

Palladium-Catalyzed Addition of Tetragermetanes to Alkynes

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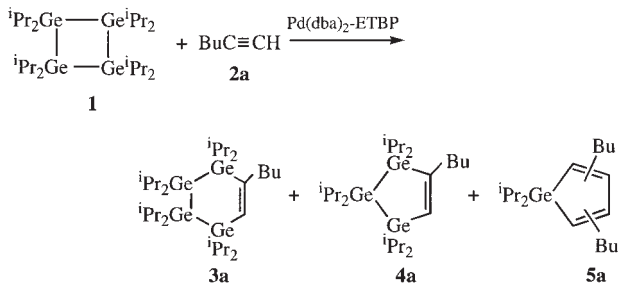
1,1,2,2,3,3,4,4-Octaisopropyltetragermetane $(^{i}Pr_2Ge)_4$ reacted with various alkynes in the presence of palladium complexes at 120 °C to afford 1,2,3,4-tetrahydro-1,2,3,4-tetragermins, Δ^4-1,2,3-trigemolene, and 1*H*-germoles, depending on the kind of alkyne and the palladium complex employed. Terminal alkynes are more reactive than internal ones. $Pd(dba)_2$-ETBP and $Pd(acac)_2$-ETBP systems were found to serve as efficient catalysts. The mechanism of alkyne insertion reactions into the germanium–germanium bonds of $(^{i}Pr_2Ge)_4$ is discussed.

A transition-metal complex-catalyzed addition of a group-14 element (Si, Ge, and Sn) catenates to unsaturated organic compounds is a useful fundamental process in group-14 element chemistry and organometallic chemistry.[1–8] The addition of group-14 element catenates to C–C triple and double bonds, i.e., bis-metallation, has attracted considerable interest in the synthesis of functional molecules and in applications to selective organic synthesis and new materials. For the bis-metallation of C–C triple bonds, palladium complexes have often been used as catalysts. In contrast to the extensive use of their bis-silylation method and considerable studies on reaction mechanisms, there have been few reports on bis-germylation reactions, except for the reaction of strained digermiranes,[9] chlorine-substituted digermanes,[10] and octamethyltrigermanes.[11] Recently, we have reported on the bis-germylation of various alkynes with organodigermanes and cyclic oligogermanes in the presence of platinum complexes.[12] In these studies we characterized bis(germyl)platinum complexes and germyl(germylvinyl)platinum complexes that are assumed to be key intermediates in these platinum-catalyzed processes, and examined their reactivities. However, in the bis-germylation of alkynes with 1,1,2,2,3,3,4,4-octaisopropyltetragermetane $(^{i}Pr_2Ge)_4$ (**1**) the strained, germanium–germanium bonds did not proceed with such platinum complexes. Instead we found that the insertion reaction of alkynes into the germanium–germanium bonds in **1** proceeded readily in the presence of palladium complexes. We report herein on the palladium-catalyzed reaction of the alkynes with **1** and attempt to provide insight into the reaction mechanism.

Results

When a degassed benzene solution of 1 molar amount of 1,1,2,2,3,3,4,4-octaisopropyltetragermetane $(^{i}Pr_2Ge)_4$ (**1**) containing 5 molar amounts of 1-hexyne (**2a**), and a catalytic amount (0.05 molar amount) of $Pd(dba)_2$ containing 0.2 molar amount of ETBP (dba = dibenzylideneacetone, ETBP = 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane) was heated at 120 °C for 16 h, 5-butyl-1,1,2,2,3,3,4,4-octaisopropyl-1,2,3,4-tetrahydro-1,2,3,4-tetragermin (**3a**, 18%), 4-butyl-1,1,2,2,3,3-hexaisopropyl-Δ^4-1,2,3-trigermolene (**4a**, 58%), and 1,1-diisopropy1-1*H*-germoles (**5a**, 39%) were obtained (Eq. 1). The rest of **1** remained unreacted. Concentration of the reaction mixture, followed by recycling preparative HPLC (ODS column), gave pure **3a** and **4a**, which showed satisfactory NMR, IR, and GC-MS data. Tetrahydrotetragermin **3a** contained only a single isomer, assigned to the *cis* configuration. An examination of the molecular models showed that the alternative *trans* form should be highly strained.



(1)

The germoles **5a** contained three isomers, assigned to 1,1-diisopropyl-2,4-dibutyl-1*H*-germole (**5a-1**), 1,1-diisopropy1-3,4-dibutyl-1*H*-germole (**5a-2**), and 1,1-diisopropyl-2,3-dibutyl-1*H*-germole (**5a-3**), in roughly a 5:1:1 ratio. The structures of **5a-1**–**5a-3** were identified based on their NMR and GC-MS spectra, and by comparing the IR and NMR data of similar previously reported compounds (Chart 1).[13,14]

Although the 2,4-disubstituted 1*H*-germole has been previously identified, the remaining two products, 3,4- and 2,3-disubstituted 1*H*-germoles, derived from germylenes, have not been reported.[13,14]

The ^{1}H NMR spectrum of **5a-1** showed two vinylic protons at 5.28 (t, 1H, $J = 1.19$ Hz) and 5.63 ppm (t, $J = 1.28$ Hz, 1H).[13] The ^{1}H NMR spectrum of **5a-2** showed a single vinylic proton at 5.72 ppm (t, $J = 0.92$ Hz, 2H). Compound **5a-3**

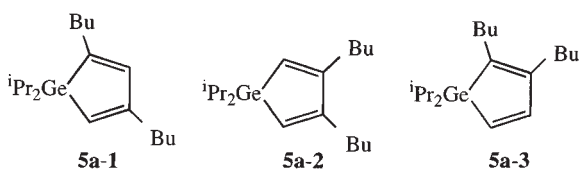


Chart 1.

Table 1. Reactions of 1,1,2,2,3,3,4,4-Octaisopropyltetragermetane (**1**) with 1-Hexyne (**2a**) in the Presence of Palladium Complexes[a)]

Pd complex	Conv./%	Products, Yields/%[b)]		
		3	**4**	**5**
$Pd(PPh_3)_4$	0	0	0	0
$PdCl_2(PPh_3)_2$	0	0	0	0
$Pd(dba)_2$	0	0	0	0
$Pd(dba)_2$ - 2 P(OMe)	5	trace	0	0
$Pd(dba)_2$ - 2 $P(OPh)_3$	5	trace	0	0
$Pd(dba)_2$ - 2 ETBP	18	0	1	15
$Pd(dba)_2$ - 4 ETBP	70	18	69	39
$Pd(acac)_2$	0	0	0	0
$Pd(acac)_2$ - 2 ETBP	78	17	70	52
$Pd(acac)_2$ - 4 ETBP	82	15	67	50

a) **1** (0.01 mol), **2a** (0.05 mmol), Pd complex (0.05 mol. amt. based on **1**), benzene (1 mL), 120 °C for 16 h. b) GC yields.

Table 2. Reactions of 1,1,2,2,3,3,4,4-Octaisopropyltetragermetane (**1**) with Acetylenes (**2**) in the Presence of $Pd(dba)_2$-4 ETBP[a)]

Acetylene (**2**)	Conv./%	Products, Yield/%[b)]		
		3	**4**	**5**
^{n}BuC≡CH (**2a**)	70	18	69	39
$Me(CH_2)_4C{\equiv}CH$ (**2b**)	70	18	69	49
PhC≡CH (**2c**)	—[c)]	26	—[c)]	9
p-$MeC_6H_4C{\equiv}CH$ (**2d**)	97	46	100	61
^{t}BuC≡CH (**2e**)	19	6	0	0
EtOC≡CH (**2f**)	50	2	6	4
$MeO_2CC{\equiv}CCO_2Me$ (**2g**)	42	0	0	0
PhC≡CPh (**2h**)	0	0	0	0
^{n}BuC≡C^{n}Bu (**2i**)	5	0	0	0

a) **1** (0.01 mmol), **2** (0.05 mmol), $Pd(dba)_2$-4 ETBP (0.05 mol. amt. based on **1**), benzene (1 mL) at 120 °C for 16 h. b) GC yields. c) Not determined by GLC.

gave two vinylic proton signals at 5.58 (dt, $J = 1.52$, 18.13 Hz) and 6.16 ppm (dt, $J = 6.41$, 18.13 Hz) in its ^{1}H NMR spectrum. The assignment of **5a-3** was established further by a spin-spin decoupling experiment. Decoupling the methylene signal in the 3-butyl group ($\underline{CH_2}CH_2CH_2CH_3$) at 2.26 ppm caused a collapse of both doublets of triplets for the vinylic protons to a pair of doublets ($J = 18.13$ Hz at 5.58 and 6.16 ppm) for **5a-3**. Decoupling the two vinylic protons at 5.58 and 6.16 ppm as two doublets of triplets causes them to collapse into two triplets ($J = 1.52$ and 6.41 Hz).

Palladium(0) and palladium(II) complexes without containing a phosphite ligand showed no catalytic activity to have the tetragermetane **1** react with 1-hexyne (**2a**), as shown in Table 1. The addition of $P(OMe)_3$ and $P(OPh)_3$ showed a sign of promoting the reaction. A striking enhancement effect of the catalytic reaction was observed upon the addition of ETBP to catalyst systems containing the Pd(0) and Pd(II) complexes. Particularly, when 4 molar amounts of ETBP were used per $Pd(dba)_2$, a considerable increase in the conversion as well as in the yields of the products were observed in comparison with the case where 2 molar amounts of ETBP was employed.

The results suggest that a Pd(0) species having the ETBP ligand serves as the catalytic species. The fact that the Pd(II) complex, Pd(acac), also served as a good catalyst in the presence of added ETBP may be understood as an indication of the occurrence of some type of reduction of the Pd(II) precursor into the Pd(0) catalyst in the catalytic system (vide infra).

The effect of other experimental conditions on the yields of **3a**–**5a** in the present process was examined using the $Pd(dba)_2$-4 ETBP system. Lowering the reaction temperature from 120 to 60 °C resulted in no reaction of **1** with alkynes, while raising the temperature to 150 °C gave lower yields of products **3a**–**5a**, owing to the preferential dimerization of alkynes. Extending the reaction time scarcely improved the yields of products **3a**–**5a**. Increasing in the concentration of $Pd(dba)_2$-4 ETBP relative to **1** did not affect the yields of products **3a**–**5a**.

The reactivities of other terminal and internal alkynes with **1** were also examined with $Pd(dba)_2$-4 ETBP as catalyst, as summarized in Table 2. 1-Heptyne (**2b**) reacted with **1** under similar reaction conditions as those for **2a** to give the corresponding 5-pentyl-1,2,3,4-tetrahydro-1,2,3,4-tetragermin (**3b**, 18%), 4-pentyl-Δ^4-1,2,3-trigermolene (**4b**, 69%), and 1*H*-germoles (**5b**, 49%). Arylacetylenes, such as phenylacetylene (**2c**) and *p*-tolylacetylene (**2d**), reacted with **1** to give the corresponding 5-aryl-1,2,3,4-tetrahydro-1,2,3,4-tetragermins (**3c**, 26% and **3d**, 46%), 4-*p*-tolyl-Δ^4-1,2,3-trigermolene (**4d**, 100%), and 1*H*-germoles (**5c**, 9% and **5d**, 61%), respectively, under similar reaction conditions. The formation of 4-phenyl-Δ^4-1,2,3-trigermolene (**4c**) was detected by means of GC, NMR, and GC-MS, but **4c** could not be isolated in these reaction mixtures. Other terminal alkynes, such as 3,3-dimethyl-1-butyne (**2e**) and ethoxylacetylene (**2f**), gave the corresponding insertion products in low yields. Internal alkynes, such as dimethyl acetylenedicarboxylate (**2g**), diphenylacetylene (**2h**), and 4-octyne (**2i**), proved to be unreactive toward **1** under similar reaction conditions.

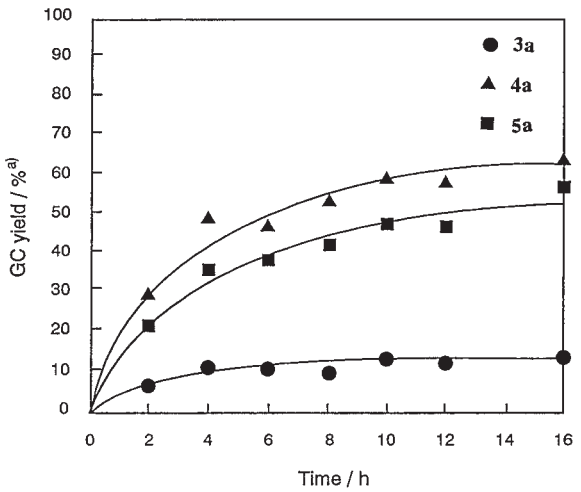
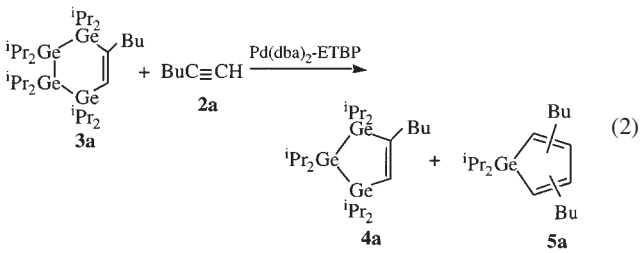


Fig. 1. Time dependence of insertion products, **3a**–**5a**.

The time course of the reaction of **1** with **2a** in the presence of the $Pd(dba)_2$-4 ETBP system, followed by GC, is shown in Fig. 1. The yield of product **3a** increased with the reaction time, but was smaller than those of other compounds, **4a** and **5a**. On the other hand, the yields of products **4a** and **5a** progressively increased at the same time. The formation of **4a**

and **5a** may be accounted for by the palladium-catalyzed bis-germylation of the 1,2,3,4-tetrahydro-1,2,3,4-tetragermin **3** and the palladium–germylene complex mechanism.

In fact, it was confirmed that Δ^4-1,2,3-trigermolene **4a** (47%) and 1*H*-germoles **5a** (5%) were produced upon the thermolysis of **3a** at 120 °C for 48 h in the presence of a catalytic amount of $Pd(dba)_2$-4 ETBP and 5 molar amounts of **2a**. The unreacted **3a** was recovered (55%). In the absence of the $Pd(dba)_2$-4 ETBP system, the reaction of **3a** with **2a** did not give **4a** and **5a** under similar reaction conditions.

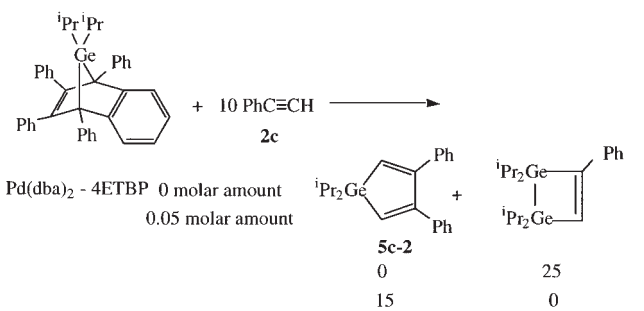


(2)

The formation of the Δ^4-1,2,3-trigermolene **4a** from **3a** indicates that a diisopropylgermylene (^{i}Pr$_2$Ge:) unit is extruded in the platinum-catalyzed thermolysis of the 1,2,3,4-tetrahydro-1,2,3,4-tetragermin **3a**. The extruded germylene is readily trapped with the 1-hexyne **2a** to give **5a**.

The Δ^4-1,2,3-trigermolene **4** is a stable compound, and did not further decompose to release germylenes in the presence of a catalytic amount of $Pd(dba)_2$-4 ETBP when treated with 5 molar amounts of **2a** under similar reaction conditions.

In order to obtain further information on the course of formation of 1*H*-germole **5**, the reactions of free germylenes with alkynes were examined. A benzene solution containing 10 molar amounts of **2c** as alkyne and 11,11-diisopropyl-11-germatricyclo[6.2.1.0^{2,7}]undeca-2,4,6,9-tetraene, which is known to generate free germylene on mild heating, was heated at 80 °C for 3 h. 3-Phenyl-1,1,2,2-tetraisopropyl-Δ^3-1,2-digermetine was formed in 25% yield. Tetraphenylnaphthalene and oligomers containing a diisopropylgermylene unit formed by untrapped germylenes were also detected by GC, HPLC, and NMR analysis. However, when we added a catalytic amount (0.05 molar amount based on the 11-germatricyclo[6.2.1.0^{2,7}]undeca-2,4,6,9-tetraene) of $Pd(dba)_2$-4 ETBP to this benzene solution, 1,1-diisopropyl-3,4-diphenyl-1*H*-germole (**5c**) was exclusively produced under similar reaction conditions in 15% yield (Eq. 3). No Δ^2-1,2-digermetine was detected by means of GC and NMR. The results suggest that germole **5** is the trapping product of germylene liberated in the presence of Pd complexes.



(3)

A similar $Pd(PPh_3)_4$-catalyzed addition of dimethylgermylene to alkynes has been reported by Neumann and co-workers.[14] Thermal reactions of 11,11-dimethyl-11-germatricyclo[6.2.1.0^{2,7}]undeca-2,4,6,9-tetraene with alkynes in the presence of the $Pd(PPh_3)_4$ complex gave 1,1-dimethyl-1*H*-germols and 1,1,4,4-tetramethyl-1,4-dihydro-1,2,3,4-tetragermins in good yields.

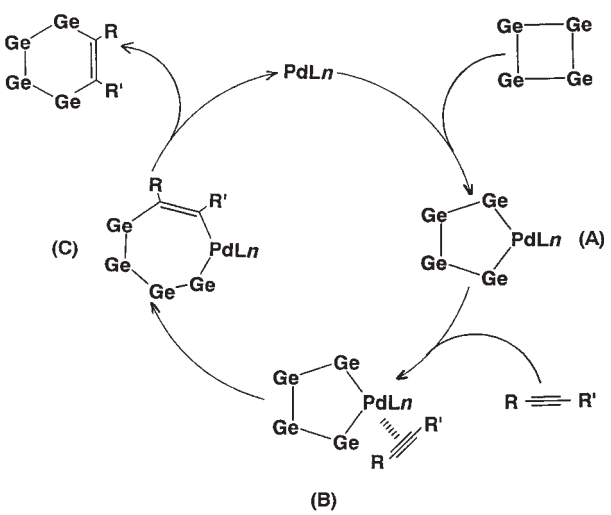
West and co-workers have reported that octaethyltetrasilane $(Et_2Si)_4$ reacts with alkynes in the presence of $Pd(PPh_3)_4$ to give tetrasilacyclohex-1-enes as main products together with small amounts of 1,4-disilacyclohexa-2,5-dienes and trisilacyclopentenes.[15]

Discussion

A mechanism for the Pd-catalyzed insertion reactions of the alkynes into the Ge–Ge bonds of tetragermetane **1** can be proposed in analogy with that suggested by us for the Pt-catalyzed bis-germylation of alkynes with organodigermanes and cyclic oligogermanes.[12] Thus, the catalytic cycle is composed of (a) the oxidative addition of **1** to the palladium species to form a tetragermapalladacyclopentane intermediate (**A**), (b) the coordination of an alkyne to **A** to form an alkyne-coordinated tetragermapalladacyclopentane complex (**B**), (c) the insertion of a coordinated alkyne into one of the Pt–Ge bonds of **1** to form an insertion product (**C**), and (d) the reductive elimination of the 1,2,3,4-tetrahydro-1,2,3,4-tetragermin from the insertion product (**C**) along with the regeneration of the active palladium species, that further carries the catalytic cycle.

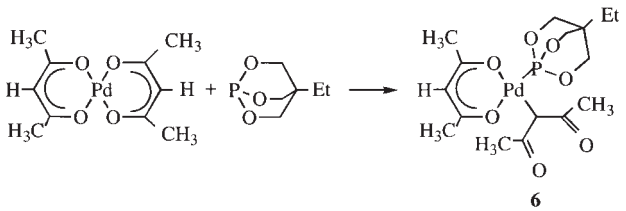
The reason for the particular effectiveness of adding ETBP is not clear, but it may arise from steric and electronic effects of the phosphine ligand. A greater activity enhancement effect of the ETBP ligand than those of the $P(OMe)_3$ and $P(OPh)_3$ ligands may be ascrible to the smaller cone angle of the ETBP ligand,[17] which allows a space to perform the elementary process, as shown in Scheme 1.

Although attempts to identify possible intermediates in the catalytic cycle with NMR were unsuccessful under various conditions, the cycle shown in Scheme 1 involving the Pd(0)–Pd(II) intermediates is compatible with the mechanism proposed for the bis-germylation of alkynes with



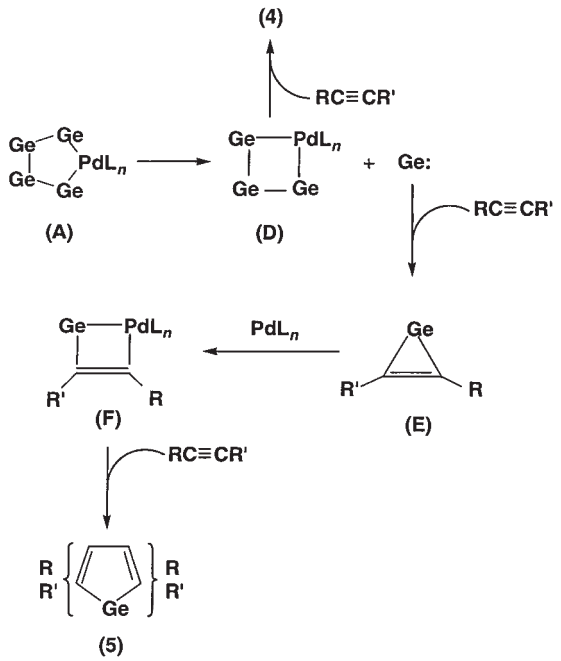
Scheme 1.

digermanes.[12] A puzzling result is that $Pd(acac)_2$ catalyst in combination with ETBP is as effective as the combination of $Pd(dba)_2$ and ETBP. If $Pd(acac)_2$ serves as a catalyst precursor for generating the Pd(0) species, a process for reducing the $Pd(acac)_2$ into Pd(0) species should be involved. A possible course for the development of a catalytically active species is a known conversion of the unusual O-bonded palladium acetylacetonate in which a chelated enol form is changed into a C-bonded acetylacetonato form **6** upon the addition of a base to $Pd(acac)_2$ (Eq. 4). Complex **6**, having C-bonded and O-bonded acetylacetonato ligands, were separately prepared, and its effect was examined. Treatments of **1** with **2a** in the presence of **6** gave a trace amount of **3a** as the alkyne insertion product into **1**. Thus, the real role of the $Pd(acac)_2$ used in combination of ETBP remains to be established.

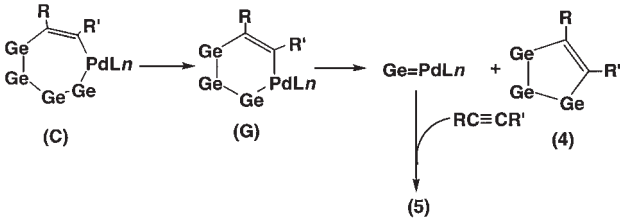


(4)

The course of forming the Δ^4-1,2,3-germolene **4** and 1*H*-germole **5** may be accounted for by the palladium-catalyzed bis-germylation of the 1,2,3,4-tetrahydro-1,2,3,4-tetragermin **3**, followed by reductive elimination, or alternatively, by the elimination of a germylene unit from the putative intermediate **A** in Scheme 1 to form trigermapalladetane **D**, as shown in Scheme 2. The intermediate complex **D** may further undergo alkyne insertion and reductive elimination to give the Δ^4-1,2,3-germolene **4**. The germylene liberated from **A** may be immediately trapped by an alkyne to form a germirene **E**. The oxidative addition of **E** to a Pd(0) species in the system



Scheme 2.



Scheme 3.

to give the Δ^3-1,2,3-germapalladetene **F**, followed by alkyne insertion and reductive elimination, may give the germole **5**. The experimental result shown in Eq. 3, employing the 11-germatricyclo[6.2.1.$0^{2,7}$]undeca-2,4,6,9-tetraene as the germylene source, provided supporting evidence for the involvement of germylene. The mechanism for the formation of the germole **5** was analyzed and substantiated in previous studies dealing with platinum-catalyzed bis-germylation of alkynes with organodigermanes and with cyclic oligogermanes.[12,13]

The formation of **4** and **5** may be rationalized by another mechanism, depicted in Scheme 3. The trigermapalladetane-germylene complex (**G**) via α-germylene group migration from the insertion product (**C**) is formed.[18–20] The intermediate **G** may decompose to give Δ^4-1,2,3-germolene **4** together with the liberation of a palladium–germylene complex (**H**). Complex **H** liberated from **G** may be trapped by an alkyne to form a germacyclopentadiene **5**.

Experimental

General Methods. The NMR spectra were obtained on a Varian Unity lnova 400 MHz NMR spectrometer. The GC-MS spectra were measured on a JEOL JMS-DX 303 mass spectrometer. The IR spectra were recorded with a Shimadzu FT IR 4200 spectrometer. Gas chromatography was performed on a Shimadzu GC 8A with a 1 m 20% SE30 column. Liquid chromatography was performed on a Shimadzu SPD 10A and on a JAI recycling preparative HPLC (ODS column). All solvents were purified and dried, as reported in the literature.

Materials. 1,1,2,2,3,3,4,4-Octaisopropyltetragermetane,[21] $Pd(dba)_2$,[22] and $Pd(acac)_2$,[23] were prepared as reported in the literature. Alkynes and other palladium complexes were commercially available.

Palladium-Catalyzed Reactions of 1,1,2,2,3,3,4,4-Octaisopropyltetragermetane (1) with Alkynes (2). As a representative example, the reaction of **1** with 1-hexyne (**2a**) is described. A mixture of **1** (0.1 mmol), **2a** (0.5 mmol) with $Pd(dba)_2$ (0.005 mmol)-4 ETBP (0.020 mmol), and benzene (1 mL) was prepared in a Pyrex tube ($\phi = 8$ mm). The solution was degassed in a vacuum and heated under argon in a sealed tube for 16 h at 120 °C. GC and GC-MS analyses of the reaction mixture showed a 78% conversion of **1** along with the formation of 5-butyl-1,1,-2,2,3,3,4,4-octaisopropyl-1,2,3,4-tetrahydro-1,2,3,4-tetragermin (**3a**, 18%), 4-butyl-1,1,2,2,3,3-hexaisopropyl-Δ^4-1,2,3-trigermolene (**4a**, 58%), and 1,1-diisopropyl-1*H*-germole (**5a**, 39%). The concentration of the reaction mixture, followed by preparative LC (ODS column), gave pure **3a**, **4a** and isomers **5a**. **3a**: ^{1}H NMR (δ in $CDCl_3$) 0.92 (t, $J = 7.2$ Hz, 3H), 1.16 (d, $J = 7.5$ Hz, 6H), 1.24–1.35 (m, 42H), 1.42–1.62 (m, 8H), 1.76–1.87 (m, 4H), 2.32 (t, $J = 7.9$ Hz, 2H), 6.60 (s, 1H); GC–MS m/z (relative intensity) 718 (1.0, M^+), 675 (100), 589 (4), 429 (11), 207 (32); mp 175–

176 °C. Found: C, 50.10; H, 9.32%. Calcd for $C_{30}H_{64}Ge_4$: C, 50.23, H, 9.28%. **4a**: ^{1}H NMR (δ in $CDCl_3$) 0.90 (t, $J = 7.2$ Hz, 3H), 1.12–1.20 (m, 36H), 1.40–1.61 (m, 8H), 1.70–1.81 (m, 2H), 2.32 (t, $J = 7.9$ Hz, 2H), 6.80 (s, 1H); GC-MS m/z (relative intensity) 558 (3.5, M^+), 515 (100), 473 (34), 431 (19), 305 (16). **5a-1**: ^{1}H NMR (δ in $CDCl_3$) 0.86–0.92 (m, 6H), 1.09 (d, $J = 7.14$ Hz, 6H), 1.14 (d, $J = 7.32$ Hz, 6H), 1.22–1.62 (m, 10H), 2.19 (t, $J = 7.51$ Hz, 2H), 2.26 (m, 2H), 5.28 (t, 1H, $J = 1.19$ Hz), 5.63 (t, 1H, $J = 1.28$ Hz); GC–MS m/z 324 (M^+). **5a-2**: ^{1}H NMR (δ in $CDCl_3$) 0.93 (t, $J = 7.23$ Hz, 6H), 1.08 (d, $J = 7.32$ Hz, 12H), 1.16–1.64 (m, 10H), 2.32 (t, $J = 7.51$ Hz, 4H), 5.72 (t, $J = 0.92$ Hz, 2H); GC-MS m/z (relative intensity) 324 (M^+, 1.3), 281 (100), 239 (39), 191 (14), 163 (17), 113 (12). **5a-3**: ^{1}H NMR (δ in $CDCl_3$) 0.87–0.94 (m, 6H), 1.08 (d, $J = 7.32$ Hz, 6H), 1.12 (d, $J = 7.32$ Hz, 6H), 1.22–1.62 (m, 10H), 2.15 (t, $J = 6.59$ Hz, 2H), 2.27 (t, $J = 6.96$ Hz, 2H), 5.58 (dt, $J = 18.13$, 1.64 Hz, 1H), 6.16 (dt, $J = 18.13$, 6.36 Hz, 1H); GC–MS m/z 324 (M^+). **3b**: ^{1}H NMR (δ in $CDC1_3$) 0.90 (t, $J = 6.96$ Hz, 3H), 1.16 (d, $J = 7.51$ Hz, 6H), 1.23–1.38 (m, 44H), 1.45–1.63 (m, 8H), 1.76–1.88 (m, 4H), 2.32 (td, $J = 7.88$, 1.34 Hz, 2H), 6.60 (t, $J = 1.28$ Hz, 1H); GC–MS m/z (relative intensity) 732 (1.0, M^+), 688 (100), 644 (30), 602 (25), 531 (25),446 (30), 304 (15). **4b**: ^{1}H NMR (δ in $CDC1_3$) 0.91 (t, $J = 6.87$ Hz, 3H), 1.18 (d, $J = 7.32$ Hz, 12H), 1.20 (d, $J = 7.51$ Hz, 6H), 1.21 (d, $J = 7.32$ Hz, 6H), 1.29–1.38 (m, 14H), 1.46–2.37 (m, 8H), 1.79 (q, $J = 7.42$ Hz, 2H), 2.35 (dt, $J = 7.69$, 1.28 Hz, 2H), 6.83 (t, $J = 1.37$ Hz, 1H); GC–MS m/z (relative intensity) 572 (1.0, M^+), 535 (100), 486 (40), 445 (20), 403 (5), 347 (40), 307 (40), 264 (80). **5b-1**: ^{1}H NMR (δ in $CDCl_3$) 0.89 (t, $J = 6.96$ Hz, 6H), 0.90 (t, $J = 7.14$ Hz, 3H), 1.09 (d, $J = 7.14$ Hz, 6H), 1.14 (d, $J = 7.32$ Hz, 6H), 1.24–1.60 (m, 14H), 2.14–2.22 (m, 2H), 2.25 (t, $J = 7.05$ Hz, 2H), 5.28 (t, $J = 1.19$ Hz, 1H), 5.63 (t, $J = 1.28$ Hz, 1H); GC–MS m/z 352 (M^+). **5b-2**: ^{1}H NMR (δ in $CDC1_3$) 0.90 (t, $J = 7.14$ Hz, 6H), 1.09 (d, $J = 7.32$ Hz, 12H), 1.27–1.38 (m, 8H), 1.39–1.54 (m, 6H), 2.26 (t, $J = 7.69$ Hz, 4H), 5.72 (t, $J = 0.92$ Hz, 2H); GC–MS m/z 352 (M^+). **5b-3**: ^{1}H NMR (δ in $CDCl_3$) 0.88 (t, $J = 6.96$ Hz, 3H), 0.90 (t, $J = 7.23$ Hz, 3H), 1.08 (d, $J = 7.14$ Hz, 3H), 1.12 (d, $J = 7.32$ Hz, 3H), 1.20 (d, $J = 6.96$ Hz, 3H), 1.22 (d, $J = 7.14$ Hz, 3H), 1.24–1.45 (m, 12H), 1.48–1.58 (m, 2H), 2.10–2.18 (m, 2H), 2.25 (t, $J = 6.96$ Hz, 2H), 5.58 (dt, $J = 18.3$, 1.52 Hz, 1H), 6.16 (dt, $J = 18.13$, 6.41 Hz, 1H); GC–MS m/z 352 (M^+). **3c**: ^{1}H NMR (δ in $CDCl_3$) 1.0–2.0 (m, 56H), 6.7 (s, 1H), 7.0–7.3 (m, 5H); GC–MS m/z (relative intensity) 736 (1.7, M^+), 695 (100), 651 (86), 537 (8), 263 (27), 161 (29). Found: C, 52.38; H, 8.50%. Calcd for $C_{32}H_{52}Ge_4$: C, 52.13, H, 8.48%. **4c**: ^{1}H NMR (δ in $CDCl_3$) 1.5–2.3 (m, 56H), 7.6–7.8 (m, 6H); GC–MS m/z (relative intensity) 578 (10, M^+), 535 (100), 493 (33), 263 (34), 161 (51), 78 (8). **5c-2**: ^{1}H NMR (δ in $CDCl_3$) 1.5–1.9 (m, 14H), 6.8 (s, 2H), 7.3–7.7 (m, 10H); GC–MS m/z (relative intensity) 364 (3.2, M^+), 321 (100), 279 (57), 175 (42), 151 (52). **3d**: ^{1}H NMR (δ in $CDCl_3$) 1.11 (d, $J = 7.51$ Hz, 6H), 1.13 (d, $J = 7.87$ Hz, 6 H), 1.20 (d, $J = 7.32$ Hz, 6H), 1.37 (d, $J = 7.69$ Hz, 6H), 1.33 (d, $J = 7.87$ Hz, 6H), 1.34 (d, $J = 7.32$ Hz, 6H), 1.37 (d, $J = 7.69$ Hz, 6H), 1.39 (d, $J = 7.87$ Hz, 6H), 1.50–1.68 (m, 4H), 1.82–1.94 (m, 4H), 2.33 (s, 3H), 6.68 (s, 1H), 6.95–7.08 (m, 4H); GC–MS m/z (relative intensity) 756 (5.0, M^+), 712 (100), 548 (55), 462 (70), 420 (60), 260 (80). **4d**: ^{1}H NMR (δ in $CDC1_3$) 1.09 (d, $J = 7.51$ Hz, 6H), 1.13 (d, $J = 7.32$ Hz, 6H), 1.23 (d, $J = 7.69$ Hz, 6H), 1.25 (d, $J = 8.24$ Hz, 6H), 1.38 (d, $J = 6.96$ Hz, 6H), 1.39 (d, $J = 6.96$ Hz, 6H), 1.53–1.71 (m, 4H), 1.80–1.93 (m, 2H), 2.34 (s, 3H), 7.08–7.10 (m, 5H); GC–MS m/z (relative intensity) 592 (5, M^+), 552 (100), 506 (20), 464 (10), 422 (5), 379 (2), 347 (10), 305 (50), 259 (70), 219 (30), 181 (40). **5d-2**: ^{1}H NMR (δ in $CDC1_3$) 1.20 (d, $J = 7.32$ Hz, 12H), 1.62 (sept, $J = 7.32$ Hz, 2H), 2.29 (s, 6H), 6.25 (s, 2H), 6.92–6.98 (m, 8H); GC–MS m/z 392 (M^+). **3e**: ^{1}H NMR (δ in $CDCl_3$) 1.15 (s, 9H), 1.22–1.90 (m, 56H), 6.63 (s, 1H); GC–MS m/z (relative intensity) 718 (0.6, M^+), 675 (100), 515 (13), 429 (21), 263 (30), 161 (23); mp 224 °C. Found: C, 48.26; H, 9.12%. Calcd for $C_{29}H_{64}Ge_4$: C, 48.52, H, 8.99%. **3f**: GC–MS m/z (relative intensity) 706 (0.6, M^+), 663 (65), 617 (100), 533 (22), 415 (11), 263 (26), 191 (27), 119 (25). **4f**: GC–MS m/z (relative intensity) 546 (0.6, M^+), 507 (100), 461 (48), 257 (29), 161 (35), 119 (75). **5f**: GC–MS m/z (relative intensity) 300 (5.1, M^+), 273 (6.2), 257 (28), 209 (81), 153 (72), 126 (95), 69 (100).

Pd(acac)$_2$ETBP-Catalyzed Reactions of Tetragermetane (1) with 1-Hexyne (2a). A mixture of **1** (0.1 mmo1), **2a** (0.5 mmol) with $Pd(acac)_2$ (0.005 mmol)-4 ETBP (0.020 mmol), and benzene (1 mL) was prepared in a Pyrex tube ($\phi = 8$ mm). The solution was degassed in a vacuum and heated under argon in a sealed tube for 16 h at 120 °C. The reaction mixture was analyzed by GC and GC–MS.

Palladium-Catalyzed Reaction of 1,2,3,4-Tetrahydro-1,2,3,-4-tetragermin 3a with 1-Hexyne (2a). A mixture of **3a** (0.01 mmo1) and **2a** (0.05 mmol) with $Pd(dba)_2$ (0.0005 mmol)-4 ETBP (0.0025 mmol) (0.05 mol. amt. based on **3a**), and benzene (1 mL) was prepared in a Pyrex tube ($\phi = 8$ mm). The solution was degassed in a vacuum and heated under argon in a sealed tube for 48 h at 120 °C. GC and GC–MS analyses of the reaction mixture showed a 45% conversion of **3a** along with the formation of 4-butyl-1,1,2,2,3,3-hexaisopropyl-Δ^4-1,2,3-trigermolene (**4a**, 47%), and 1,1-diisopropy1-1*H*-germoles (**5a**, 5%).

Preparation of 11,11-Diisopropyl-1,8,9,10-tetraphenyl-11-germatricyclo[6.2.1.0^{2,7}]undeca-2,4,6,9-tetraene. The 11-germatricyclo[6.2.1.0^{2,7}]undeca-2,4,6,9-tetraene was prepared by a reaction of 1,1-diisopropyl-2,3,4,5-tetrapheny1-1*H*-germole with benzyne, as reported in the literature.[24] mp 196 °C, ^{1}H NMR (δ in $CDC1_3$) 0.88 (d, $J = 6.9$ Hz, 6H), 1.38 (d, $J = 6.9$ Hz, 6H), 1.30–2.80 (m, 2H), 6.80–7.80 (m, 24H). Anal. Calcd for $C_{40}H_{42}Ge$: C, 80.69; H, 7.11%. Found: C, 80.72; H, 7.25%.

Palladium-Catalyzed Reaction of 11-Germatricyclo[6.2.-1.0^{2,7}]undeca-2,4,6,9-tetraene with Phenylacetylene (2c). A mixture of 11,11-diisopropyl-1,8,9,10-tetraphenyl-11-germatricyclo[6.2.1.0^{2,7}]undeca-2,4,6,9-tetraene (0.1 mmol), **2c** (1.0 mmol) with $Pd(dba)_2$ (0.005 mmol)-4 ETBP (0.020 mmol) (0.05 mol. amt. based 11-germatricyclo[6.2.1.0^{2,7}]undeca-2,4,6,9-tetraene), and benzene (0.5 mL) was prepared in a Pyrex tube ($\phi = 8$ mm). The solution was degassed in a vacuum and heated under argon in a sealed tube for 3 h at 70 °C. GC and GC–MS analyses of the reaction mixture showed the formation of 1,1-diisopropyl-1*H*-germole in 15% yield.

Thermal Reaction of 11-Germatricyclo[6.2.1.0^{2,7}]undeca-2,4,6,9-tetraene with Phenylacetylene (2c). A mixture of 11,-11-diisopropyl-1,8,9,10-tetraphenyl-11-germatricyclo[6.2.1.0^{2,7}]-undeca-2,4,6,9-tetraene (0.1 mmol), **2c** (1.0 mmol), and benzene (0.5 mL) was prepared in a Pyrex tube ($\phi = 8$ mm). The solution was degassed in a vacuum and heated under argon in a sealed tube for 3 h at 70 °C. GC and GC–MS analyses of the reaction mixture showed the formation of 3,3,4,4-tetraisopropyl-2-phenyl-Δ^3-1,2-digermetene in 25% yield. Tetraphenylnaphthalene and oligomers containing a diisopropylgermylene unit were also detected. The concentration of the reaction mixture, followed by preparative TLC (silica gel, hexane), gave pure Δ^3-1,2-digermetene.

^{1}H NMR (δ in $CDC1_3$) 1.26 (d, $J = 4.7$ Hz, 12H), 1.28 (d, $J = 4.7$ Hz, 12H), 1.7 (m, 4H), 7.0–7.4 (m, 5H), 7.83 (s, 1H); GC–MS m/z (relative intensity) 418 (9.6, M^+), 377 (76), 249 (53), 189 (57), 149 (100), 89 (48).

Preparation of Bis(acetylacetonate)(ETBP)palladium (6). A mixture of $Pd(acac)_2$ (0.304 g, 0.1 mmol) and ETBP (0.162 g, 0.1 mmol) was stirred in benzene (6 mL) at room temperature in an atmosphere of nitrogen for 1 h until the solution became clear. Petroleum ether was then added to precipitate the product $Pd(acac)_2$ETBP in 70% yield. ^{1}H NMR (δ in $CDCl_3$) -0.13 (t, $J = 7.60$ Hz, 3H), 0.01 (q, $J = 7.69$ Hz, 2H), 1.82 (s, 6H), 2.58 (s, 6H), 3.52 (d, $J = 4.94$ Hz, 6H), 4.59 (d, $J = 4.58$ Hz, 1H), 5.12 (s, 1H).

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