

Preparation, structural characterization of 1,2-digermacyclobut-3-enes, and their palladium-catalyzed insertion of alkynes

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Abstract

1,2-Digermacyclobut-3-enes were prepared by the treatment of *Z*- α,β -bis(chlorodialkylgermyl)ethenes with Na metal in boiling toluene and their structures were fully established by spectroscopic methods coupled with X-ray crystallography. In the presence of an appropriate catalyst, 1,2-digermacyclobut-3-enes reacted smoothly with alkynes to give the corresponding insertion products, 1,4-digermacyclohexa-2,5-dienes in moderate to good yields. Conventional complexes, such as [Pd(PPh₃)₄] and [Pt(PPh₃)₄], serve as efficient catalysts. The mechanism of the insertion reaction of alkynes into the germanium–germanium bond of 1,2-digermacyclobut-3-enes is discussed in terms of a key intermediate, a 1,4-digerma-2-buten-1,4-diylpalladium.

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1. Introduction

The chemical and physical properties of Group 14 element (Si, Ge, etc.) – Group 14 element bonds have been extensively studied and are the subject of current interest in view of the potential applications of Group 14 element compounds to organic synthesis and advanced materials [1]. In contrast to the extensive studies of the Si–Si bond, there have been only a few reports on those of the Ge–Ge bond.

Group 14 element – Group 14 element σ bonds are formally similar to a C–C σ bond but are well-known to be much more reactive than the latter under various

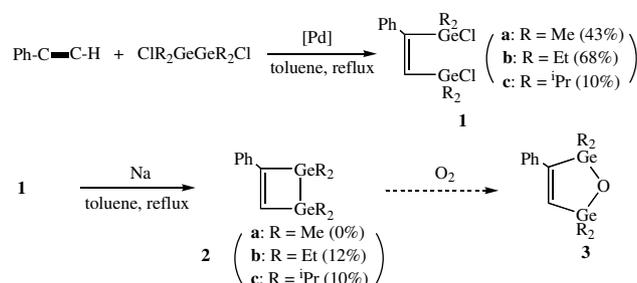
reaction conditions [2]. The σ bond of Group 14 element catenates is reactive as the corresponding C–C π bond [3]. Recently, we have reported the synthesis, structure, and unique properties of 1,2-digermacyclohexa-3,5-dienes [4a–4e]. During the course of our studies of 1,2-dimetallacyclopolyenes, we describe in this paper the preparation, structural characterization of 1,2-digermacyclobut-3-enes, and their palladium-catalyzed insertion reaction of alkynes. Two research groups have reported on the study of 1,2-digermacyclobut-3-ene derivatives. Namely, Weidenbruch et al. [4f] have described briefly the preparation and crystal structure of tetra-*tert*-butyl-1,2-digermacyclobut-3-ene produced by photolysis of hexa-*tert*-butylcyclotrigermane in the presence of phenylacetylene. Synthesis and chemical properties of 3,4-benzo-1,1,2,2-tetraethyl-1,2-digermacyclobut-3-ene have been reported by Nakadaira and co-workers [4g].

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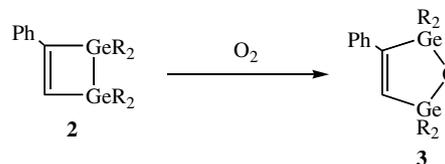
2. Results and discussion

2.1. Preparation and structural characterization of 1,2-digermercyclobut-3-enes

New types of 1,2-digermercyclobut-3-enes were prepared by intramolecular cyclization of *Z*- α,β -bis(chlorodialkylgermyl)ethenes with sodium (Na) metal. At first, *Z*- α,β -bis(chlorodialkylgermyl)styrenes (**1**) were prepared by the insertion reactions of phenylacetylene into the germanium–germanium bond of 1,2-dichlorotetraalkyldigermanes in the presence of [Pd(dba)₂] (0.05 molar amount) containing ETBP (0.2 molar amount) in boiling toluene (R = Me (**a**): 43%, Et (**b**): 68%, ^{*i*}Pr (**c**): 10%), (dba = dibenzylideneacetone, ETBP = 4-ethyl-2,6,7-trioxa-1-phospha-bicyclo[2.2.2]octane)) [5]. The conventional palladium catalysts such as [Pd(PPh₃)₄] were not effective for the insertion reactions of alkynes into the germanium–germanium bond of 1,2-dichlorotetraalkyldigermanes. 1,4-*Z*- α,β -bis(chlorodialkylgermyl)styrenes (**1b**, **c**) were cyclized by Na metal in boiling toluene to give the corresponding 3-phenyl-1,2-digermercyclobut-3-enes (**2**) in low yields (R = Et (**b**): 12%, ^{*i*}Pr (**c**): 10%). At the same time, 1,3-digerma-2-oxacyclopent-4-enes (**3**) and unidentified products showing ¹H NMR signals assignable to those of the dialkylgermanium units (R₂Ge) were also formed. On the other hand, 1,4-bis(chlorodimethylgermyl)styrene (**1a**) was treated by Na metal in boiling toluene to give mainly 1,1,3,3-tetramethyl-4-phenyl-1,3-digerma-2-oxacyclopent-4-ene (**3**) together with unidentified compounds containing Me₂Ge units. The formation of cyclic germoxanes **3** may be ascribed to accidental oxidation of **2** by oxygen which could not be excluded completely during preparation and/or the subsequent work-up.



New germacycles **2b**, **c** are colorless oils and highly reactive toward oxygen, but can be purified by rapid chromatography with a short packed column with silica-gel followed by simple distillation (Kugelrohr) under reduced pressure. 1,2-Digermercyclobut-3-enes (**2b**, **c**) in toluene are gradually oxidized in air at room temperature to give the corresponding 1,3-digerma-2-oxacyclopent-4-enes (**3**).



1,1,2,2-Tetraethyl-3-phenyl-1,2-digermercyclobut-3-ene (**2b**) and 1,1,2,2-tetra-*iso* propyl-3-phenyl-1,2-digermercyclobut-3-ene (**2c**) were determined by inspection of ¹H, ¹³C NMR, and GC–MS data. The structure of 1,2-digermercyclobut-3-ene (**2c**) was finally established by the X-ray diffraction method at 120 K as described in Fig. 1. The ¹H NMR of **2b** in CDCl₃ displayed signals assignable to those of ethyl groups in the range of 0.99–1.31 ppm, that of a phenyl group in the range of

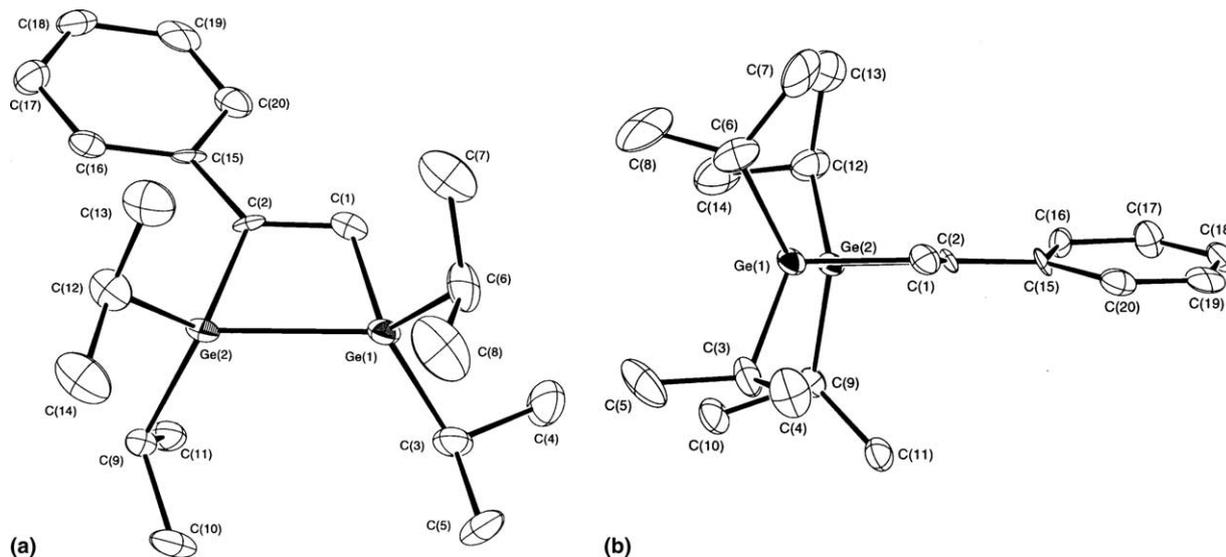


Fig. 1. Molecular structure of **2c**. Hydrogen atoms are omitted for clarity. (a) Top view and (b) side view.

Table 1

The selected bond length (Å) and bond angles (°) of 1,2-digermacyclobut-2-ene (**2c**)

Ge(1)–Ge(2)	2.439(7)
Ge(1)–C(3)	1.971(7)
Ge(2)–C(2)	1.993(6)
Ge(2)–C(12)	1.970(7)
Ge(1)–C(1)	1.959(6)
Ge(1)–C(6)	1.987(7)
Ge(2)–C(9)	1.979(6)
Ge(2)–C(2)–C(1)	104.5(4)
C(1)–Ge(1)–Ge(2)	74.0(2)
Ge(1)–Ge(2)–C(2)	74.0(9)
C(2)–C(1)–Ge(1)	107.5(5)

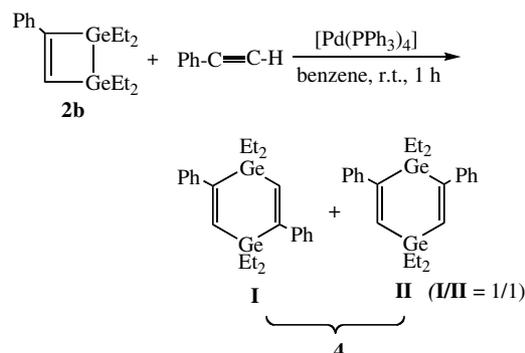
7.10–7.33 ppm, and that due to the olefinic proton at 7.69 ppm, respectively. Compound **2c** exhibited ^1H NMR spectrum of signals due to *iso* propyl groups in the range of 1.12–1.71 ppm, that due to a phenyl group in the range of 7.08–7.26 ppm, and that due to the olefinic proton at 7.70 ppm, respectively. Fortunately, 1,2-digermacyclobut-2-ene (**2c**) was crystallized from toluene at $-78\text{ }^\circ\text{C}$ (mp ca. $-60\text{ }^\circ\text{C}$). The molecular structure of **2c** at 120 K is shown in Fig. 1. The crystallographic data, selected bond lengths, and angles are summarized in Section 3 and Table 1, respectively.

The Ge–Ge distance of **2c** is 2.439(7) Å, which is slightly shorter than that of 1,1,2,2-tetra-*tert*-butyl-3-phenyl-1,2-digermacyclobut-3-ene (2.531(6) Å) on account of a less steric repulsion of substituent on germanium atom [4f]. The bond distance of **2c** is somewhat longer than those of 1,2-digermacyclohexa-3-enes (2.3893–2.40 Å) due to the difference of ring [4a]. The Ge–C bonds are in the range of 1.959(6)–1.993(6) Å, and the bond angles of Ge–Ge–C and C–C–Ge are 74.0° and $104.5(4)$ – $107.5(5)^\circ$, respectively. The structure of **2c** is that its four-membered ring is planar.

2.2. Palladium-catalyzed insertion reactions of 1,2-digermacyclobut-3-ene (**2b**) with alkynes

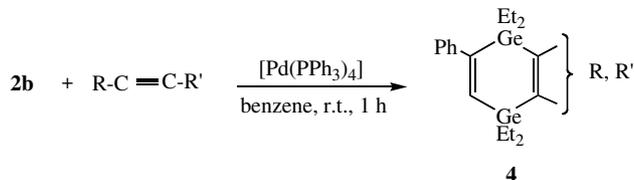
Reactions of 1,2-digermacyclobut-3-enes (**2**) with alkynes in the presence of palladium complexes were examined. A degassed benzene solution of 1 mol equiv of **2b** containing 5 mol equiv of phenylacetylene, and $[\text{Pd}(\text{PPh}_3)_4]$ (0.05 mol equiv based on the acetylene) was stirred at room temperature for 1 h to afford readily a 1:1 mixture of 2,5-diphenyl-1,4-digermacyclohexa-2,5-diene (**4I**) and 3,5-diphenyl-1,4-digermacyclohexa-2,5-diene (**4II**) in a total yield of 98% (GC yield). Evaporation of benzene followed by preparative TLC with silica-gel gave diphenyl-1,4-digermacyclohexa-2,5-dienes (**4**) (in pure 77% isolated yield), which showed satisfactory NMR and MS data. In contrast to the bis-germylation of phenylacetylene with various digermanes previously

reported, **2b** reacted with alkynes to give the corresponding insertion products under very mild conditions due to the ring strain caused by a longer Ge–Ge bond [4d].



Besides $[\text{Pd}(\text{PPh}_3)_4]$, a zero-valent palladium complex, such as $[\text{Pd}(\text{dba})_2]$ and $[\text{Pd}(\text{PMePh}_2)_4]$, also catalyzed the alkyne insertion into the Ge–Ge bond of **2b** to give **4** in moderate to good yields. Under the same conditions, the use of zero-valent platinum complex, $[\text{Pt}(\text{PPh}_3)_4]$ resulted similarly in good yields of insertion products.

The reactivities of other terminal and internal alkynes for **2b** were also examined with $[\text{Pd}(\text{PPh}_3)_4]$ as a catalyst, as summarized in Table 2.



1-Hexyne reacted with **2b** under the same conditions as those for phenylacetylene to give a 1:1 mixture of 2-butyl-5-phenyl-1,4-digermacyclohexa-2,5-diene and 3-butyl-5-phenyl-1,4-digermacyclohexa-2,5-diene in total 86% isolated yields. Other terminal alkynes, such as methyl propionate, gave the corresponding insertion products, 2-carboxylate- and 3-carboxylate-5-phenyl-1,4-digermacyclohexa-2,5-dienes in the ratio of 1:1 in 69% isolated yield. The reactions of internal alkynes with **2b** were also examined. 1-Phenyl-1-propyne and dimethyl acetylenedicarboxylate reacted with **2b** under the same conditions resulted in formation of the corresponding insertion products in moderate to good yields. So far as we know, these results are the first examples of internal alkynes, except for those having electron-withdrawing groups in insertion reactions of Ge–Ge bonds. Other internal alkynes, such as bis(trimethylsilyl)acetylene and diphenylacetylene, proved to be unreactive toward **2b** at even $70\text{ }^\circ\text{C}$ for 5 h probably due to steric hindrance caused by these substituents on alkynes.

Table 2
Reactions of 1,2-digermacyclobut-3-ene (**2b**) with alkynes in the presence of [Pd(PPh₃)₄]

Run	1,2-Digermacyclobut-3-ene	Alkynes	Conditions	Yield (%)	Product ratio
1	2b	Bu-C≡C-H	r.t., 1 h	86 ^a (98) ^b	1:1
2	2b	Ph-C≡C-H	r.t., 1 h	77 (95)	1:1
3	2b	MeO ₂ C-C≡C-H	r.t., 1 h	69 (90)	1:1
4	2b	Ph-C≡C-Me	r.t., 1 h	56 (85)	1:1
5	2b	MeO ₂ C-C≡C-C-CO ₂ Me	r.t., 1 h	52 (85)	–
6	2b	Me ₃ Si-C≡C-SiMe ₃	70 °C, 5 h	0	–
7	2b	Ph-C≡C-Ph	70 °C, 5 h	0	–

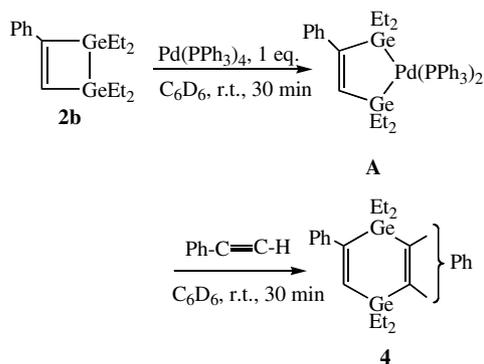
^a Isolated yields.

^b GC yields.

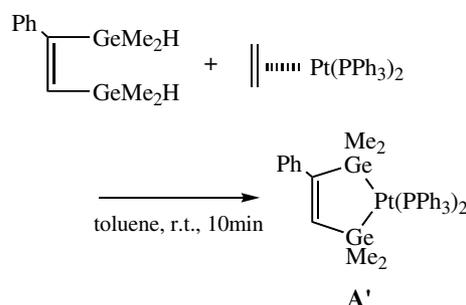
2.3. Preparation and identification of 1,4-digermabut-2-ene-1,4-diylpalladium

In the palladium-catalyzed reaction of **2b** with alkynes, 1,4-digermabut-2-ene-1,4-diylpalladium complex is conceivable to be a possible intermediate for the insertion of alkynes and this gives the alkyne-insertion products **4**.

To examine intervention of 1,4-digermabut-2-ene-1,4-diylpalladium intermediate (**A**), a mixture of 1,2-digermacyclobut-3-ene (**2b**) and one mol equiv of [Pd(PPh₃)₄] in C₆D₆ was placed in an NMR tube at room temperature. After 30 min inspection of the ¹H NMR spectrum, it was revealed that most of **2b** in the reaction mixture disappeared and instead the complex **A** was formed. The structure of **A** was confirmed by comparing its ¹H, ¹³C, and ³¹P NMR data with those of related palladium and platinum complexes [4f–4h]. The ¹H NMR spectrum of **A** displays signals due to ethyl groups on germanium in the range of 0.6–1.4 ppm and those due to phenyl groups in the range of 6.90–7.79 ppm, respectively. The ¹³C NMR spectrum of **A** shows four peaks at 12.22, 12.33, 13.64, and 13.75 ppm, due to ethyl carbons. In addition, **A** revealed a ³¹P NMR signal at 13.9 (br) ppm. The broad ³¹P NMR signals of **A** suggest the rapid exchange between the two PPh₃ ligands on the Pd atom. All ¹H, ¹³C, and ³¹P NMR signals due to **A** locate at higher field than those due to **2b**. The intermediate **A** smoothly reacted with phenylacetylene to afford a 1:1 mixture of 1,4-digermacyclohexa-2,5-dienes (**4I** and **4II**) in quantitative yields, as confirmed by NMR spectroscopy.

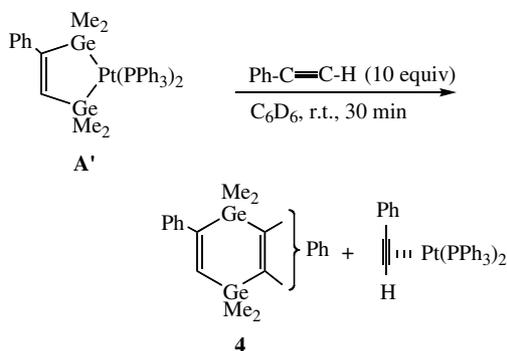


To obtain further information, we attempted to isolate 1,4-digermabut-2-ene-1,4-diylpalladium **A** under various conditions without success. Next, we set about to prepare a platinum analogue of intermediate **A** by the treatment of (η-ethylene)bis(triphenylphosphine)platinum with excess amounts of *Z*-α,β-bis(dimethylgermyl)styrene at room temperature for 10 min. A model complex 1,4-digermabut-2-ene-1,4-diylplatinum (**A'**) was formed quantitatively and obtained as a white powder. The structure of **A'** was established by inspection of spectral data, such as NMR, IR, and MS spectra. Platinum complex **A'** was sensitive to air and moisture at room temperature.



The ¹H NMR of platinum complex **A'** in C₆D₆ displayed two methyl signals due to methyl groups on germanium at 0.41 ppm (*J*_{Pt-H} = 15 Hz) and 0.47 ppm (*J*_{Pt-H} = 15 Hz). The ³¹P NMR showed two singlet signals with two satellites at 29.0 ppm (*J*_{Pt-P} = 2198 Hz, *J*_{P-P} = 17 Hz) and 29.9 ppm (*J*_{Pt-P} = 2219 Hz, *J*_{P-P} = 17 Hz). The small *J*_{Pt-P} value in **A'** is consistent with that of *cis*-(digermyl)bis(*tert*-phosphine)platinum complexes and bis(germyl)platinum complexes having chelating diphosphines [4d].

The platinum complex **A'** reacted with excess amounts of phenylacetylene at room temperature for 30 min in C₆D₆ to give a 1:1 mixture of the corresponding insertion products **3** in quantitative yields, and at the same time, (η-acetylene)bis(triphenylphosphine)platinum was also formed. All products were identified by NMR and GC–MS analysis.

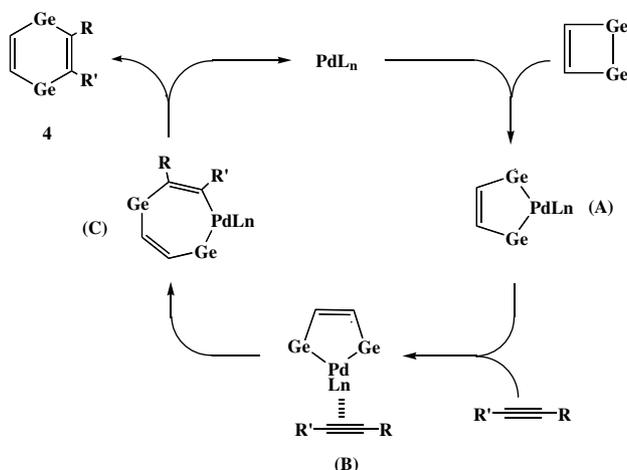


2.4. Catalytic cycle

A mechanism for the Pd-catalyzed insertion reaction of the alkyne into the Ge–Ge bond of 1,2-digermapent-3-enes (**2**) can be proposed in analogy with the above results and was previously suggested by the use for the Pt-catalyzed insertion of alkynes with 1,2-digermapent-3,5-dienes [4d]. Thus, the catalytic cycle is composed of four steps: (a) the oxidative addition of **2** to a palladium complex, PdL_n, to form a 1,4-digermapent-2-ene-1,4-diylpalladium intermediate **A**, (b) the coordination of an alkyne to **A** to form a 1,4-digermapent-2-ene-1,4-diylpalladium intermediate having an alkyne as a ligand, (c) the insertion of a coordinated alkyne into one of the Pd–Ge bonds of **2** to form an insertion product **C**, and (d) the reductive elimination of the 1,4-digermapent-2,5-dienes (**4**) from the insertion product **C** along with the regeneration of the active palladium species, that further carries the catalytic cycle (see Scheme 1).

3. Experimental

¹H, ¹³C, ³¹P NMR spectra were recorded on Varian Unity Inova-400 MHz spectrometer. GC–MS spectra



Scheme 1. Catalytic cycle.

were measured with JEOL JMS-DX 303 mass spectrometer. The UV and UV–vis spectra were recorded with a Shimadzu UV 2200 spectrometer. IR spectra were recorded on Shimadzu FT-IR 4200 spectrometer. Gas chromatographic analyses were performed with Shimadzu GC-8A equipped with 1 m of 20% SE30. X-ray crystallographic data and diffraction intensities were collected on a MacScience DIP2030 diffractometer utilizing graphite-monochromated Mo K α ($\lambda = 0.71073$ Å) radiation. The structures were solved by direct methods using the program system SIR-92 [6] and refined with all data on F^2 by means of SHELXL-97 [7]. Refinement was performed by a SILICON Graphics O₂ with maXus. Crystallographic data for **2c**: molecular formula = C₂₀H₃₄Ge₂, molecular weight = 419.672, monoclinic, $P2_1/a$, $a = 16.6670(19)$ Å, $b = 8.1500(7)$ Å, $c = 17.1340$ Å, $\beta = 114.624(6)^\circ$, $V = 2115.8(4)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.317$ g/cm³, GOF = 1.802, $R = 0.0640$, $R_w = 0.1996$.

3.1. Materials

Diethylether, hexane, pentane, benzene, and toluene were dried by refluxing over sodium benzophenone ketyl under atmosphere of nitrogen and distilled just before use. Methanol was dried with magnesium metal and distilled before use. Phenylacetylene, 1-phenyl-1-propyne, 1-hexyne, methyl propionate, and dimethyl acetylenedicarboxylate were commercially available. [Pd(dba)₂], [Pd(PPh₃)₄], [Pd(PMePh₂)₃], [Pt(PPh₃)₄], [Pt(acac)₂], and ETBP are commercially available. Compounds (ClMe₂Ge)₂ [8], (ClEt₂Ge)₂ [9], Z-C₆H₅C (ClMe₂Ge)=CH(ClMe₂Ge) [10], (η -ethylene)bis(triphenylphosphine), and (η -phenylacetylene)bis(triphenylphosphine) [11] were prepared according to reported procedures.

3.2. Preparation of 1,2-tetraiso-propyl-1,2-dichlorodigermane

To a benzene solution (100 ml) of (Ph^{*i*}Pr₂Ge)₂ (4.7 g, 10 mmol) and AlCl₃ (catalytic amounts), HCl gas was carefully bubbled for 30 h. The reaction was followed by GC. 1,2-Dichlorodigermane was purified simply by distillation under reduced pressure in 1.37 g (3.2 mmol, 32%), bp 92–94 °C/0.3 mmHg. ¹H NMR (δ , CDCl₃) 1.18–1.22 (dd, $J = 7.3$ Hz, 24H), 1.62–1.76 (sept., $J = 7.3$ Hz, 4H); ¹³C NMR (δ , CDCl₃) 17.7, 21.3; MS m/z : 388 (M⁺). Anal. Calc. for C₁₂H₂₈Ge₂Cl₂: C, 37.12; H, 7.27. Found: C, 37.30; H, 7.34%.

3.3. Preparation of Z- α,β -bis(chlorodiethylgermyl)-styrene (**1b**)

A toluene solution (70 mol) of (ClEt₂Ge)₂ (13 g, 0.047 mol), 3 equiv phenylacetylene (12 ml, 0.11 mol), 0.05 equiv of [Pd(dba)₂] (1.04 mg, 1.8 mmol), and 0.1 equiv

of ETBP (0.58 mg, 3.6 mmol) was placed in a two-necked flask under argon atmosphere. After stirring for 12 h in boiling toluene, the toluene, ETBP, and unreacted phenylacetylene were evaporated. Then, *Z*- α,β -bis(chlorodiethylgermyl)styrene (**1b**) was purified simply by distillation (Kugelrohr) under reduced pressure to give **1b** (7.71 g, 0.20 mol, 43%). **1b**: bp 80–140 °C/0.02 mmHg; ¹H NMR (δ , CDCl₃) 1.09 (m, 10H, EtGe), 1.25 (m, 10H, EtGe), 6.90 (s, 1H, CH=), 7.10–7.42 (m, 5H, phenyl ring protons); ¹³C NMR (δ , CDCl₃) 8.19, 8.72, 12.99, 15.94, 126.06, 127.36, 128.55, 144.62, 148.15, 158.84. MS *m/z* (relative intensity): 405 (88), 370 (11), 341 (10), 268 (33), 239 (30), 166 (100). Anal. Calc. for C₁₆H₂₆Ge₂Cl₂: C, 44.23; H, 6.03. Found: C, 44.46; H, 6.38%.

3.4. Preparation of *Z*- α,β -bis(chlorodiisopropylgermyl)styrene (**1c**)

A toluene solution (70 mol) of (ClⁱPr₂Ge)₂ (6.23 g, 16.03 mmol), 2 equiv of phenylacetylene (3.52 ml, 32.1 mmol), 0.05 equiv of [Pd(dba)₂] (461 mg, 32.1 mmol), and 0.1 equiv of ETBP (260 mg, 1.60 mmol) was placed in a two-necked flask under argon atmosphere. After stirring for 37 h in boiling toluene, the toluene, ETBP, and unreacted phenylacetylene were evaporated. *Z*- α,β -bis(chlorodiisopropylgermyl)styrene (**1c**) was purified simply by distillation (Kugelrohr) under reduced pressure in 1.57 g (3.20 mol, 10.0%). **1c**: bp 103–133 °C/0.05 mmHg. ¹H NMR (δ , CDCl₃) 1.04 (d, *J* = 7.3 Hz, 3H, CH₃), 1.14 (d, *J* = 7.3 Hz, 3H, CH₃), 1.17 (d, *J* = 7.3 Hz, 3H, CH₃), 1.24 (d, *J* = 7.3 Hz, 3H, CH₃), 1.71 (sept., *J* = 7.3 Hz, 2H, CH), 2.07 (sept., *J* = 7.3 Hz, 2H, CH), 6.89 (s, 1H, CH=), 7.03–7.38 (m, 5H, Ph); ¹³C NMR (δ , CDCl₃) 18.36, 18.72, 19.20, 19.53, 21.62, 24.69, 126.35, 127.31, 128.51, 145.52, 149.68, 158.05. MS *m/z* (relative intensity): 490 (M⁺, 13), 447 (100), 404 (26). Anal. Calc. for C₂₀H₃₄Ge₂Cl₂: C, 47.25; H, 6.74. Found: C, 47.48; H 6.90%.

3.5. Preparation of 1,1,2,2-tetraethyl-3-phenyl-1,2-digermercyclobut-3-ene (**2b**)

A solution of bis(chlorodiethylgermyl)styrene (7.62 g, 17.5 mmol) in toluene (80 ml) was slowly added to sodium (1.29 g, 56.1 mmol) in refluxing toluene (100 ml). After the mixture continued to reflux for 48 h, the resulting salt was filtered off. Then, the filtrate was concentrated under reduced pressure at below 30 °C. To remove the germoxane, the crude solution thus obtained was chromatographed rapidly over a silica-gel short column with hexane. After evaporation of the solvent, the residue was Kugelrohr-distilled (94–99 °C/0.048 mmHg) to afford 1,1,2,2-tetraethyl-3-phenyl-1,2-digermercyclobut-3-ene (**2b**) (760 mg, 2.1 mmol, 12% yield). Pure com-

pound **2b** was stored below –20 °C in argon. Under these conditions, **2b** was stable for one month. **2b**: ¹H NMR (δ , CDCl₃) 0.99–1.31 (m, 20H, EtGe), 7.10–7.33 (m, 5H, Ph), 7.69 (s, 1H, CH=); ¹³C NMR (δ , CDCl₃) 8.85, 9.55, 10.70, 10.90, 126.52, 127.74, 128.53, 140.88, 149.72, 161.74. MS *m/z* (relative intensity): 364 (M⁺, 41), 349 (46), 335 (27), 320 (8), 262 (100), 233 (47), 204 (24), 175 (31), 160 (49). Anal. Calc. for C₁₆H₂₆Ge₂: C, 52.86; H, 7.21. Found: C, 53.05; H, 7.42%. 1,1,3,3-Tetraethyl-4-phenyl-1,3-digerma-2-oxacyclopent-4-ene (**3b**) was obtained as by-product by chromatography with a short column packed with silica-gel eluted with diethylether and Kugelrohr-distilled (84–95 °C/0.085 mmHg) in 6.8% yield (450 mg, 1.19 mmol). **3b**: ¹H NMR (δ , CDCl₃) 0.91–1.22 (m, 20H, EtGe), 7.24 (s, 1H, CH=), 7.16–7.30 (m, 5H, phenyl); MS *m/z* (relative intensity): 380 (M⁺, 18), 351 (100), 322 (53).

3.6. Preparation of 1,1,2,2-tetra-isopropyl-3-phenyl-1,2-digermercyclobut-3-ene (**2c**)

A solution of bis(chlorodiisopropylgermyl)styrene (**1c**) (7.62 g, 17.5 mmol) in toluene (80 ml) was slowly added to sodium (1.29 g, 56.1 mmol) in refluxing toluene (100 ml). After the mixture continued to reflux for 48 h, the resulting salt was filtered off. The filtrate was concentrated under reduced pressure at below 30 °C. The crude solution was chromatographed over a short column packed with short column and rapidly eluted with hexane to give pure 1,1,2,2-tetra-isopropyl-3-phenyl-1,2-digermercyclobut-3-ene (**2c**) (730 mg, 1.74 mmol, 10% yield). **2c**: mp –48 °C. ¹H NMR (δ , CD₂Cl₂, 23 °C) 1.12 (d, *J* = 7.3 Hz, 6H, CH₃), 1.14 (d, *J* = 7.3 Hz, 6H, CH₃), 1.17 (d, *J* = 7.3 Hz, 6H, CH₃), 1.18 (d, *J* = 7.3 Hz, 6H, CH₃), 1.60 (sept., *J* = 7.3 Hz, 2H, CH), 1.71 (sept., *J* = 7.3 Hz, 2H, CH), 7.08–7.26 (m, 5H, Ph), 7.70 (s, 1H, CH=); ¹³C NMR (23 °C, δ , CDCl₃) 18.4, 18.7, 21.2, 21.3, 21.5, 21.7, 126.2, 126.8, 128.1, 141.6, 150.4, 171.6; MS *m/z* (relative intensity): 420 (M⁺, 11), 390 (100), 377 (74), 347 (14), 291 (12), 248 (27), 203 (13), 160 (159, 117 (9). Anal. Calc. for C₂₀H₃₄Ge₂: C, 57.26; H, 8.17. Found: C, 57.36; H, 8.25%.

3.7. Reaction of bis(chlorodimethylgermyl)styrene (**1a**) with sodium metal

A solution of bis(chlorodimethylgermyl)styrene (6.64 g, 17.5 mmol) in toluene (80 ml) was slowly added to sodium (1.29 g, 56.1 mmol) in refluxing toluene (100 ml). After the mixture was refluxed for 48 h, the resulting salt was filtered off. The filtrate was concentrated under reduced pressure at below 30 °C. GC–MS analysis of the crude concentrate (0.9 g) showed that the main component thus obtained was 1,1,3,3-tetramethyl-4-phenyl-1,2-digerma-3-oxacyclopent-4-ene (**3a**).

3.8. Preparation of *Z*- α,β -bis(dimethylgermyl)styrene

A diethylether solution (40 ml) of bis(chloro-dimethylgermyl)styrene (7.71 g, 20.3 mmol) and LiAlH₄ (0.77 g, 20.3 mmol) was stirred at 40 °C for 3 h. After hydrolysis with water, *Z*- α,β -bis(dimethylgermyl)styrene was obtained in pure form by chromatography a silica gel over short column packed with silica-gel eluted with hexane (1.98 g, 6.4 mmol, 31.5% yield). ¹H NMR (δ , C₆D₆) 0.34 (d, *J* = 3.4 Hz, 6H, MeGe), 0.34 (d, *J* = 3.3 Hz, 6H, MeGe), 4.57–4.67 (m, 1H, HGe), 4.76 (sept., *J* = 3.4 Hz, 1H, HGe), 6.72 (d, *J* = 5.5 Hz, 1H, CH=), 7.00–7.22(m, 5H); ¹³C NMR (δ , CDCl₃) –2.6, –2.2, 126.1, 126.3, 128.1, 144.0, 147.2, 160.9; GC–MS *m/z* (relative intensity) 310 (M⁺, 21), 295 (28), 207 (100). Anal. Calc. for C₁₂H₂₀Ge₂: C, 44.04; H, 6.16. Found: C, 44.36; H, 6.51%.

3.9. Pd-catalyzed reactions of acetylenes with 1,2-digermacyclobut-3-enes (**2b**)

As a representative example, the reaction of **2b** with phenylacetylene is described. A mixture of **2b** (3.6 mg, 10 μ mol), phenylacetylene (5.5 μ L, 50 μ mol) with [Pd(PPh₃)₄] (0.6 mg, 0.5 μ mol) and toluene (0.6 ml) was placed in a 5-ml flask. The solution was degassed under vacuum and stirred at room temperature for 1 h. GC and GC–MS analyses of the reaction mixture showed **2b** was completely consumed and thus led to the formation of 1,1,4,4-tetraethyl-2,5-diphenyl-1,4-digermacyclohexa-2,5-dienes (**4**). The crude solution was chromatographed over silica-gel TLC to give a 1:1 mixture of 1,1,4,4-tetraethyl-2,5-diphenyl-1,4-digermacyclohexa-2,5-diene and 1,1,4,4-tetraethyl-2,6-diphenyl-1,4-digermacyclohexa-2,5-diene (77% isolated yield). ¹H NMR (δ , C₆D₆) 0.89–1.17 (m, 40H, EtGe), 6.90 (s, 2H, CH=), 6.97 (s, 2H, CH=), 7.07–7.35 (m, 20H, phenyl); ¹³C NMR (δ , CDCl₃) 7.23, 7.40, 7.97, 9.14, 9.39, 9.45, 11.23, 12.42, 125.90, 126.06, 126.07, 126.15, 126.23, 126.44, 127.56, 128.10, 128.11, 128.21, 128.22, 128.28, 128.64, 129.99, 130.23, 133.19, 140.00, 142.63, 142.70, 146.39, 147.30, 159.07, 160.11; MS *m/z* (relative intensity) 466 (M⁺, 7), 437 (100), 408 (18), 161 (18), 132 (16). Anal. Calc. for C₂₄H₃₂Ge₂: C, 61.90; H, 6.93. Found: C, 62.05; H, 6.71%. 1,1,4,4-Tetraethyl-2-butyl-5-phenyl-1,4-digermacyclohexa-2,5-diene and 1,1,4,4-tetraethyl-3-butyl-5-phenyl-1,4-digermacyclohexa-2,5-diene (86% isolated yield). ¹H NMR (δ , C₆D₆) 0.84–1.24 (m, 40H, EtGe), 1.24–1.53 (m, 18H, C–Bu), 6.57 (s, 1H, CH=), 6.62 (s, 1H, CH=), 6.91 (s, 1H, CH=), 6.93 (s, 1H, CH=), 7.02–7.36 (m, 10H, phenyl); ¹³C NMR (δ , CDCl₃) 7.10, 7.41, 8.11, 8.42, 9.65, 10.66, 12.66, 14.46, 22.87, 30.06, 30.84, 31.08, 31.46, 38.16, 40.53, 41.47, 125.89, 125.96, 126.08, 126.22, 128.03, 128.09, 128.25, 128.62, 129.97, 133.07, 136.45, 137.18, 137.42, 142.60, 143.04, 147.36; MS *m/z* (relative intensity) 417

(M⁺ – Et) (100), 386 (13), 335 (23), 316 (10), 161 (11). Anal. Calc. for C₂₂H₂₈Ge₂: C, 60.38; H, 6.45. Found: C, 59.40; H, 6.50%. 1,1,4,4-Tetraethyl-2-methyl-3,5-diphenyl-1,4-digermacyclohexa-2,5-diene and 1,1,4,4-tetraethyl-3-methyl-2,5-diphenyl-1,4-digermacyclohexa-2,5-diene (56% isolated yield). ¹H NMR (δ , C₆D₆) 0.83–1.38 (m, 40H, EtGe), 1.53 (s, 6H, C–Me), 6.93 (s, 1H, CH=), 6.95 (s, 1H, CH=), 7.01–7.35 (m, 20H, phenyl); ¹³C NMR (δ , CDCl₃) 6.18, 6.35, 6.42, 6.49, 9.10, 9.34, 9.36, 9.50, 19.87, 20.03, 125.16, 125.21, 125.95, 126.26, 126.31, 127.10, 127.20, 127.25, 128.01, 128.03, 128.12, 128.15, 128.24, 128.29, 128.31, 130.00, 133.20, 142.99, 143.12, 143.45, 143.72, 146.88, 148.05, 159.65; MS *m/z* (relative intensity) 480 (M⁺, 8), 451 (100), 436 (18), 407 (18), 350 (19), 335 (43), 306 (8), 205 (16), 160 (32). Anal. Calc. for C₂₅H₃₄Ge₂: C, 62.59; H, 7.14. Found: C, 62.94; H, 6.81%. 1,1,4,4-Tetraethyl-2-carboxylate-5-phenyl-1,4-digermacyclohexa-2,5-diene and 1,1,4,4-tetraethyl-2-carboxylate-5-phenyl-1,4-digermacyclohexa-2,5-diene (69% isolated yield). ¹H NMR (δ , C₆D₆) 0.79–1.39 (m, 40H, EtGe), 3.41 (s, 3H, CO₂Me), 3.42 (s, 3H, CO₂Me), 6.76 (s, 1H, CH=), 6.91 (s, 1H, CH=), 8.34 (s, 1H, CH=), 8.36 (s, 1H, CH=), 6.94–7.35 (m, 10H, phenyl); ¹³C NMR (δ , CDCl₃) 6.97, 7.38, 7.60, 7.79, 8.07, 9.27, 9.33, 9.39, 51.79, 52.01, 125.85, 125.99, 126.39, 126.59, 128.15, 128.27, 129.99, 140.88, 143.22, 147.14, 149.14, 158.87, 159.81, 160.33, 160.68, 67.42, 243.14, 143.15; MS *m/z* (relative intensity) 448 (M⁺, 9), 419 (54), 390 (100), 361 (23), 332 (21), 317 (11), 259 (9), 230 (7). Anal. Calc. for C₂₀H₃₀O₂Ge₂: C, 53.66; H, 6.76. Found: C, 54.02; H, 6.51%. 1,1,4,4-Tetraethyl-2,3-dicarboxylate-5-phenyl-1,4-digermacyclohexa-2,5-diene (52% isolated yield). ¹H NMR (δ , C₆D₆) 1.09–1.18 (m, 20H, EtGe), 3.39 (s, 3H, CO₂Me), 3.45 (s, 3H, CO₂Me), 6.77 (s, 1H, CH=), 6.94–7.36 (m, 5H, phenyl); ¹³C NMR (δ , CDCl₃) 7.67, 7.75, 9.07, 9.28, 51.93, 52.02, 125.88, 125.92, 126.83, 128.35, 128.26, 141.88, 146.04, 221.85, 239.64; MS *m/z* (relative intensity) 506 (M⁺, 10), 477 (68), 448 (100), 419 (23), 390 (21), 286 (26). Anal. Calc. for C₂₂H₃₂O₄Ge₂: C, 52.26; H, 6.38. Found: C, 52.60; H, 6.51%.

3.10. Pt-catalyzed reactions of acetylenes with 1,2-digermacyclobut-3-enes (**2b**)

As a representative example, the reaction of **2b** with phenylacetylene is described. A mixture of **2b** (3.6 mg, 10 μ mol), phenylacetylene (5.5 μ L, 50 μ mol), [Pt(PPh₃)₄] (0.6 mg, 0.5 μ mol), and toluene (0.6 ml) was placed in 5 ml flask. The solution was degassed under vacuum and stirred at room temperature for 1 h. GC and GC–MS analyses of the reaction mixture showed **2b** was completely consumed along with the formation of 1,1,4,4-tetraethyl-2,5-diphenyl-1,4-digermacyclohexa-2,5-dienes. The crude solution was chromatographed over silica-gel to give a 1:1 mixture of

1,1,4,4-tetraethyl-2,5-diphenyl-1,4-digermacyclohexa-2,5-diene and 1,1,4,4-tetraethyl-2,6-diphenyl-1,4-digermacyclohexa-2,5-diene (75% isolated yield).

3.11. Reactions of 1,2-digermacyclobut-3-ene (**2b**) with one mol equiv of $[Pd(PPh_3)_4]$

In a Pyrex NMR tube with a septum seal were placed 1,2-digermacyclobut-3-ene (**2b**) (0.62 mg, 1.73 μ mol), $[Pd(PPh_3)_4]$ (2.0 mg, 1.73 μ mol) and C_6D_6 (0.7 ml) carefully degassed and sealed under vacuum. The sealed tube was allowed to stand at 23 °C for 30 min. 1H NMR (δ , CD_2Cl_2 , 23 °C) 0.01–1.23 (m, 20H), 6.90–7.79 (m, 36H); ^{31}P NMR (δ , C_6D_6 , 23 °) 13.9 (br); ^{13}C NMR (δ , CD_2Cl_2 , 23 °C) 12.22, 12.33, 13.64, 13.75, 124.4, 126.5, 127.2, 127.4, 129.2, 129.4, 131.7, 134.1, 134.2, 135.5, 147.9, 150.5, 165.1.

3.12. Reactions of 1,4-digermabut-2-ene-1,4-diylpalladium with phenylacetylene

To an NMR tube containing 1,4-digermabut-2-ene-1,4-diylpalladium ((**2b** (8 μ mol), $[Pd(PPh_3)_4]$ (8 μ mol)), 10 mol equiv of phenylacetylene (80 μ mol) was added under argon atmosphere. The reaction products formed were identified by means of NMR. The reaction mixture was separated by preparative silica-gel TLC eluted with hexane (ca. 1.0 mg, 2 μ mol).

3.13. Reactions of Z - α,β -(dimethylgermyl)styrene with η -ethylene)bis(triphenylphosphine)

A solution of bis(dimethylgermyl)styrene (161 mg, 521 μ mol), (η -ethylene)bis(triphenylphosphine)platinum (208 mg, 278 η mol) in degassed toluene (4 ml) was placed in a 25-ml Schlenk tube. After the mixture was stirred at room temperature for 10 min, toluene was removed under reduced pressure. After the resulting solid was washed with hexane, a platinum complex **A'** was obtained in pure form (241 mg, 235 μ mol, 84.4% yield). **A'**: 1H NMR (δ , C_6D_6) 0.41 (s with a couple of satellite peaks, $J_{Pt-H} = 15$ Hz, 6H), 0.47 (s with a couple of satellite peaks, $J_{Pt-H} = 15$ Hz, 6H), 6.77–7.64 (m, 35H, phenyl, 1H, CH=); ^{31}P NMR (δ , C_6D_6) 29.0 (d with two satellites, $J_{Pt-P} = 2198$ Hz, $J_{P-P} = 17$ Hz), 29.9 (d with two satellites, $J_{Pt-P} = 2219$ Hz, $J_{P-P} = 17$ Hz); ^{13}C NMR (δ , CD_2Cl_2) 4.1, 5.8, 124.8, 126.7, 127.5, 127.7, 127.8, 128.4, 129.5, 134.1, 134.2, 134.4, 135.2, 135.7, 146.5, 152.1. Anal. Calc. for $C_{48}H_{48}Ge_2P_2Pt$: C, 56.13; H, 4.71. Found: C, 56.22; H, 4.92%.

3.14. Reactions of 1,4-digermabut-2-ene-1,4-diylplatinum with phenylacetylene

In an NMR tube with a septum seal were placed 1,4-digermabut-2-ene-1,4-diylplatinum (20 mg, 19.4 μ mol),

phenylacetylene (21 μ L, 194 μ mol) and C_6D_6 (0.7 ml) at ambient temperature. After bubbling with argon through a needle to remove oxygen, they were allowed to stand at room temperature for 10 min. The reaction mixture was separated by preparative silica-gel TLC eluted with hexane (8.6 mg, 18.4 μ mol, 95% yield, **4I**/**4II** = 4/3).

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