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A 3,4-benzo-1,2-germacyclobut-3-ene and related compounds. Palladium-catalyzed σ-metathesis, dehydrogenative coupling and hydrogermylation of the Ge–Ge σ-bond

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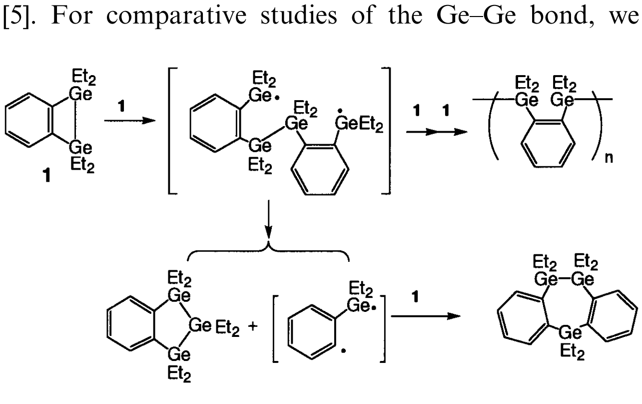
Abstract

In the presence of catalytic amounts of $Pd(PPh_3)_4$, 3,4-benzo-1,1,2,2-tetraethyl-1,2-germacyclobut-3-ene (**1**) readily undergoes the reversible σ-bond metathesis to give a dimer, 1,2,5,6-dibenzo-3,4,7,8-tetragermacycloocta-1,5-diene (**6**) below 100°C. However, at 160°C in toluene containing catalytic amounts of $Pd(PPh_3)_4$, both **1** and **6** afford an unsymmetrical dimer, 1,2,4,5-dibenzo-3,6,7,8-tetragermacycloocta-1,4-diene (**8**) with two isomeric products. In the presence of $Pd(PPh_3)_4$, 1,2-bis(diethylgermyl)benzene (**18**) undergoes dehydrocouling to give **1**, which is smoothly converted to **6** under these conditions. The metal-metal σ-bonds of **1** and its silicon analogue are highly susceptible to hydrogermylation but not to hydrosilylation in the presence of $Pd(PPh_3)_4$.

Keywords: Benzo-1,2-germacyclobutene; 1,2-Germacyclobutene; Metathesis; σ-Bond metathesis; 1,2-Silacyclobutene; Hydrogermylation; Germanium compound; Organogermane

1. Introduction

Reactions of a Si–Si bond with various kinds of transition metal complexes have been investigated extensively and now constitute one of the most useful methods to form a new Si–Si bond or Si–C bond [1]. However, much less studies have been carried out on the chemistry of its higher homologue Ge–Ge bond [2]. Recently, to examine the chemical properties of the activated Ge–Ge bond in detail [3], we have prepared the readily accessible organogermacycle, 3,4-benzo-1,1,2,2-tetraethyl-1,2-germacyclobut-3-ene (**1**) in which the Ge–Ge bond is activated primarily by ring strain [4]. As expected, **1** is highly reactive and undergoes thermo-chemical ring-opening polymerization to give polymers with molecular weight of hundreds of thousands. Furthermore on thermolysis **1** undergoes formally redistribution of a diethylgermylene unit to yield 4,5-benzo-1,2,3-trigermacyclopent-4-ene and 3,4,6,7-dibenzo-1,2,5-trigermacyclohept-3,6-diene, respectively as shown in Scheme 1. In this report we describe the chemical properties of the Ge–Ge bond of **1** toward a transition metal complex, in particular a palladium complex; insertion, σ-bond metathesis, hydrogermylation and hydrosilylation of the Ge–Ge bond along with dehydrocoupling of 1,2-bis(diethylgermyl)benzene (**18**) [5]. For comparative studies of the Ge–Ge bond, we



Scheme 1.

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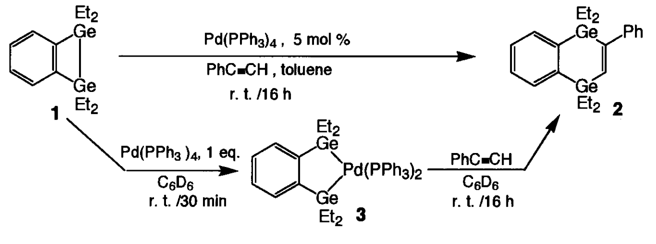
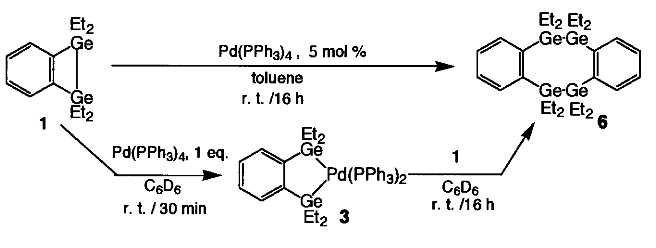


Scheme 2.



Scheme 3.

have also examined hydrogermylation and hydrosilylation of the Si–Si bond of a silicon analogue, 3,4-benzo-1,1,2,2-tetramethyl-1,2-disilacyclobut-3-ene **4a** [6]. On the other hand, much attention has been devoted to chemistry of 3,4-benzo-1,2-disilacyclobutenes **4**, the silicon analogue of **1** toward transition–metal complexes [7,8]. In addition to transition-metal induced cycloaddition with unsaturated compounds, recently the intermolecular metathesis of the Si–Si bond coupled with interesting isomerization of the dimer formed has been reported [8b].

2. Results and discussion

*2.1. Insertion of phenylacetylene into the Ge–Ge bond of **1** in the presence of Pd(PPh$_3$)$_4$*

As reported, thermolysis of **1** in the presence of phenylacetylene in toluene gave 2,3-benzo-4-phenyl-1,1,4,4-tetraethyl-1,4-digermacyclohexa-2,5-diene (**2**) in 91% yield [4]. Here, in the presence of a catalytic amount of Pd(PPh$_3$)$_4$ the reaction of **1** with phenylacetylene at ambient temperature also afforded **2** in 88% as a sole product (Scheme 2). To examine intervention of the intermediate such as 3,4-benzo-1-pallada-2,5-digermacyclopent-3-ene **3**, first **1** and one equivalent of Pd(PPh$_3$)$_4$ in C_6D_6 were placed in an NMR tube at room temperature and after 30 min inspection of the ^{1}H-NMR spectrum showed that most of **1** in the reaction mixture disappeared and instead the complex **3** was formed quantitatively. Then, a slightly excess amount of phenylacetylene was added into the NMR tube under argon, and after 16 h at room temperature the ^{1}H-NMR spectrum showed that the reaction of **3** with the acetylene added afforded **2** in a quantitative manner. The structure of **3** was confirmed by comparing its ^{1}H- and ^{13}C-NMR data with those of related compounds shown in Table 1 [7b]. The ^{13}C-NMR spectrum of **3** displays two peaks, at 12.48 and 14.29 ppm, due to ethyl carbons which locate at higher field than those due to **1**. In addition, there observed three peaks at 127.21, 132.04 and 158.23 ppm due to the symmetrically substituted phenylene carbons and four peaks at 128.48, 129.35, 134.32 and 138.59 ppm assignable to those due to triphenylphosphine.

Naturally, the silicon analog **4a** reacted with phenylacetylene to afford a similar type of the product, 2,3-benzo-1,1,4,4-tetraethyl-1,4-disilacyclohexa-2,5-diene **5** in the presence of catalytic amount of Pd(PPh$_3$)$_4$ [7b].

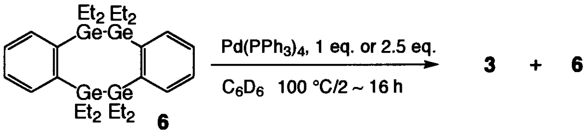
*2.2. Ge–Ge σ-bond metathesis of benzo-1,2-digemacyclobutene **1***

On the other hand, in the presence of a catalytic amount of Pd(PPh$_3$)$_4$ without acetylene, **1** readily underwent Ge–Ge σ-bond metathesis to give a dimer, 1,2,5,6-dibenzo-3,4,7,8-tetragermacycloocta-1,5-diene **6**, which was disclosed to be produced again through **3** (Scheme 3). Structure of **6** is fully compatible with spectral data shown in Table 1. Thus, the ^{1}H and ^{13}C spectra of **6** exhibit only one each kind of signals assignable to the ethyl group on the Ge atom and symmetrically substituted phenylene, respectively and these spectral data indicate **6** to be highly symmetrical [9].

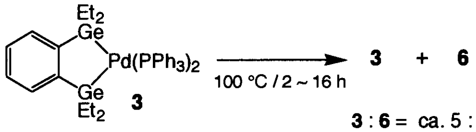
Complex **3** must play an important role also in the dimerization of **1**. After formation of **3** in C_6D_6 being monitored by ^{1}H-NMR, another mole of **1** was added into the NMR tube. After 16 h at ambient temperature complex **3** completely disappeared and instead dimer **6** was formed quantitatively.

For the transition metal-catalyzed σ-bond metathesis [10], the Si–Si σ-bond forming step has been proven to be reversible [11,12]. However in the presence of a catalytic amount of Pd(PPh$_3$)$_4$ a dimer **6** is produced from **1** in a quantitative yield, occurrence of the reverse process, namely, from **6** to **1** is not distinct at all. So, the step from **6** to **3** has been examined in detail. Although at ambient temperature **6** remained unchanged for a long time in the presence of Pd(PPh$_3$)$_4$, **6** and one equivalent of Pd(PPh$_3$)$_4$ in C_6D_6 were heated at 100°C for 2 h and this caused the backward reaction of **6** to **3** to yield the reaction mixture composed of **3** and **6** in the ratio of ca. 2:3 (Eq. (1)).

Furthermore, on the treatment of the (1:2.5) mixture of **6** and Pd(PPh$_3$)$_4$ under similar conditions, the ratio of **6** to **3** was changed to ca. 3:2 (Eq. (1)). This ratio of **6** to **3** remained unchanged on prolonged heating. These observations indicate that **6** should be in equilibrium with **3** and probably **1** under these reaction conditions. However, **1** once formed is so reactive under the conditions and is likely to return readily to **6** probably by the reaction with **3**. Next, the forward reaction from **3** to **6** has been examined by NMR spectroscopy. Thus, **3** once generated in the NMR tube at ambient temperature in C_6D_6 was heated at 100°C for 16 h to afford the mixture composed of **3** and **6** in the 1:1 ratio (Eq. (2)). Furthermore, **3** generated from **6** was finally trapped to yield **2** quantitatively when dimer **6** was heated with a catalytic amount of $Pd(PPh_3)_4$ in the presence of phenylacetylene (Eq. (3)). Here, **6** is not likely to be generated from two molecules of **3** but most reasonably explained by the reaction of **3** with **1** which may be formed first from **3**. In the presence of a catalytic amount of the Pd catalyst, **6** underwent the metathesis at around 100°C in *n*-eicosane and **1** produced was immediately distilled out under the pressure of 0.1 mmHg (Eq. (4)).

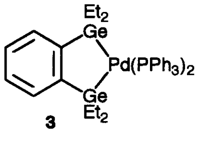
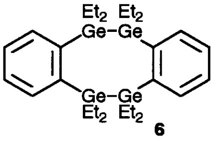
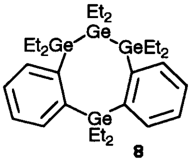
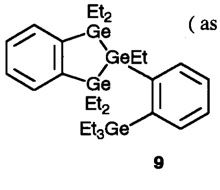
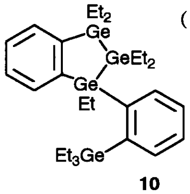


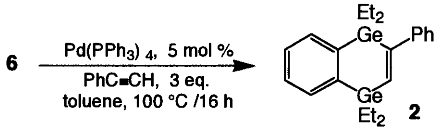
$Pd(PPh_3)_4$ - 1 eq. ; **3** : **6** = ca. 2 : 3
$Pd(PPh_3)_4$ - 2.5 eq. ; **3** : **6** = ca. 3 : 2
(1)



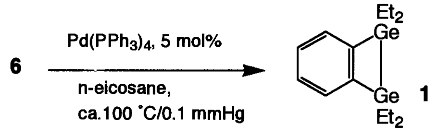
3 : **6** = ca. 5 : 5 (2)

Table 1
NMR and MS spectroscopic data for 3, 6, 8, 9 and 10

	^{1}H NMR (CDCl$_3$, δ ppm)	^{13}C NMR (CDCl$_3$, δ ppm)	MS m/z (rel. intensity)
 **3**	(C_6D_6) 0.84 - 0.91, 1.05 - 1.15, 1.25, 6.80 - 7.80	(C_6D_6) 12.48, 14.29, 127.21, 132.04, 158.23, 128.48, 129.35, 134.32, 138.59	
 **6**	1.00 - 1.32, 7.13 - 7.41	8.31, 9.53, 126.91, 134.75, 146.67	(20eV) 647 (M$^+$-Et, ^{74}Ge$_2$, ^{72}Ge$_2$, 3)
 **8**	0.78 - 1.26 , 7.22 - 7.54	5.31, 6.80, 8.45, 9.15, 9.57, 11.85, 126.66, 127.26, 134.32, 135.31, 146.89, 148.38	647 (M$^+$-Et, ^{74}Ge$_2$, ^{72}Ge$_2$, 15)
 **9**	(as a mixture of **9** and **10**) 0.78 - 1.50, 6.97 - 7.58	5.67, 8.22, 8.27, 8.32, 9.07, 9.82, 10.09, 13.13, 126.75, 127.00, 127.21, 133.72, 135.73, 138.25, 144.85, 145.68, 150.87	647 (M$^+$-Et, ^{74}Ge$_2$, ^{72}Ge$_2$, 15)
 **10**	(as a mixture of **9** and **10**) 0.78 - 1.50, 6.97 - 7.58	4.64, 4.93, 5.94, 7.76, 8.06, 9.16, 9.94, 10.13, 10.85, 11.67, 11.69, 12.41, 126.59, 126.97, 127.24, 127.67, 133.57, 134.97, 135.21, 136.78, 145.39, 148.32, 151.45, 151.87	676 (M$^+$, ^{74}Ge$_2$, ^{72}Ge$_2$, 13), 647 (M$^+$-Et, ^{74}Ge$_2$, ^{72}Ge$_2$, 14)



(3)



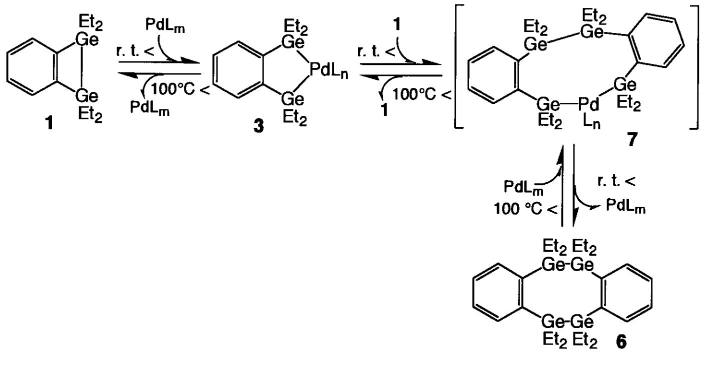
(4)

At even ambient temperature the Ge–Ge bond of **1** readily undergoes oxidative addition with $Pd(PPh_3)_4$ to give bis(germyl)palladium complex **3** and then this reacts with another molecule of **1** to give a dimeric intermediate such as **7**, which is finally converted to **6** by way of reductive elimination of the palladium as shown in Scheme 4. On the other hand, the metathesis of dimer **6** only proceeds at elevated temperature, and so **6** is presumably not strained enough to react smoothly with the Pd complex. However the metathesis of simple Ge–Ge and Si–Si bonds does not occur even at higher temperature with the palladium complex [10], the Ge–Ge bond of **6** should be activated somewhat possibly by the phenylene group coupled with the steric strain caused by the ethyl groups [9]. Thus, insertion of the palladium into the Ge–Ge bond affords **7**, and then this eliminates possibly **1** to afford **3** which is able to give **1** by elimination of the palladium complex at around 100°C.

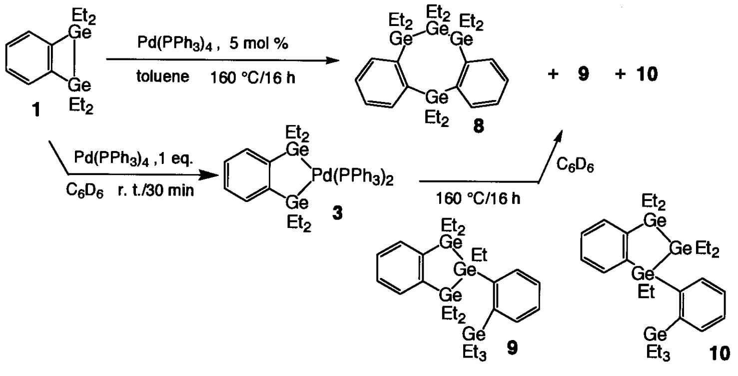
*2.3. Metathesis of benzo-1,2-digemacyclobutene **1** at higher temperature*

So, at around 100°C **6** goes back competitively to give **3** and probably **1** by way of the metathesis as shown in Scheme 4. Furthermore, at 160°C in toluene in a sealed tube containing a catalytic amount of $Pd(PPh_3)_4$, **1** gave unsymmetrical dimer, 1,2,4,5-dibenzo-3,6,7,8-tetragermacycloocta-1,4-diene **8** in 24% yield together with two minor isomers **9** and **10** in 9 and 4% yields, respectively as shown in Scheme 5. Bis(germyl)palladium **3** once generated in an NMR tube was transferred into a sealed tube and was heated at 160°C for 16 h to afford dimer **8**. Meanwhile under similar conditions symmetrical dimer **6** was also converted to the unsymmetrical dimer **8** in 38% yield, and at the same time two minor isomers **9** and **10** were also isolated in 9 and 4% yields, respectively.

The structure of the dimer **8** was determined based on the spectroscopic data described in Table 1. Thus, **8** shows the molecular ion peak corresponding to that of the dimer of **1**. In higher field region, the ^{13}C-NMR of **8** shows six resonances at 5.31, 6.80, 8.45, 9.15, 9.57, and 11.85 ppm in 1:2:1:1:2:1 ratio indicating **8** to have



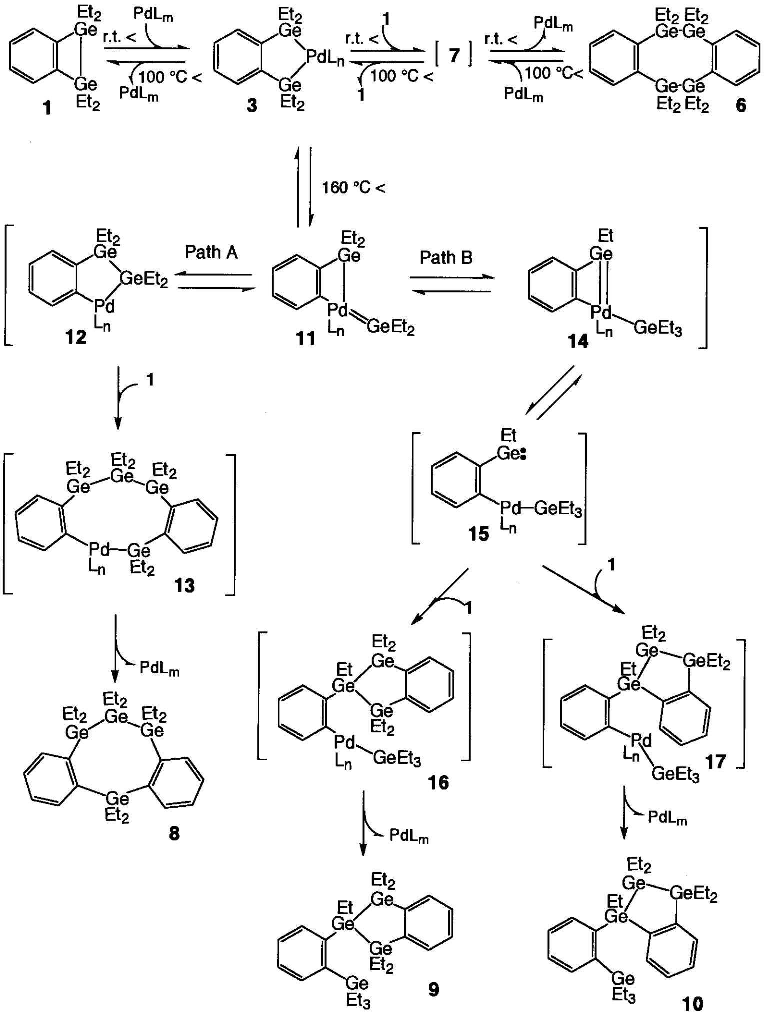
Scheme 4.



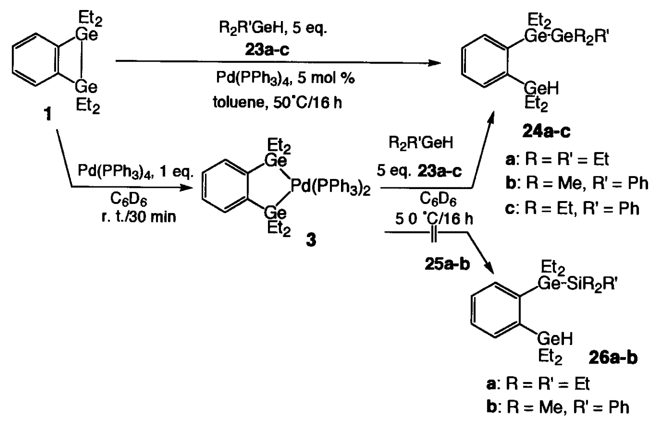
Scheme 5.

three kinds of the ethyl group on the germanium atoms in 1:1:2 ratio in the molecule. On the other hand, in lower field region, there are six peaks at 126.66, 127.26, 134.32, 135.31, 146.89, and 148.38 ppm assignable to those due to the phenylene group substituted unsymmetrically. The silicon analog **4a** has been reported to give the dimeric product having analogous structure to that of **8** [7b,8b]. In the thermolysis, two minor isomers **9** and **10** were isolated along with **8** and their structures were also assigned based on the spectroscopic data shown in Table 1.

On the thermolyses of **1** and dimer **6** at 160°C, the ratios of **8**, **9**, and **10** obtained are quite similar in both cases. This is reasonably interpreted that these three products must be formed after the equilibrium in Scheme 4 being established. Careful examination of the molecular structure of unsymmetrical dimer **8** indicates that at least one of the Ge-phenylene linkages should be cleaved by possibly the palladium catalyst during thermolysis. On the other hand, to the two isomers **9** and **10** being constructed one of the ethyl groups on the germanium should be shifted to the other germanium atom and this leads to give EtGe and Et_3Ge groups, respectively. This type of rearrangement on silicon and germanium atoms is reported to occur by way of silylene and germylene complexes [13,14]. So we assume that the transformations observed here proceed by way of a key intermediate germylene complex **11** as described in Scheme 6. At around 100°C the equilibrium among **1** and **6** has been readily established through palladium complexes **3** and **7**. At higher temperature one of the phenylene carbons of the complex **3** rearranges from the germanium atom to the palladium center to give a germylene complex **11** which is conceivable to participate in the equilibrium as shown in Scheme 6. Now, the release of the ring strain of **11** facilitates isomerization to **12** that is the positional isomer of **3** (Path A). Activated Ge–Ge bond of **1** is expected to react readily with the Pd–Ge bond of **12** to give intermediate **13** that affords unsymmetrical dimer **8** with reductive elimination of palladium. On the other hand, in key intermediate **11**, another type of rear-



Scheme 6.



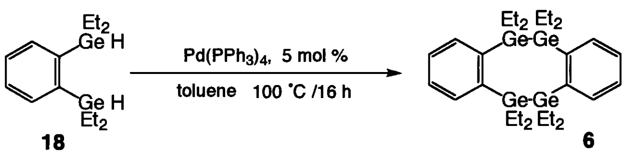
Scheme 7.

rangement, namely the ethyl group on the sp^3 germanium atom shifts to the sp^2 germanium to give another germylene complex **14** (Path B) [13]. Since a metal–metal double bond, such as a silicon–silicon double bond is well known to be cleaved thermally to give divalent species, a silylene [15], **14** is expected reasonably to be transformed to a germylene **15**. Now, germylene **15** readily inserts into either the Ge–Ge or Ge-phenylene bond to give **16** or **17**. Finally the reductive elimination would afford **9** from **16**, and **10** from **17**, respectively.

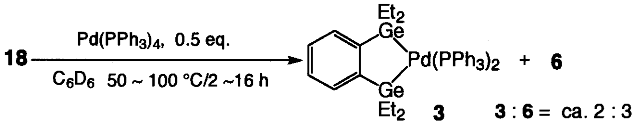
For silicon analogue **4a**, a similar type of the intermolecular metathesis followed by the isomerization to the unsymmetrical dimer analogous to dimer **8** has been reported with a plausible mechanism [8b].

*2.4. Dehydrocoupling of 1,2-bis(diethylgermyl)benzene (**18**) and hydrogermylation of benzo-1, 2-digemacyclobutene **1** and related silane **4b***

As expected from a silicon analogue, 1,2-bis-(dimethylsilyl)benzene (**26**), in the presence of $Pd(PPh_3)_4$ 1,2-bis(diethylgermyl)benzene (**18**) underwent dehydrocoupling [2e,16] and was also smoothly converted to **6** probably by way of palladium complex **3** [17]. Actually being heated in toluene containing the palladium catalyst at 100°C for 16 h **18** afforded dimer **6** in 82% yield (Eq. (5)). The reaction path was followed by ^{1}H-NMR spectroscopy, and in fact this showed that even at 50°C **18** was converted to **3** and then dimer **6** was formed slowly from **18** by way of **3**. When **18** was reacted with 0.5 equivalent of $Pd(PPh_3)_4$ at 100°C to give the reaction mixture composed of **3** and **6** in around 2:3 ratio (Eq. (6)). The ratio is close to those obtained from thermolyses of **1**, **3**, and **6**, respectively, under similar conditions as mentioned (Eq. (1)). This implies that the equilibrium ($1 \rightleftarrows 3 \rightleftarrows 6$) should be established also under these reaction conditions.



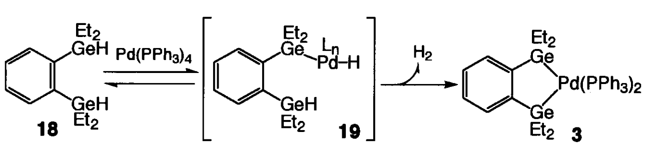
(5)



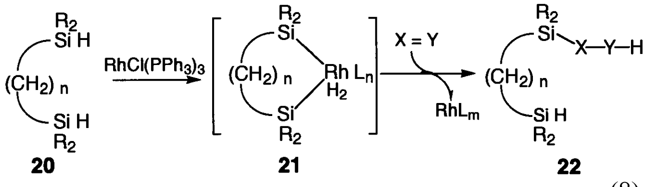
(6)

At first, the insertion of palladium occurs into one of the Ge–H bonds of **18** to afford intermediate **19** and subsequently insertion of another Ge–H bond followed by dehydrogenation would give **3** (Eq. (7)). The silicon analogue **26** has been reported to undergo a similar type of dehydrogenation to give the corresponding bis-silylated metal complex in the presence of a low coordinated catalyst such as ethylene platinum complex $Pt(CH_2{=}CH_2)(PPh_3)_2$ but not high coordinated complex such as $Pd(PPh_3)_4$ [17]. This is due to the fact that in general a hydrogermane is more reactive than a hydrosilane toward a transition metal complex.

Hydrosilane **20** having two hydrosilyl groups in the molecule has been reported to undergo the hydrosilylation of olefins with a rhodium catalyst such as $RhCl(PPh_3)_3$ more efficiently when the two hydrosilane moieties are connected by two or three atoms [17c]. This is ascribed to the formation of an intermediate **21** having a chelate ring which would undergo readily hydrosilylation to give **22** as illustrated in Eq. (8). In this respect, higher reactivity of **18** toward catalytic dehydrogenation is conceivable that the two hydrogermyl groups are connected with a two carbon atom unit each other. Hence **18** forms the chelate ring quite readily and this leads its facile conversion to **3**. In fact monohydrogermane such as diethylphenylgermane (**23c**) is quite unreactive in the presence of $Pd(PPh_3)_4$ toward dehydrogenation.



(7)

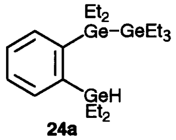
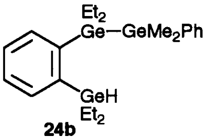
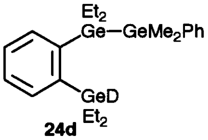
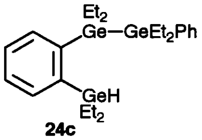


(8)

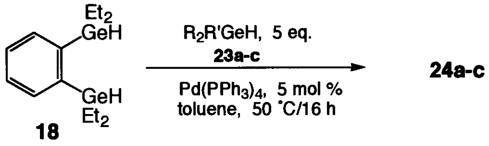
The Ge–Ge bond of **1** was subjected to hydrogermylation with the palladium catalyst in the presence of excess amounts of hydrogermane **23** at 50°C for 16 h and this afforded **24** in high yields as shown in Scheme 7 [18a]. The ^{1}H-NMR spectrum of the reaction mixture of **3** and excess amounts of hydrogermane **23** showed clean conversion to **24**. This indicates that **3** should be the intermediate of hydrogermylation of this type. The structure of **24** has been fully established on the basis of spectroscopic data summarized in Table 2. Interestingly, **3** did not react with hydrosilanes **25** such as triethylsilane (**25a**) and dimethylphenylsilane (**25b**) [18b,c]. Palladium complex **3** generated first in an NMR tube was allowed to react with excess amounts of the hydrosilane **25**. However the ^{1}H-NMR spectrum showed no resonance due to that of **26** but only the presence of **3** and dimer **6** in the reaction mixture as observed in the absence of hydrosilane **25**.

Similarly, in the presence of large excess amounts of hydrogermane **23** bis(hydrogermyl)benzene **18** was readily converted to **24** by the treatment with the palladium catalyst in high yields (Eq. (9)). Meanwhile, this constitutes formally dehydrocoupling of the two hydrogermanes **18** and **23** by the palladium catalyst, interestingly only the cross coupling reaction between **18** and **23** has been observed. In conformity with this, in the absence of **18**, the simple hydrogermane **23** and hydrosilane **25** turned out to be unreactive even in the presence of the palladium catalyst. This would be attributable to the lack of driving force leading to formation of the chelate ring such as that of **3**. Furthermore, highly reactive **18** underwent the catalytic self-coupling to give a dimeric product **6** in the absence of hydrogermane **23**. So, since **6** should be formed by way of key intermediate **3** that would preferentially react with hydrogermane **23** but not with **18**. This may be simply due to the concentration of **23** being higher than that of **18**. As expected, the hydrogermynation with deuterated hydrogermane **23d** gave only mono-deuterated product

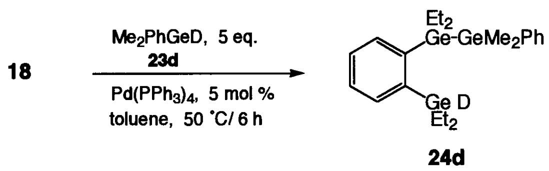
Table 2
NMR and MS spectroscopic data for 24a, 24b, 24c and 24d

	^{1}H NMR (CDCl$_3$, δ ppm)	^{13}C NMR (CDCl$_3$, δ ppm)	MS m/z (rel. intensity)
 **24a**	0.87 - 1.26, 4.56, 7.21 - 7.50	5.48, 6.03, 7.66, 9.79, 9.82, 9.98, 126.83, 127.47, 134.57, 135.05, 145.51, 148.04	469 (M^{+}-Et, ^{74}Ge, ^{72}Ge$_{2}$, 6), 339 (M^{+}-Et$_{3}$^{72}Ge, ^{74}Ge, ^{72}Ge, 100)
 **24b**	0.53, 0.92 - 1.27, 4.48, 7.21 - 7.43	-1.71, 5.91, 7.47, 9.79, 9.96, 127.10, 127.53 127.66, 127.76, 133.55, 134.68, 135.22, 142.71, 145.73, 146.64	489 (M^{+}-Et, ^{74}Ge, ^{72}Ge$_{2}$, 4), 339 (M^{+}-Me$_{2}$Ph^{72}Ge, ^{74}Ge, ^{72}Ge, 100)
 **24d**	0.53, 0.92 - 1.27, 7.21 - 7.43	-1.71, 5.79, 7.46, 9.79, 9.95, 127.10, 127.53, 127.66, 127.76, 133.55, 134.70, 135.21, 142.71, 145.68, 146.64	490 (M^{+}-Et, ^{74}Ge, ^{72}Ge$_{2}$, ^{2}H, 1), 340 (M^{+}-Me$_{2}$Ph^{72}Ge, ^{74}Ge, ^{72}Ge, ^{2}H, 100)
 **24c**	0.92 - 1.25, 4.47, 7.20 - 7.44	5.92, 6.14, 7.74, 9.71, 9.74, 9.95, 126.98, 127.50, 127.53,127.66, 134.34, 134.63, 135.16, 140.55, 145.73, 147.20	517 (M^{+}-Et, ^{74}Ge, ^{72}Ge$_{2}$, 3), 339 (M^{+}-Et$_{2}$Ph^{72}Ge, ^{74}Ge, ^{72}Ge, 100)

24d in high yields (Eq. (10)). This clearly indicates that at first **18** was converted to **3** which reacts with deuterated hydrogermane **23d** to afford **24d** in 72% yield.

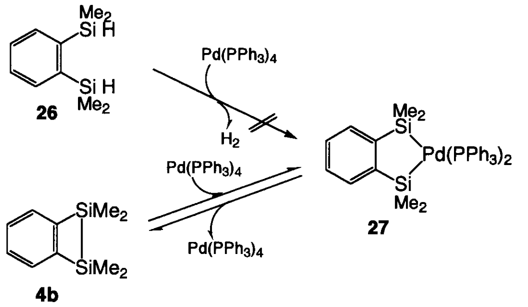


(9)

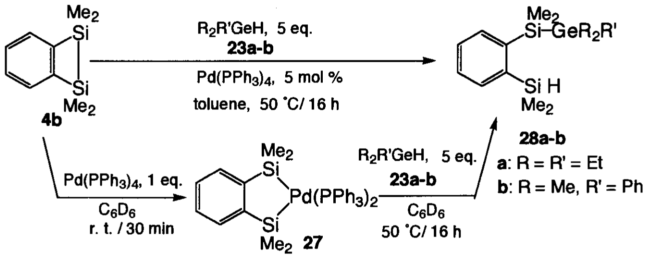


(10)

1,2-Bis(hydrosilyl)benzene **26** is unreactive to $Pd(PPh_3)_4$ but benzo-1,2-disilacyclobutene **4** is readily converted to the corresponding palladium complex **27** as shown in Scheme 8 [17d]. For comparative studies of the reactivity of germanium complex **3**, reactions of the corresponding silicon analog **27** with hydrogermane **23** and hydrosilane **25** have been examined. As summarized in Scheme 9, in the presence of a catalytic amount of $Pd(PPh_3)_4$ benzodisilacyclobutene **4b** was reacted at 50°C for 16 h with excess amounts of hydrogermanes **23** to afford hydrogermylated products **28** in 70–80% yields. Bissilylated complex **27** prepared first at room temperature was allowed to react readily with excess amounts of hydrogermane **23** at 50°C to give **28**, and this indicates that as in the case of germanium analog **3**, **27** should be the key intermediate of the hydrogermylation. The structures of **28a–b** are fully compatible with spectroscopic data shown in Table 3. As in the case of germanium analogue **1**, **4b** was reacted with deuterated hydrogermane **23d** to give only **28d** having a Ge–Si



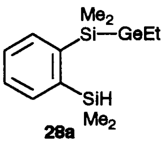
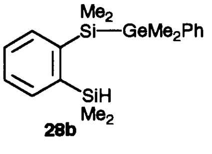
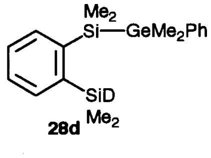
Scheme 8.



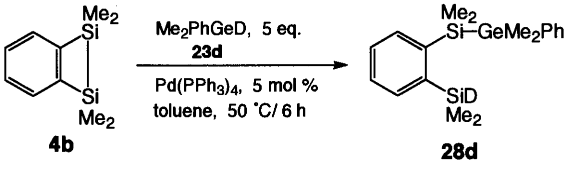
Scheme 9.

Table 3

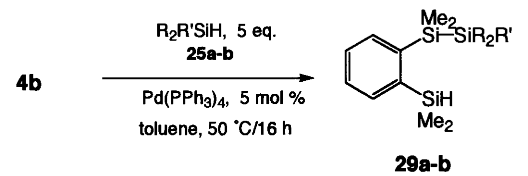
NMR and MS spectroscopic data for 28a, 28b and 28d

	^{1}H NMR (CDCl$_3$, δ ppm)	^{13}C NMR (CDCl$_3$, δ ppm)	MS m/z (rel. intensity)
 **28a**	0.32, 0.50, 0.78 - 0.97, 4.69, 7.29 - 7.54	-2.36, 0.94, 4.33, 9.81, 127.61, 128.15, 134.14, 134.28, 144.43, 146.63	339 (M^+-Me, ^{74}Ge, 2), 325 (M^+-Et, ^{74}Ge, 21), 193 (M^+-Et$_3$^{74}Ge, 100)
 **28b**	0.22, 0.41, 0.46, 4.59, 7.21 - 7.52	-3.35, -2.52, -0.03, 127.49, 127.71, 127.92, 128.22, 133.68, 134.20, 134.44, 142.51, 144.79, 144.91	359 (M^+-Me, ^{74}Ge, 0.4), 193 (M^+-Me$_2$Ph^{74}Ge, 100)
 **28d**	0.22, 0.41, 0.46, 7.21 - 7.52	-3.33, -2.59, -0.03, 127.49, 127.70, 127.91, 128.20, 133.67, 134.21, 134.42, 142.50, 144.75, 144.89	360 (M^+-Me, ^{74}Ge, ^{2}H, 3), 194 (M^+-Me$_2$Ph^{74}Ge, ^{2}H, 100)

bond in 72% yield (Eq. (11)). On the other hand hydrosilylation of **4b** with hydrosilanes **25** did not proceed smoothly. Actually, in the presence of the palladium catalyst **4b** did not give **29a** with triethylsilane **25a** but it gave **29b** with dimethylphenylsilane **25b** in only 17% yield (Eq. (12)). However, the tetraethyl derivative of **4**, 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobutane **4a** has been reported to give the hydrosilylated product in 31% yield with **25a** and 52% yield with **25b** at higher temperature 150°C [5c].



(11)

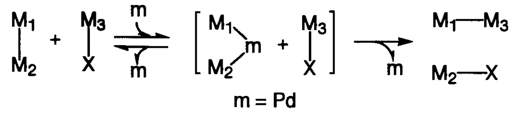


(12)

a: R = R' = Et
b: R = Me, R' = Ph

The hydrogermylation described can be conceivable to proceed in a similar manner as the metathesis of a Ge–Ge bond as shown in Eq. (13). Benzopallada-digemacyclopentene **3** reacts with hydrogermane **23** to form an intermediate **30** having a newly formed Ge–Ge bond (Eq. (14)). This undergoes reductive elimination to afford **24**. The corresponding silicon analogue **27** shows similar reactivities to give **28** and **29** as mentioned above. In conformity with Eq. (14), the deuterium of hydrogermane **23d** is transferred to one of the germanium atoms of product **24d** together with formation of a new Ge–Ge bond.

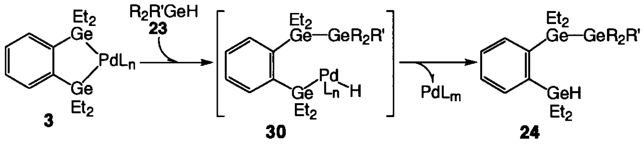
Formation of **24d** suggests that the Ge–Pd and Ge–H bonds may be activated in two ways as illustrated in Scheme 10. At first, in the transition state such as **31** these bonds are simultaneously activated in a five-centered manner [19]. In conformity with this, recently a tetrakis(silyl)platinum (IV) complex has been isolated and characterized during the studies of reactions of disilylbenzene with a platinum(0) complex [17c]. Although the substituents on silicon atoms in the platinum complex are all hydrogens in the model system, there seems to be enough room to accommodate the required five-centered transition state **31** for the germanium systems. Then, the corresponding product of the σ-bond metathesis and the dehydrocoupling will be formed after the reductive elimination of the central metal. On the other hand, there seems to be another possible transition state, namely four-centered transition state **32** proposed for the dehydrocoupling of hydrosilanes by early transition metal catalysts [20,21]. Since the metathesis, the dehydrocoupling and the hydrometalation observed above are conceivable to be sorts of concerted [2 + 2] cycloaddition reactions, the transition states for these processes may be depicted as **32**. Unlike the case of early-transition metal catalyzed dehydrocoupling the corresponding product will be produced formally after reductive elimination of the central metal.



m = Pd

(13)

σ-Bond Metathesis : M = X = Si or Ge
Hydrometalation to M-M bond : M = Si or Ge, X = H

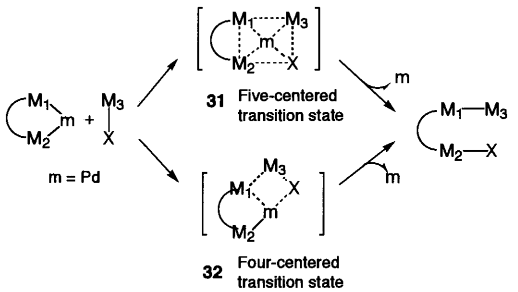


(14)

3. Experimental

3.1. General methods

All reactions were carried out under an atmosphere of argon. THF and toluene were dried by refluxing over sodium benzophenone ketyl and distilled just before use. GLC-analyses were carried out on a Shimadzu GC-14A equipped with an FID detector and a 0.25 mm × 25 m CBP1 capillary column. Gel permeation chromatography was used for separation of reaction products using a series of JAIgel 1H and 2H columns with a flow of toluene on an LC-908 liquid chromatograph of Japan Analytical Industry Co. Ltd. NMR spectra were obtained on Varian Unity plus 300 and 500 MHz spectrometers. Mass spectral data were measured on a Shimadzu QP-1000 and High-resolution mass spectral data were obtained on a Hitachi M-2500 spectrometers.



σ-Bond Metathesis : M = X = Si or Ge
Hydrometalation to M-M bond : M = Si or Ge, X = H

Scheme 10.

Tetrakis(triphenylphosphine)palladium, dimethylphenylsilane, and triethylsilane were purchased and were used as received. Et_3GeH, Me_2PhGeH and Et_2PhGeH were prepared by $LiAlH_4$ reduction of the corresponding chlorogermanes derived from tetrachlorogermane. Me_2PhGeD was prepared by reduction of $Me_2PhGeCl$ with $LiAlD_4$. 3,4-Benzo-1,1,2,2-tetraethyl-1,2-digermabut-3-ene [4], 1,2-bis(diethylgermyl)benzene [4], 3,4-benzo-1,1,2,2-tetramethyl-1,2-disilabut-3-ene [6] and 1,2-bis(dimethylsilyl)benzene [22] were prepared according to the literature.

*3.2. Reaction of 3,4-benzo-1,1,2,2-tetraethyl-1,2-germacyclobut-3-ene (**1**) with phenylacetylene in the presence of a catalytic amount of $Pd(PPh_3)_4$*

In a 30 ml two-necked flask fitted with a magnetic stirrer and a reflux condenser were placed **1** (100 mg, 0.30 mmol), $Pd(PPh_3)_4$ (17 mg, 0.015 mmol), phenylacetylene (91 mg, 0.89 mmol), and toluene (5 ml). After stirred for 16 h at room temperature, the reaction mixture was separated by preparative silica gel TLC to give 2,3-benzo-1,1,4,4-tetraethyl-1,4-digermacyclohexa-2,5-diene (**2**, 115 mg, 0.26 mmol, 88%).

*3.3. Reaction of palladium complex **3** formed from **1** and one equivalent of $Pd(PPh_3)_4$ with phenylacetylene*

At first in an NMR tube with a septum seal were placed **1** (10 mg, 0.030 mmol), $Pd(PPh_3)_4$ (34 mg, 0.030 mmol), and C_6D_6 (0.4 ml). After bubbled with argon through a needle to remove oxygen, they were subjected to ultrasonic wave to be dissolved into solution and then allowed to stand for 30 min at ambient temperature. After formation of complex **3** being monitored by ^{1}NMR spectroscopy phenylacetylene (9 mg, 0.089 mmol) was added to the tube. After 6 h, ^{1}H- and ^{13}C-NMR spectra of **2** were obtained. **3**: ^{1}H-NMR (C_6D_6) δ 0.84–0.91 (m, 4H, CH_2Ge), 1.05–1.15 (m, 4H, CH_2Ge), 1.25 (t, 12H, CH_3, $J = 7.8$ Hz), 6.80–7.80 (m, 64H, aromatic protons); ^{13}C-NMR (C_6D_6) δ 12.48, 14.29 (EtGe), 127.21, 132.04, 158.23 (phenylene ring carbons), 128.48, 129.35, 134.32, 138.59 (phenyl ring carbons).

*3.4. Dimerization of **1** in the presence of a catalytic amount of $Pd(PPh_3)_4$*

In a 30 ml two-necked flask equipped with a magnetic stirrer bar and a reflux condenser were placed **1** (100 mg, 0.30 mmol), $Pd(PPh_3)_4$ (70 mg, 0.015 mmol), and toluene (5 ml) and were stirred at ambient temperature for 16 h. Then, the reaction mixture was separated by preparative TLC (silica gel, hexane) to give **6** (87 mg, 0.13 mmol, 87%). **6**: colorless crystals; m.p. 207–210°C; ^{1}H-NMR($CDCl_3$) δ 1.00–1.32 (m, 40H, EtGe), 7.13–7.41 (m, 8H, phenylene ring protons); ^{13}C-NMR ($CDCl_3$) δ 8.31, 9.53(EtGe), 126.91, 134.75, 146.75, 146.67 (phenylene ring carbons); MS (20 eV) m/z (rel. intensity) 647 ($M^+ - Et$, ^{74}Ge, ^{72}Ge, 3); HRMS calc. for $C_{26}H_{43}{}^{74}Ge_2{}^{72}Ge_2$ ($M^+ - Et$) 647.0230, found 647.0225. Anal. Calc. for $C_{28}H_{48}Ge_4$: C, 49.82; H, 7.17. Found: C, 49.67; H, 6.99%.

*3.5. Reaction of **1** with palladium complex **3***

In an NMR tube with a septum seal were placed **1** (10 mg, 0.030 mmol), $Pd(PPh_3)_4$ (34 mg, 0.030 mmol), and C_6D_6 (0.4 ml). After formation of **3** was monitored by NMR spectroscopy, another lot of **1** (30 mg, 0.089 mmol) was added. After 16 h, formation of dimer **6** was confirmed by the ^{1}H- and ^{13}C-NMR spectra.

*3.6. Reaction of **6** with one equivalent of $Pd(PPh_3)_4$*

In an NMR tube with a septum seal were placed **6** (10 mg, 0.015 mmol), $Pd(PPh_3)_4$ (17 mg, 0.015 mmol), and C_6D_6 (0.4 ml). After bubbled with argon through a needle to remove oxygen, they were subjected to ultrasonic wave. After stood for 16 h at ambient temperature, **6** was shown to remain unchanged by NMR measurements. Then, the NMR tube was heated at 100°C for 2 h and the ^{1}H- and ^{13}C-NMR spectra at this moment indicated that palladium complex **3** and dimer **6** should be found in the ratio of around 2:3 in C_6D_6. The ratio observed here did not change on further heating of the tube. The similar experiment using 2.5 equivalents of $Pd(PPh_3)_4$ gave the ratio of around 3:2 between **3** and **6** on heating at 100°C for 2 h and the ratio was not changed on further heating of the mixture.

*3.7. Reaction of **6** with phenylacetylene in the presence of a catalytic amount of $Pd(PPh_3)_4$*

In a 30 ml two-necked flask equipped with a magnetic stirrer bar and a reflux condenser were placed **6** (50 mg, 0.074 mmol), $Pd(PPh_3)_4$ (4 mg, 0.0037 mmol), phenylacetylene (23 mg, 0.22 mmol) and toluene (5 ml). The reaction mixture was stirred at 100°C for 16 h, and then was separated by preparative TLC (silica gel, hexane) to give **2** (62 mg, 0.14 mmol, 96%).

*3.8. Thermolysis of palladium complex **3***

At first in an NMR tube were placed palladium complex **3** prepared from **1** (10 mg, 0.030 mmol), $Pd(PPh_3)_4$ (34 mg, 0.030 mmol), and C_6D_6 (0.4 ml) at ambient temperature. After degassed and sealed in vacuo, the NMR tube containing **3** was heated at 100°C for 2 h. After allowed to stand for a few hours at ambient temperature its ^{1}H-NMR showed that the ratio of **3** and **6** was around 1:1 in the solution. The ratio remained unchanged on further heating at 100°C.

3.9. Formation of **1** from **6** in the presence of $Pd(PPh_3)_4$

In a 10 ml round flask equipped with a magnetic stirrer and connected to a chilled trap (0°C) by way of a vacuum pump were placed dimer **6** (200 mg, 0.30 mmol), $Pd(PPh_3)_4$ (17 mg, 0.015 mmol), and *n*-eicosane (500 mg). On heated around 100–120°C volatile fractions were distilled into the trap under reduced pressure (0.1 mmHg). Then, these distillates were analyzed to contain a certain amount of **1** by GC and GC-MS.

3.10. Dimerization of **1** at higher temperature (160°C) in the presence of a catalytic amount of $Pd(PPh_3)_4$

In a Pyrex tube **1** (100 mg, 0.30 mmol), $Pd(PPh_3)_4$ (70 mg, 0.015 mmol), and toluene (1 ml) were placed, degassed and sealed in vacuo. The sealed tube was heated at 160°C for 16 h. The reaction mixture was separated by preparative TLC (silica gel, hexane) to give **8** (24 mg, 0.036 mmol, 24%) and the mixture of **9** and **10** (13 mg, **9**: **10** = ca. 2:1). All attempts to separate **9** and **10** by GC and LC failed. **8**: ^{1}H-NMR ($CDCl_3$) δ 0.78–1.26 (m, 40H, EtGe), 7.22–7.54 (m, 8H, phenylene ring protons); ^{13}C-NMR ($CDCl_3$) δ 5.31, 6.80, 8.45, 9.15, 9.57, 11.85 (EtGe), 126.66, 127.26, 134.32, 135.31, 146.89, 148.38 (phenylene ring carbons); MS *m*/*z* (rel. intensity) 647 ($M^+ - Et$, $^{74}Ge_2$, $^{72}Ge_2$, 15); HRMS calc. for $C_{26}H_{43}^{74}Ge_2^{72}Ge_2$ ($M^+ - Et$) 647.0230, found 647.0231. Anal. Calc. for $C_{28}H_{48}Ge_4$: C, 49.82; H, 7.17. Found: C, 49.59; H, 7.01. **9**: ^{1}H-NMR (analyzed as a mixture of **9** and **10**) ($CDCl_3$) δ 0.78–1.50 (m, EtGe), 6.97–7.58 (m, 8H, phenylene ring protons); ^{13}C-NMR ($CDCl_3$) δ 5.67, 8.22, 8.27, 8.32, 9.07, 9.82, 10.09, 13.13 (EtGe), 126.75, 127.00, 127.21, 133.72, 135.73, 138.25, 144.85, 145.85, 150.87 (phenylene ring carbons); MS *m*/*z* (rel. intensity) 647 ($M^+ - Et$, $^{74}Ge_2$, $^{72}Ge_2$, 15). **10**: ^{1}H-NMR (analyzed as a mixture of **9** and **10**) ($CDCl_3$) δ 0.78–1.50 (m, EtGe), 6.97–7.58 (phenylene ring protons); ^{13}C-NMR ($CDCl_3$) δ 4.64, 4.93, 5.94, 7.76, 8.06, 9.16, 9.94, 10.13, 10.85, 11.67, 11.69, 12.41 (EtGe), 126.59, 126.97, 127.24, 127.76, 133.57, 134.97, 135.21, 136.78, 145.39, 148.32, 151.45, 151.87 (phenylene ring carbons); MS *m*/*z* (rel. intensity) 676 (M^+, $^{74}Ge_2$, $^{72}Ge_2$, 13), 647 ($M^+ - Et$, $^{74}Ge_2$, $^{72}Ge_2$, 14).

3.11. Isomerization of **6** in the presence of $Pd(PPh_3)_4$ at higher temperature (160°C)

In a Pyrex tube **6** (100 mg, 0.15 mmol), $Pd(PPh_3)_4$ (9 mg, 0.0074 mmol), and toluene (1 ml) were placed, carefully degassed and sealed in vacuo. The sealed tube was heated at 160°C for 16 h. The reaction mixture was separated by preparative TLC (silica gel, hexane) to give **8** (38 mg, 0.056 mmol, 24%) and the mixure of **9** and **10** (22 mg, **9**: **10** = ca. 2:1).

3.12. Formation of dimer **6** from 1,2-bis(dimethylsilyl)benzene **18** in the presence of $Pd(PPh_3)_4$

In a Pyrex tube **18** (100 mg, 0.29 mmol), $Pd(PPh_3)_4$ (17 mg, 0.015 mmol), and toluene (1 ml) were placed, carefully degassed and sealed in vacuo. The sealed tube was heated at 160°C for 16 h. The reaction mixture was separated by preparative TLC (silica gel, hexane) to give **6** (82 mg, 0.012 mmol, 82%).

3.13. Reaction of **18** with $Pd(PPh_3)_4$

At first in an NMR tube with a septum seal were placed **18** (10 mg, 0.029 mmol), $Pd(PPh_3)_4$ (17 mg, 0.015 mmol), and C_6D_6 (0.4 ml) at ambient temperature. After bubbled with argon through a needle to remove oxygen, they were warmed at 50°C for 16 h. From the ^{13}C-NMR measured molar ratio of **18**, **3** and **6** in the tube were estimated to be around 53:31:16. On the other hand, the ratio between **3** and **6** changed to around 2:3 on heated at 100°C.

3.14. Reactions of **1** with excess amounts of hydrogermanes

In a 30 ml two-necked flask equipped with a magnetic stirrer and a reflux condenser were placed **1** (100 mg, 0.30 mmol), $Pd(PPh_3)_4$ (17 mg, 0.015 mmol), triethylgermane (**23a**) (238 mg, 1.48 mmol) and toluene (5 ml). The reaction mixture was stirred at 50°C for 16 h, and then was separated by preparative TLC (silica gel, hexane) to give **24a** (116 mg, 0.23 mmol, 79%). Similarly, reaction of **1** and dimethylphenylgermane (**23b**) gave **24b** in 80%, and that of **1** and diethylphenylgermane (**23c**) yielded **24c** in 76%. **24a**: a colorless oil; ^{1}H-NMR ($CDCl_3$) δ 0.87–1.26 (m, 35H, EtGe), 4.56 (quint, 1H, $J = 2.8$ Hz, HGe), 7.21–7.50 (m, 4H, aromatic protons); ^{13}C-NMR ($CDCl_3$) δ 5.48, 6.03, 7.66, 9.79, 9.82, 9.98 (EtGe), 126.83, 127.47, 134.57, 135.05, 145.51, 148.04 (aromatic carbons); MS *m*/*z* (rel. intensity) 469 ($M^+ - Et$, $^{74}Ge_2$, $^{72}Ge_2$, 6), 339 ($M^+ - Et_3^{74}Ge$, ^{72}Ge, 100); Anal. Calc. for $C_{20}H_{40}Ge_3$: C, 48.21; H, 8.10. Found: C, 48.24; H, 7.87. **24b**: a colorless oil; ^{1}H-NMR ($CDCl_3$) δ 0.53 (s, 6H, MeGe), 0.92–1.27 (m, 20H, EtGe), 4.48 (quint, 1H, $J = 2.8$ Hz, HGe), 7.21–7.43 (m, 9H, aromatic protons); ^{13}C-NMR ($CDCl_3$) δ −1.71 (MeGe), 5.91, 7.47, 9.79, 9.96 (EtGe), 127.10, 127.53, 127.66, 127.76, 133.55, 134.68, 135.22, 142.71, 145.73, 146.64 (aromatic carbons); MS *m*/*z* (rel. intensity) 489 ($M^+ - Et^{74}Ge$, ^{72}Ge, 4), 339 ($M^+ - Me_2Ph^{74}Ge$, ^{72}Ge, 100); Anal. Calc. for $C_{24}H_{40}Ge_3$: C, 52.76; H, 7.38. Found: C, 52.56; H, 7.39. **24c**: a colorless oil; ^{1}H-NMR ($CDCl_3$) δ 0.92–1.25 (m, 30H, EtGe), 4.47 (quint, 1H, $J = 2.8$ Hz, HGe), 7.20–7.44 (m, 9H, aromatic protons); ^{13}C-NMR ($CDCl_3$) δ 5.92, 6.14, 7.74, 9.71, 9.74, 9.95 (EtGe), 126.98, 127.50, 127.53, 127.66, 134.34, 134.34, 134.63, 135.16, 140.55, 145.73, 147.20 (aromatic carbons); MS m/z (rel. intensity) 517 ($M^+ - Et$, ^{74}Ge, ^{72}Ge, 3), 339 ($M^+ - Et_2Ph^{74}Ge$, ^{72}Ge, 100); Anal. Calc. for $C_{24}H_{40}Ge_3$: C, 52.76; H, 7.38. Found: C, 52.56; H, 7.39%.

*3.15. Reaction of **3** with hydrogermanes*

At first in an NMR tube with a septum seal were placed **1** (10 mg, 0.030 mmol), $Pd(PPh_3)_4$ (34 mg, 0.030 mmol), and C_6D_6 (40 ml). After bubbled with argon through a needle into the solution to remove oxygen, the reaction mixture was allowed to stand for 30 min at ambient temperature.

After palladium complex **3** in the NMR tube was confirmed by ^{1}H-NMR spectroscopy triethylgermane (**23a**) (24 mg, 0.15 mmol) was added into the tube, and was subjected to ultrasonic wave for 30 min. The reaction mixture was heated at 50°C for 16 h. At this moment the ^{1}H- and ^{13}C-NMR spectra of the mixture showed that **24a** was formed. Similarly, in the presence of $Pd(PPh_3)_4$, reactions of **1** with dimethylphenylgermane (**23b**), diethylphenylgermane (**23c**), and deuteriodimethylphenylgermane (**23d**) were shown to yield **24b**, **24c**, and **24d**, respectively. Under similar reaction conditions, reactions of **3** with triethylsilane (**25a**) and dimethylphenylsilane (**25b**) were examined. Thus, NMR spectra of the reaction mixture in the NMR tube obtained as above showed that **3** and the hydrosilanes remained unchanged under these conditions.

*3.16. Reactions of **18** with excess amounts of hydrogermanes in the presence of a catalytic amount of $Pd(PPh_3)_4$*

In a 30 ml two-necked flask equipped with a magnetic stirrer and a reflux condenser were placed **18** (100 mg, 0.29 mmol), $Pd(PPh_3)_4$ (17 mg, 0.015 mmol), diethylphenylgermane (**23c**) (308 mg, 1.47 mmol), and toluene (5 ml). The reaction mixture was stirred at 50°C for 16 h and was separated by preparative TLC (silica gel, hexane) to give **24c** (116 mg, 0.21 mmol, 72%). Similarly, reactions of **18** with triethylgermane (**23a**), dimethylphenylgermane (**23b**), and deuteriodimethylphenylgermane (**23d**) gave **24a**, **24b**, and **24d** in 70%, 72%, and 72% yields, respectively. **24d**: a colorless oil; ^{1}H-NMR ($CDCl_3$) δ 0.53 (s, 6H, MeGe), 0.92–1.27 (m, 20H, EtGe), 7.21–7.43 (m, 9H, aromatic protons); ^{13}C-NMR ($CDCl_3$) δ -1.71 (MeGe), 5.79, 7.46, 9.79, 9.95 (EtGe), 127.10, 127.53, 127.66, 127.76, 133.55, 134.70, 135.21, 142.71, 145.68, 146.64 (aromatic carbons); MS m/z (rel. intensity) 490 ($Et^+ - Et$, ^{74}Ge, ^{72}Ge, ^2H, 1), 340 ($M^+ - Me_2Ph^{72}Ge$, ^{74}Ge, ^{74}Ge, ^{72}Ge, ^2H, 100).

*3.17. Reaction of 2,3-benzo-1,1,2,2-tetramethyl-1,2-disilacyclopent-3-ene (**4b**) with excess amounts of hydrogermanes in the presence of a catalytic amount of $Pd(PPh_3)_4$*

In a 30 ml two-necked flask fitted with a magnetic stirrer and a reflux condenser were placed **4b** (100 mg, 0.52 mmol), $Pd(PPh_3)_4$ (30 mg, 0.026 mmol), triethylgermane (**23a**, 418 mg, 2.60 mmol), and toluene (5 ml). After stirred for 16 h at 50°C, the reaction mixture was separated by preparative silica gel TLC to give **28a** (134 mg, 0.38 mmol, 73%). Similarly, under these conditions, reactions of **4a** with dimethylphenylgermane (**23b**) and deuteriodimethylphenylgermane (**23d**) yielded **28b** and **28d** in 71 and 72% yields, respectively. **28a**: a colorless oil; ^{1}H-NMR ($CDCl_3$) δ 0.32 (d, 6H, $J = 3.8$ Hz, MeSiH), 0.50 (s, 6H, MeSiGe), 0.78–0.97 (m, 15H, EtGe), 4.69 (sep, 1H, $J = 3.8$ Hz, HSi), 7.29–7.54 (m, 4H, phenylene ring protons); ^{13}C-NMR ($CDCl_3$) δ -2.36 (MeSiH), 0.94 (MeSiGe), 4.33, 9.81 (EtGe), 127.61, 128.15, 134.14, 134.28, 144.43, 146.63 (phenylene ring carbons); MS m/z (rel. intensity) 339 ($M^+ - Me$, ^{74}Ge, 2), 325 ($M^+ - Et$, ^{74}Ge, 21), 193 ($M^+ - Et_3^{74}Ge$, 100); Anal. Calc. for $C_{16}H_{32}Si_2Ge$: C, 54.41; H, 8.97. **28b**: a colorless oil; ^{1}H-NMR ($CDCl_3$) δ 0.22 (d, 6H, $J = 3.6$ Hz, MeSiH), 0.41 (s, 6H, MeSiGe), 0.46 (s, 6H, MeGe), 4.59 (sept, 1H, $J = 3.6$ Hz, HSi), 7.21–7.52 (m, 9H, phenylene ring protons); ^{13}C-NMR ($CDCl_3$) δ -3.35 (MeSiGe), -2.52 (MeSiH), -0.03 (MeGe), 127.49, 127.71, 127.92, 128.22, 133.68, 134.20, 134.44, 142.51, 144.79, 144.91 (phenylene ring carbons); MS m/z (rel. intensity) 359 ($M^+ - Me$, ^{74}Ge, 0.4), 193 ($M^+ - Me_2Ph^{74}Ge$, 100); Anal. Calc. for $C_{18}H_{28}Si_2Ge$: C, 57.93; H, 7.56. Found: C, 57.70; H, 7.77. **28d**: a colorless oil; ^{1}H-NMR ($CDCl_3$) δ 0.22 (s, 6H, MeSiD), 0.41 (s, 6H, MeSiGe), 0.46 (s, 6H, MeGe), 7.21–7.52 (m, 9H, phenylene ring protons); ^{13}C-NMR ($CDCl_3$) δ -3.33 (MeSiGe), -2.59 (MeSiD), -0.03 (MeGe), 127.49, 127.70, 127.91, 128.20, 133.67, 134.21, 134.42, 142.50, 144.75, 144.89 (phenylene ring carbons); MS m/z (rel. intensity) 360 ($M^+ - Me$, ^{74}Ge, ^2H, 3), 194 ($M^+ - Me_2Ph^{74}Ge$, ^2H, 100).

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