.0 ppm and NICS(1): –5.8 ppm] for the ring. Moreover, its triplet state is by 25.1 kcal/mol less stable (without ZPE correction) than the singlet close shell state.
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33. Calculated at the GIAO-HF/6-311G(3df,p)//M062x/6-311G(3df,p) level of theory. On account of the non-planar structures of the 1,2-digermabenzene, it is unfortunately difficult to isolate the contribution from the π-electrons to the NICS values. Therefore, the mean planes of the $H_6C_4E_2$ (E = C, E = Si for **21**, E = Ge for **20**) models were put on the *x-y* plane, and the "bq"s (probe points) were added with *z*-coordinates. NICSzz(r) values were adopted to evaluate the out-of-plane π-electron contribution of the corresponding NICS(r) values.
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Graphical Abstract

<Title>

Reaction of a Stable Digermyne with Acetylenes: Synthesis of a 1,2-Digermabenzene and a 1,4-Digermabarrelene

<Authors' names>

Tomohiro Sugahara, Jing-Dong Guo, Takahiro Sasamori, Yusaku Karatsu, Yukio Furukawa, Arturo Espinosa Ferao, Shigeru Nagase, and Norihiro Tokitoh

<Summary>

Reactions between acetylenes and a stable digermyne afforded the corresponding stable 1,2-digermabenzenes together with the respective 1,4-digermabarrelenes. The properties of the obtained products and the reaction mechanism are discussed on the basis of experimental and theoretical results.

<Diagram>