

Mono- and Dinuclear Germapalladacycles Obtained via the Ge–Ge Bond Forming Reactions Promoted by Palladium Complexes

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Heating a toluene solution of bis(germyl)palladium complex [Pd(GeHPh₂)₂(dmpe)] (**2**) (dmpe = 1,2-bis(dimethylphosphino)ethane) at 70 °C produced a mixture of dipalladium complexes, one with bridging digermene and germylene ligands, [$\{\text{Pd}(\text{dmpe})\}_2(\mu\text{-GePh}_2)(\mu\text{-Ge}_2\text{Ph}_4)$] (**3**), and also a mononuclear tetragerpalladacyclopentane, [Pd(GePh₂GePh₂GePh₂GePh₂)(dmpe)] (**4**), in 92:8 molar ratio, respectively. The reaction of H₂GePh₂ with **2** in 10:1 molar ratio formed complex **4** as the main product (**3**:**4** = 4:96). Complexes **3** and **4** were isolated from the above reactions and characterized by X-ray crystallography and NMR spectroscopy. Complex **3** reacted with H₂GePh₂ (Pd:Ge = 1:10) at 80 °C to yield **4** quantitatively, whereas simple heating of **3** at the same temperature did not form **4** at all. Reaction pathways for the Ge–Ge bond formation are discussed.

Introduction

Si–Si bond forming reactions promoted by transition metal complexes are of great importance and are relevant to the preparation of organic compounds containing Si–Si bonds and the polysilanes.¹ Catalysis using early transition metal complexes (Ti, Zr, and Hf) is useful for dehydrocoupling of organosilanes, which forms new Si–Si bonds, and the mechanism for the reactions has been accepted as σ -bond metathesis.² Late transition metal complexes (Rh,³ Ni,⁴ Pt⁵) promote different kinds of the Si–Si bond-forming reactions. A commonly proposed route involves reductive elimination of disilanes (or oligosilanes) from the complexes with two silyl ligands at *cis* positions.⁶ The reverse reactions, oxidative addition of disilanes

to Pd(0) and Pt(0) complexes, are also well known.^{7,8} Alternative important Si–Si bond formation in chemistry of late transition metal complexes takes place via migration of a silyl group bonded to the metal center to silylene ligands.⁹ Kumada and co-workers found that Pt complex-catalyzed redistribution of disilanes formed a mixture of the oligosilanes with Si₂–Si₆ units. They proposed the mechanism involving formation of the intermediate Pt complexes with the silyl and silylene ligands and migration of the silyl ligand to the electrophilic silylene ligands.¹⁰ This type of Si–Si bond-forming reactions promoted by late transition metal complexes have been investigated over a wide range of transition metal complexes by Tobita,¹¹ Pannell,¹² Tilley,¹³ and their respective co-workers. Thus, silylene complexes of transition metals have attracted significant attention as the important intermediate of transformation of

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organosilicon complexes, although such complexes are too unstable to be isolated in most cases.

Ge–Ge bond formation promoted by transition metal complexes has received limited attention partly because of the lower reactivity of M–Ge bonds than the corresponding M–Si bonds in late transition metal complexes.¹⁴ Cp₂TiMe₂ catalyzes dehydrocoupling of PhGeH₃ and Ph₂GeH₂ to produce the polygermanes having Ph substituents.¹⁵ Tertiary germanes such as HGeMe₃ and HGeMe₂Ar (Ar = C₆H₅, C₆H₄F-*p*, C₆H₄Me-*p*, C₆H₄OMe-*p*, etc.) are polymerized to form the polygermanes via demethanation in the presence of Ru(II)-PMe₃ catalysts.¹⁶ Stoichiometric coupling reactions of halogermanes with one-electron reducing reagent SmI₂ also form a new Ge–Ge bond under mild conditions.¹⁷ Germanium amide and germanium hydride serve as precursors of linear and branched oligogermanes.¹⁸ Heating of [Pt(GeMe₂Cl)₂(PPh₃)₂] at 120 °C produces ClMe₂Ge–GeMe₂Cl as one of the products.¹⁹ The digermene is formally the product of reductive elimination, but another mechanism involving platinum-germylene species is also proposed, based on the occurrence of scrambling of Me and Cl substituents attached to Ge during the reaction and on the report on α-chloro elimination of [Pt(GeMe₂Cl)₂(PEt₃)₂].²⁰ 3,4-Benzo-1,2-germacyclobut-3-ene dimerizes via cleavage and formation of the Ge–Ge bond promoted by Pd(PPh₃)₄ catalyst.²¹ The complexes having a $\text{Pd}-\text{Ge}-\text{C}-\text{C}-\text{Ge}$ five-membered ring are observed in the reaction mixture, and they react further with the digermene to form the cyclic dimer. Heating the complex at high temperature (175 °C) yields the product having new Ge–Ge bonds.

Oxidative addition of digermanes to Pt(0) or Pd(0) complexes, accompanied by Ge–Ge bond activation, was studied by many research groups in relation to bisgermylation of alkynes.^{19–22}

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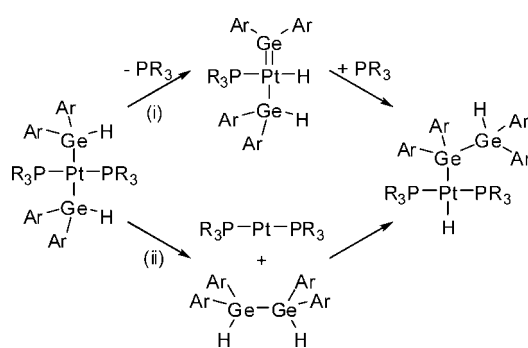
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Scheme 1



There have been much fewer reports of the reverse reaction, reductive elimination of digermene from the Pt(II) or Pd(II) complexes having two germyl ligands. Mochida and co-workers found that thermolysis of *cis*-[Pt(GePh₂Me)₂(PMe₂Ph)₂] in the presence of PPh₃ gave MePh₂Ge–GePh₂Me in quantitative yield via reductive elimination.²³ Wells and Banaszak Holl reported that a bis(germyl)platinum complex with electron-withdrawing groups, *trans*-[Pt(GeAr₂H)₂(PEt₃)₂] (Ar = C₆H₃(CF₃)₂-3,5), underwent thermal rearrangement to yield a digermyl(hydrido)platinum complex, *trans*-[Pt(H)(GeAr₂GeAr₂H)(PEt₃)₂].²⁴ A pathway to form the Ge–Ge bond in the complexes is suggested to involve platinum-germylene intermediates that were formed through α-migration of the substituent attached to Ge, as shown in Scheme 1(i).^{20,24,25} Another pathway via reductive elimination of digermene and reoxidative addition of H–Ge bond cleavage may also account for the products (Scheme 1(ii)).

Bis(germyl)palladium complexes were expected to promote similar reactions, producing a Ge–Ge bond, more easily than the corresponding Pt–Ge complexes. Early studies by Glockling and co-workers revealed that bis(germyl)palladium complexes with monodentate phosphine ligands were thermally unstable and decomposed in solution.²⁶ In this paper, we present the preparation and structure of mono- and dinuclear germapalladacycles via Ge–Ge bond forming reactions starting from a bis(germyl)palladium complex with a chelating phosphine ligand.

Results and Discussion

Treatment of the bis(silyl)palladium complex [Pd(SiHPh₂)₂(dmpe)] (**1**)²⁷ with an excess amount of H₂GePh₂ at room temperature yielded a palladium complex with two germyl ligands, [Pd(GeHPh₂)₂(dmpe)] (**2**), in 76% yield (eq 1). Similar exchange reaction of [Pt(SiMe₃)₂(dppe)] with HGeMe₃ produced the mononuclear Pt complex [Pt(GeMe₃)₂(dppe)].²⁸ A dinuclear platinum complex with bridging Si ligands was also reported to react with Ph₂GeH₂, yielding [{Pt(PPh₃)₂]₂(μ-GeHPh₂)].²⁹

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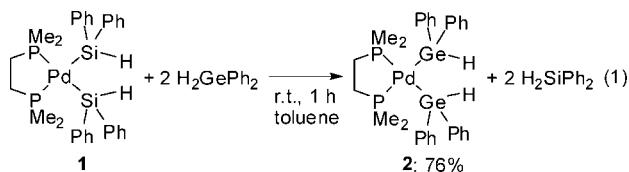
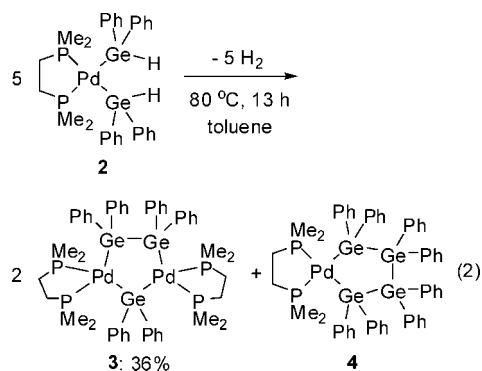


Figure 1 shows the molecular structure of **2** determined by X-ray crystallography. The Pd–Ge bonds of **2** (2.4259(2), 2.4266(3) Å) are longer than the Pd–Si bonds of analogous silyl complex **1** (2.3548(9), 2.3550(7) Å) by virtue of the larger covalent radius of Ge relative to that of Si, while the Pd–P bond distances of **2** (2.3066(6), 2.3147(7) Å) are shorter than those of **1** (2.3395(9), 2.3356(7) Å) due to smaller degree of *trans* influence of Ge than Si atoms. The Ge–Pd–Ge bond angle (81.27(1)°) is slightly larger than the Si–Pd–Si bond angle of **1** (79.74(3)°). Although NMR signals of the E–H hydrogens (E = Si, Ge) of complexes **1** and **2** display close chemical shifts to each other (**1**, E = Si; δ 5.69; **2**, E = Ge; δ 5.63), the coupling constant of **2** attributed to the two phosphorus nuclei (14.3 Hz) is larger than the corresponding *J* value of **1** (9.9 Hz). The $^{31}\text{P}\{^1\text{H}\}$ NMR signal of **2** (δ 19.9) was slightly shifted to lower field compared with the chemical shift of **1** (δ 12.6).

Heating a toluene solution of **2** at 80 °C for 13 h produced a mixture of a dipalladium complex with bridging digermene and germylene ligands, $[\{\text{Pd}(\text{dmpe})\}_2(\mu\text{-GePh}_2)(\mu\text{-Ge}_2\text{Ph}_4)]$ (**3**), and a tetragermapalladacyclopentane, $[\text{Pd}(\text{GePh}_2\text{GePh}_2\text{GePh}_2\text{Ge-Ph}_2)(\text{dmpe})]$ (**4**). The former complex was isolated in 36% yield from the reaction mixture, while isolation of complex **4** was not feasible due to a low yield in this reaction. Isolation and characterization of **4** are presented shown below.



Complex **3** was characterized by X-ray crystallography, as shown in Figure 2a. A molecule of **3** contains a twisted five-membered ring including two Pd atoms, which have square-planar coordination with two Ge atoms and a chelating dmpe ligand. The long distances between two Pd atoms (4.4669(4) Å) and of diagonal Pd...Ge lines (3.7736(4), 3.8178(4) Å) indicate the absence of a Pd–Pd bond and no significant interaction inside the five-membered ring. The two bond distances between Ge1 and Pd1 or Pd2 atoms (Pd1–Ge1 2.5024(4) Å, Pd2–Ge1 2.4875(4) Å) are elongated compared with Pd–Ge bond distances of the digermene ligand (Pd1–Ge2 2.4399(4) Å, Pd2–Ge3 2.4324(4) Å) and of bis(germyl)palladium complex **2** (2.4259(2), 2.4266(3) Å). The Ge2–Ge3 bond distance (2.4296(4) Å) is slightly shorter than the Ge–Ge bonds of digermene $\text{Ph}_3\text{Ge-GePh}_3$ (2.437(2) Å)³⁰ and cyclic Ge compounds such as cyclopentagermane (Ph_2Ge)₅ (2.438(3)–

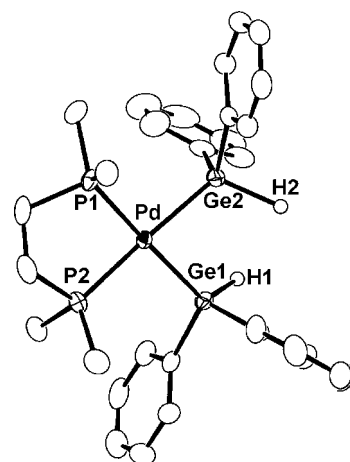
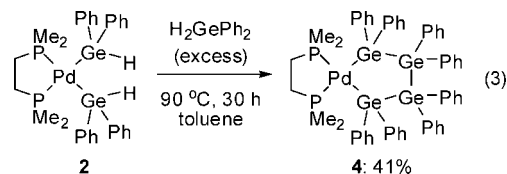


Figure 1. ORTEP drawing of **2** with thermal ellipsoids shown at the 50% probability level. Selected bond distances (Å) and angles (deg): Pd–Ge1 2.4259(2), Pd–Ge2 2.4266(3), Pd–P1 2.3066(6), Pd–P2 2.3147(7), Ge1–H1 1.61(2), Ge2–H2 1.76(2), Ge1–Pd–Ge2 81.27(1), Ge1–Pd–P2 95.82(2), Ge2–Pd–P1 96.99(2), P1–Pd–P2 85.93(2).

2.473(3) Å)³¹ and cyclohexagermane (Ph_2Ge)₆ (2.456(2)–245.8(2) Å).³² The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3** contains two signals at δ 15.2 and 14.2, whose coupling pattern indicates an AA'BB' spin system ($J_{\text{P-P}} = 7.8, 11.2$ Hz). Two phosphorus atoms of the dmpe ligands are magnetically inequivalent with different environments, germylene and digermene ligands at the *trans* position. In the ^1H NMR spectrum of **3**, two aromatic hydrogen peaks at δ 7.93 and 7.40 in 2:1 ratio are assigned as the *ortho* hydrogens of $\mu\text{-Ge}_2\text{Ph}_4$ and $\mu\text{-GePh}_2$ ligands. There have been a limited number of transition metal complexes with bridging disilene or digermene ligands. A diiron complex with $\mu\text{-Ge}_2\text{Me}_4$ and $\mu\text{-GeMe}_2$ ligands, $[\{\text{Fe}(\text{CO})_4\}_2(\mu\text{-Ge}_2\text{Me}_4)(\mu\text{-GeMe}_2)]$, was obtained from the interaction of $[\text{Na}_2\text{Fe}(\text{CO})_4]$ with the dichlorogermene $\text{ClMe}_2\text{GeGeMe}_2\text{Cl}$.³³ A diplatinum complex with bridging disilene and silylene ligands, $[\{\text{Pt}(\text{H})(\text{dmpe})\}_2(\mu\text{-SiHPh}_2)(\mu\text{-SiHPh}_2)]$, was prepared via a Si–Si bond forming reaction of the mononuclear trisilyl(hydrido)platinum(IV) complex *fac*- $[\text{Pt}(\text{H})(\text{SiH}_2\text{Ph})_3(\text{dmpe})]$.³⁴



Reaction of excess H_2GePh_2 with **2** at 90 °C for 30 h afforded **4**, which was isolated as yellow crystals in 41% yield (eq 3). Mochida et al. proposed tetragermapalladacyclopentane as the crucial intermediates in Pd-catalyzed ring-opening addition of tetragermene, $(\text{Ge}^i\text{Pr}_2)_4$, to alkynes to give the five- and six-membered cyclic organogermanium compounds.³⁵ Isolation of the PdGe_4 intermediates was not reported probably due to the labile nature of the intermediates under the reaction conditions. The crystal of **4** involves three independent molecules due to

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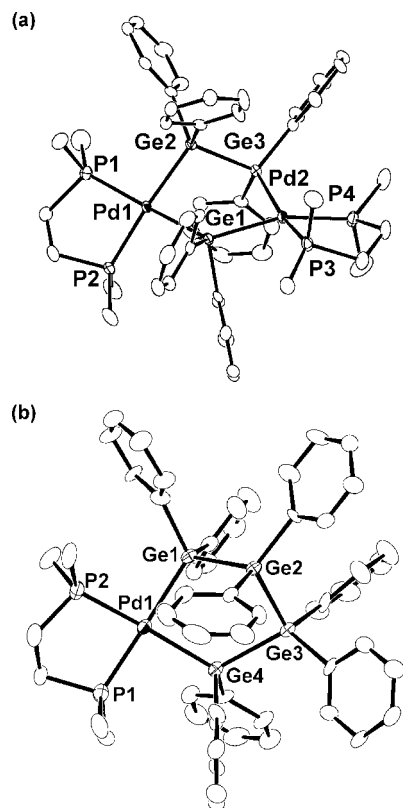
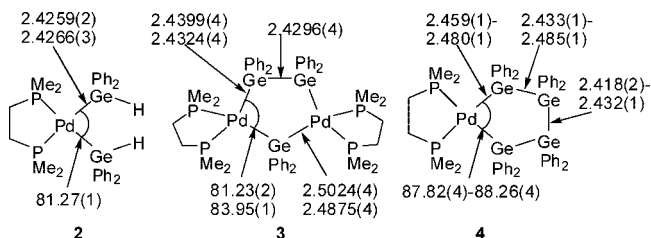


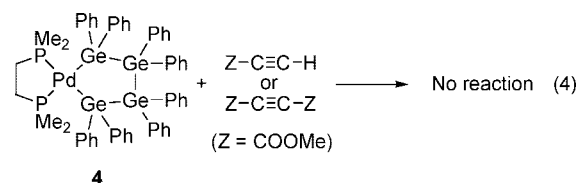
Figure 2. ORTEP drawings of (a) **3** and (b) **4** with thermal ellipsoids shown at the 50% probability level. The crystal structure of **4** contains three independent molecules in the unit cell. Selected bond distances (Å) and angles (deg) for **3**: Pd1–Ge1 2.5024(4), Pd1–Ge2 2.4399(4), Pd1–P1 2.3166(9), Pd1–P2 2.311(1), Pd2–Ge1 2.4875(4), Pd2–Ge3 2.4324(4), Pd2–P3 2.3185(9), Pd2–P4 2.307(1), Ge2–Ge3 2.4296(4), Ge1–Pd1–Ge2 81.23(2), Ge1–Pd2–Ge3 83.95(1), Pd1–Ge1–Pd2 127.06(2), Pd1–Ge2–Ge3 101.60(2), Pd2–Ge3–Ge2 103.48(2). Selected bond distances (Å) and angles (deg) for **4**: Pd–Ge 2.459(1)–2.480(1), Pd–P 2.038(2)–2.346(2), (Pd–)Ge–Ge 2.433(1)–2.485(1), (Ge–)Ge–Ge 2.418(2)–2.432(1), Ge–Pd–Ge 87.82(4)–88.26(4), Pd–Ge–Ge 105.38(4)–116.81(4), Ge–Ge–Ge 96.42(4)–97.63(5).

Chart 1



the different orientation of the Ph groups in the unit cell. Each molecule of **4** involves a five-membered PdGe₄ ring with an envelope conformation (Figure 2b). The Pd atom has a square-planar environment and is occupied by two terminal Ge atoms of a tetragermylene fragment. Chart 1 summarizes the bond parameters of complexes **2–4**. The Pd–Ge bonds of **4** (2.459(1)–2.480(1) Å) are slightly longer than those of bis(germyl)palladium complex **2** (2.4259(2), 2.4266(3) Å) and of dipalladium complex **3** (Pd1–Ge2: 2.4399(4) Å, Pd2–Ge3: 2.4324(4) Å). The Ge–M–Ge bond angles of complexes with digermly ligands might be interpreted as a criterion of Ge...Ge interaction. The Ge–Pd–Ge angles of two germapalladacycles **3** and **4** (**3**, 81.23(2)°, 83.95(1)°; **4**, 87.82(4)–88.26(4)°) are larger than that of the mononuclear palladium complex **2**

(81.27(1)°), suggesting no significant interaction between two Ge atoms. A similar tetragermacyclopentane structure involving the ytterbium atom, [Yb(GePh₂GePh₂GePh₂GePh₂)(THF)₄], was reported to form a slightly twisted cyclic five-membered structure.³⁶ The Ge–Ge–Ge bond angles of **4** (96.42(4)–97.63(5) Å) are significantly smaller than the Pd–Ge–Ge bond angles (105.38(4)–116.81(4)°) and the Yb–Ge–Ge and Ge–Ge–Ge bond angles (116.0(1)° and 107.6(1)°) of the ytterbium complex. The Ge2–Ge3 bond distances (2.418(2)–2.432(1) Å) opposite the Pd atoms of **4** are slightly shortened compared with the Ge1–Ge2 (or Ge3–Ge4) bonds proximal to Pd atoms (2.433(1)–2.485(1) Å), while all Ge–Ge bonds of the ytterbium complex are within the range 2.479(2)–2.489(2) Å. Thus, complex **4** and the YbGe₄ complex have different conformations of the five-membered chelate rings.



Cyclic Pd or Pt complexes with two Ge atoms coordinated to the metal center were reported to undergo insertion of alkynes into the M–Ge bonds.^{21b,22} Reactions of tetragermapalladacycle **4** with a 5-fold amount of dimethyl acetylenedicarboxylate or 3-fold amount of methyl propiolate at rt and 70 °C, however, did not afford a product with new C–Ge bonds (eq 4).

Figure 3a shows a change in the concentration of complexes **2–4** during the thermal reaction of **2** at 70 °C in C₆D₆, which is monitored by ¹H NMR spectroscopy. Decrease of **2** and formation of **3** take place smoothly, although they are accompanied by much slower formation of **4**. The reaction is completed in 5 h to produce a mixture of **3** and **4** in a 92:8 molar ratio of the complexes. The time-dependent change of the reaction of H₂GePh₂ with **2** (Ge: Pd = 10:1) at 70 °C is shown in Figure 3b. The decrease in **2** is slower than the reaction without added H₂GePh₂. The major product is the mononuclear complex **4** rather than the dinuclear complex **3**, from the beginning of the reaction. At the initial stage (0–1.5 h) of the reaction, total amounts of **2**, **3**, and **4** are not balanced due to the presence of a small amount of intermediates in the reaction mixture, which is mentioned below. After 44 h, the NMR spectrum exhibited signals of **4** and no signal due to **2** and **3**, indicating that complexes **2** and **3** were completely converted into **4**.

The reaction of **3** with excess H₂GePh₂ in C₆D₆ at 80 °C was monitored by ³¹P{¹H} NMR spectroscopy, as shown in Figure 4. Figure 4a shows the signals of **3** with an AA'BB' spin system. Heating of the solution for 3 h (Figure 4b) leads to the signals due to bis(germyl)palladium complex **2** (δ 19.9), tetragermapalladacycle **4** (δ 21.8), and remaining dinuclear complex **3** (δ 15.2 and 14.2). Small signals with an AB spin system were observed at different positions from complexes **2–4** (δ 19.3 and 18.4). After 47 h, the signals other than **4** become negligible, indicating that complex **4** is the final product of the reaction (Figure 4c). These results suggest that complex **3** reacts with H₂GePh₂ to form **2** and uncharacterized species (³¹P NMR: δ 19.3 and 18.4) as the initial products and transformation from **2** and H₂GePh₂ into **4** takes place, as shown in reaction 3.

(36) Bochkarev, L. N.; Makarov, V. M.; Zakharov, L. N.; Fukin, G. K.; Yanovsky, A. I.; Struchkov, Y. T. *J. Organomet. Chem.* **1995**, *490*, C29–C31.

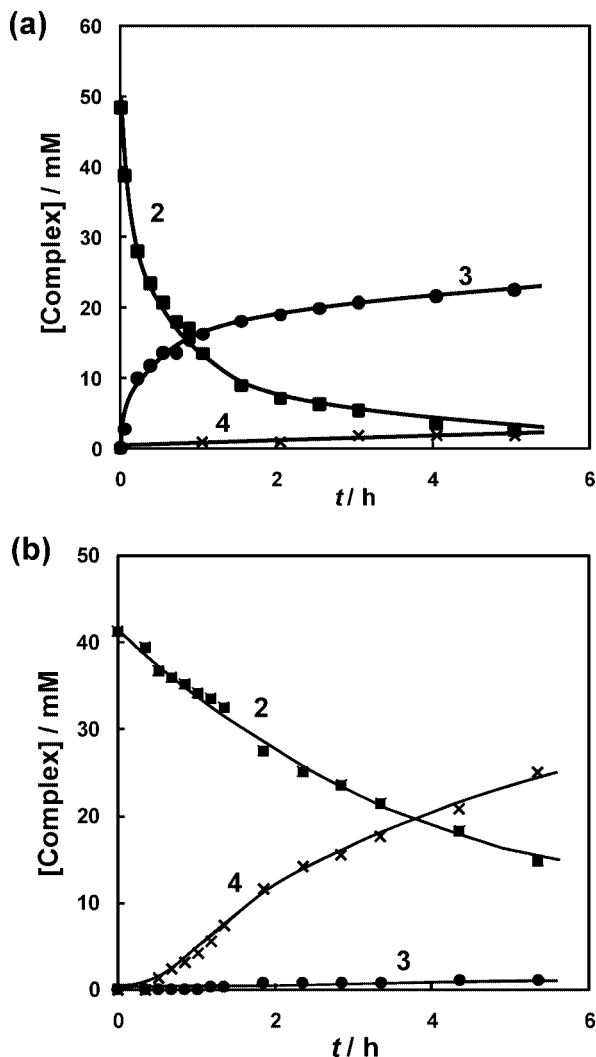


Figure 3. Change in amounts of **2** (■), **3** (●), and **4** (×) during the thermal reaction of **2** at 70 °C in benzene-*d*₆ (a) with no additive ([**2**] = 49 mM) and (b) with a 10-fold molar amount of H₂GePh₂ ([**2**] = 42 mM).

Although complex **3** is prepared from **2** together with elimination of H₂GePh₂, the reaction is reversible to regenerate **2** from **3** and added H₂GePh₂. In contrast, simple heating of **3** in the absence of H₂GePh₂ at 80 °C did not change the ¹H NMR spectra of the reaction mixture at all for 48 h.

Mononuclear bis(silyl)palladium complex **1** was reported to be in equilibrium with a dinuclear complex, [{Pd(dmpe)}₂(μ-SiPh₂)₂], having a four-membered Pd₂Si₂ core with bridging silylene ligands in solution.²⁷ The reversible reaction accompanies elimination and addition of H₂SiPh₂ to the Pd complex, as shown in Scheme 2. Addition of H₂SiPh₂ to [{Pd(dmpe)}₂(μ-SiPh₂)₂] cleaves a bridging Pd–Si bond and forms a new Pd–Si bond. A σ-bond metathesis type reaction³⁷ involving an intermediate (**A**) causes smooth cleavage of the bridging coordination bond. Further cleavage of the bridging Pd–Si–Pd bond by addition of H₂SiPh₂ generates mononuclear complex **1**. Conversion of **3** into **2** by added H₂GePh₂ may also similarly involve Pd–Ge bond cleavage. It is not clear whether the Ge–Ge bond of **3** is cleaved directly by addition of H₂GePh₂ or not.

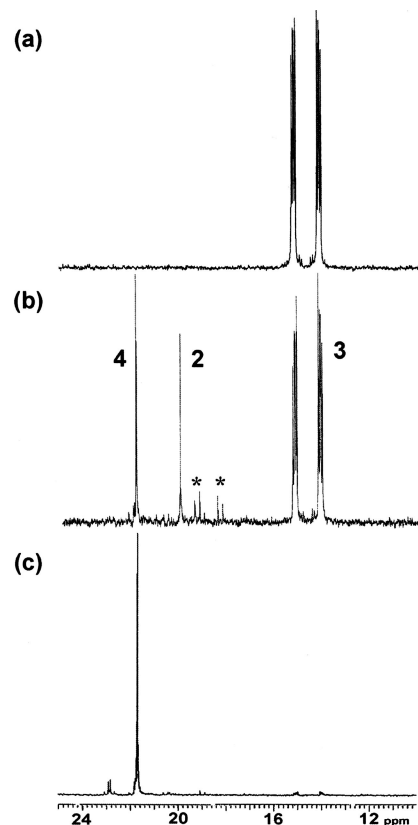
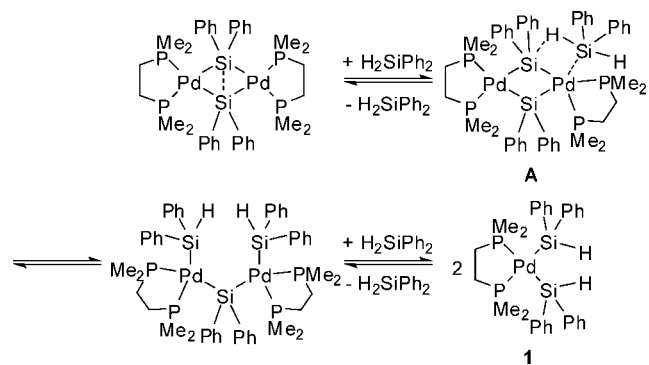
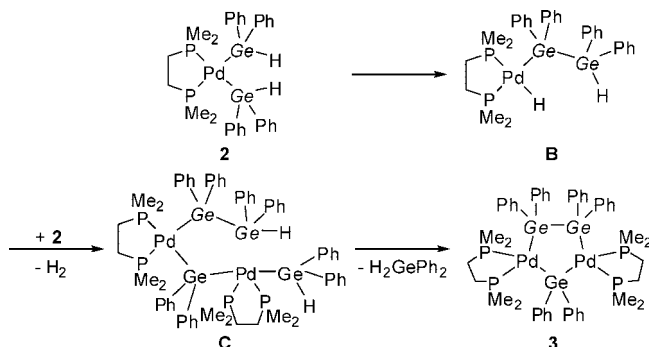


Figure 4. Monitoring of ³¹P{¹H} NMR spectra during the conversion of **3** into **4** in the presence of H₂GePh₂ (a) at 0 h, (b) after 3 h at 80 °C, and (c) after 47 h at 80 °C. The two doublets (δ 19.3 and 18.4) with an asterisk may be assigned as one of intermediate **D** or **F**.

Scheme 2



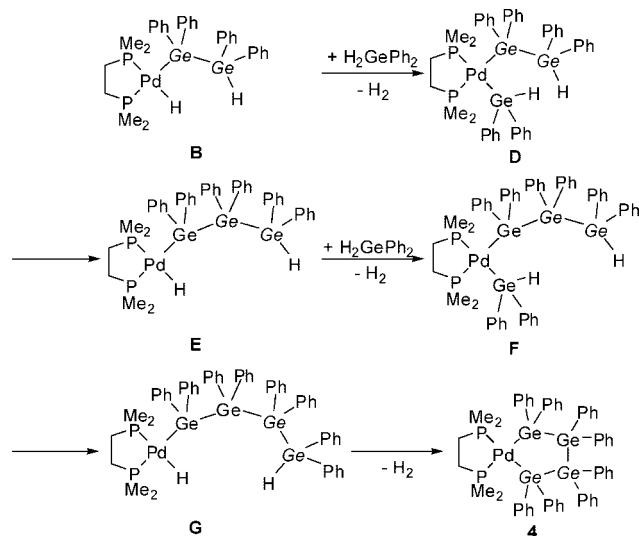
Scheme 3



(37) (a) Koizumi, T.; Osakada, K.; Yamamoto, T. *Organometallics* **1998**, *17*, 5721–5727. (b) Maruyama, Y.; Yamamura, K.; Sagawa, T.; Katayama, H.; Ozawa, F. *Organometallics* **2000**, *19*, 1308–1318.

Schemes 3 and 4 depict the plausible mechanisms for the formation of **3** and **4**, respectively. Rearrangement of bis(ger-

Scheme 4



myl)palladium complex **2** gives a digermyl(hydrido)palladium complex (**B**) via migration of the germyl group to the germylene ligand, which is generated by α -migration of hydrogen at the Ge atoms, similarly to Scheme 1(i). The NMR study of the reaction mixture did not provide direct evidence for the presence of Pd-germylene species probably due to their instability. The Pd–H bond in structure **B** is expected to be reactive toward the Ge–H bond of the unreacted starting material **2** to form the dinuclear complex with a bridging germylene ligand (**C**). Subsequent intramolecular cyclization of **C** via a σ -bond metathesis of Pd–Ge and Ge–H bonds forms the five-membered ring structure **3**, accompanied by elimination of H_2GePh_2 . Instead of the σ -bond metathesis pathway, a six-coordinated Pd(IV) intermediate formed by oxidative addition of the Ge–H bond of the germyl ligand may also be proposed for the ligand exchange. An octahedral platinum(IV) complex with three silyl and a hydrido ligand, *fac*-[Pt(H)(SiH₂-Ph)₃(dmpe)], was prepared and characterized by Tilley et al.³⁴

Scheme 4 shows the plausible pathway for preparation of **4** starting from digermyl(hydrido)palladium complex **B**. The addition of excess H_2GePh_2 to the solution of **2** leads to faster σ -bond metathesis of the Pd–H bond of **B** with the Ge–H bonds of H_2GePh_2 than those of complex **2** to form a digermyl(germyl)palladium complex (**D**), followed by rearrangement of digermyl(germyl) ligands to trigermyl(hydrido) groups (**E**). Repeated exchange of a hydrido with GePh_2H ligands (**F**) and migration of the germylene moiety afford a tetragermyl(hydrido)palladium complex (**G**), propagating the GePh_2 unit. Finally, tetragermapalladacycle **4** is formed by intramolecular cyclization of **G**. Mochida and co-workers reported that the intramolecular cyclization of hydrido(germyl)platinum complexes, [PtH(GePh_2 - $(\text{SiMe}_2)_n\text{GePh}_2\text{H}$)(PPh₃)₂] ($n = 1, 2$), produced four- or five-membered germaplatinacycles, [Pt(GePh_2 (SiMe_2)_{*n*} GePh_2)-(PPh₃)₂].³⁸ Complexes symmetrically coordinated by tri- and tetragermylene ligands such as trigermapalladacyclobutane, [Pd($\text{GePh}_2\text{GePh}_2\text{GePh}_2$)(dmpe)], and pentagermapalladacyclohexane, [Pd($\text{GePh}_2\text{GePh}_2\text{GePh}_2\text{GePh}_2\text{GePh}_2$)(dmpe)], were not detected during the reaction mixture. On the other hand, the minor $^{31}\text{P}\{^1\text{H}\}$ NMR signals at δ 19.3 and 18.4 in Figure 4b suggest the presence of palladium intermediates having an

unsymmetrical structure. Species **D** and/or **F** may be assigned to this intermediate. Since the ^1H NMR spectra of the reaction mixture do not contain any signals due to Pd–H hydrogen, intermediates **E** and **G** do not correspond to the $^{31}\text{P}\{^1\text{H}\}$ NMR signals. Other pathways, for example, involving intermediate [Pd($\text{GePh}_2\text{GePh}_2\text{H}$)₂(dmpe)], can also be considered.

Conclusion

We demonstrated the preparation and structure of five-membered germacycles containing one or two palladium atoms from simple thermolysis of a bis(germyl)palladium complex. The chemoselectivity to produce complexes **3** and **4** depends on the presence or absence of H_2GePh_2 in the reaction mixture. Compared with the analogous silyl complexes, bis(germyl) complexes undergo facile formation of Ge–Ge bonds promoted by Pd complexes. The preparations of **3** and **4** might be important to form a digermyl(hydrido)palladium complex by rearrangement of germylene species of **2**. Use of the chelating dmpe ligand enabled the formation of the complexes with new Ge–Ge containing ligands. Ge–Ge bond formation reported by Mochida also employed complexes with chelating digermyl ligands.²¹ This may facilitate Ge–Ge bond formation via germyl group migration to the germylene ligand.

Experimental Section

General Procedures. All manipulations of the complexes were carried out using standard Schlenk techniques under an argon or nitrogen atmosphere. Hexane and toluene were purified by passing through a solvent purification system (Glass Contour). ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on Varian Mercury 300 or JEOL EX-400 spectrometers. Chemical shifts in ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were referenced to the residual peaks of the solvents used. The peak positions of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were referenced to external 85% H_3PO_4 (δ 0) in C_6D_6 . The reagent H_2GePh_2 was obtained from a reduction reaction of Cl_2GePh_2 (Sigma-Aldrich) by LiAlH_4 . The compound [Pd(SiHPh_2)₂(dmpe)] (**1**)²⁷ was prepared according to the reported procedure. IR absorption spectra were recorded on a Shimadzu FT/IR-8100 spectrometer. Elemental analysis was carried out using a LECO CHNS-932 or Yanaco MT-5 CHN autorecorder.

Preparation of [Pd(GeHPh_2)₂(dmpe)] (2**).** To a toluene solution (4 mL) of complex **1** (812 mg, 1.30 mmol) was added excess H_2GePh_2 (1.49 g, 6.51 mmol). The solution was stirred at room temperature for 1 h. The solvent was removed under reduced pressure to produce a white solid, which was washed with 2 mL of hexane three times and dried *in vacuo* to yield **2** (706 mg, 76%). Recrystallization of **2** from hexane/toluene (5:1) at room temperature gave colorless crystals suitable for X-ray crystallography. Anal. Calcd for $\text{C}_{30}\text{H}_{38}\text{Ge}_2\text{P}_2\text{Pd} \cdot 1/2\text{C}_7\text{H}_8$: C, 53.06; H, 5.58. Found: C, 52.96; H, 5.53. ^1H NMR (300 MHz, C_6D_6 , room temperature): δ 7.80 (dd, 8H, C_6H_5 *ortho*, $J_{\text{H-H}} = 8.1, 1.2$ Hz), 7.23–7.14 (m, 12H, C_6H_5 *meta* and *para*), 5.63 (apparent triplet, 2H, GeH , $J_{\text{P-H}} = 14.3$ Hz), 0.72 (d, 4H, CH_2 , $^2J_{\text{P-H}} = 17.4$ Hz), 0.66 (d, 12H, PCH_3 , $^2J_{\text{P-H}} = 8.4$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6 , room temperature): δ 146.7 (t, C_6H_5 *ipso*, $^3J_{\text{P-C}} = 7.2$ Hz), 136.6 (C_6H_5 , *ortho*), 127.6 (C_6H_5 , *meta*), 127.0 (C_6H_5 , *para*), 28.8 (t, PCH_2 , $J_{\text{P-C}} = 23$ Hz), 12.4 (t, PCH_3 , $J_{\text{P-C}} = 9.5$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, C_6D_6 , room temperature): δ 19.9. IR data (KBr): 1952 ($\nu_{\text{Ge-H}}$) cm^{-1} .

Preparation of [Pd(dmpe)]₂(μ - GePh_2)(μ - Ge_2Ph_4) (3**).** A toluene solution (20 mL) of **2** (706 mg, 0.99 mmol) was heated at 80 °C for 13 h, and the solution changed from colorless to yellow. Removal of the solvent under reduced pressure gave a solid, which was reprecipitated with toluene/hexane (3:1) twice and was washed with Et_2O three times, followed drying *in vacuo* to give **3** as yellow

(38) Usui, Y.; Hosotani, S.; Ogawa, A.; Nanjo, M.; Mochida, K. *Organometallics* **2005**, *24*, 4337–4339.

powder (212 mg, 36%). Anal. Calcd for $C_{48}H_{62}Ge_3P_4Pd_2$: C, 48.30; H, 5.24. Found: C, 48.26; H, 5.29. 1H NMR (300 MHz, C_6D_6 , room temperature): δ 7.93 (m, 8H, C_6H_5 ortho), 7.40 (m, 4H, C_6H_5 ortho), 7.06–7.13 (m, 18H, C_6H_5 meta and para), 0.84 (br, 4H, PCH_2), 0.79 (m, 16H, PCH_3 and PCH_2 , $^2J_{P-H} = 6.9$ Hz), 0.51 (d, 12H, PCH_3 , $^2J_{P-H} = 6.9$ Hz). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6 , room temperature): δ 156.0 (m, C_6H_5 ipso), 152.3 (m, C_6H_5 ipso), 137.4 (C_6H_5 ortho), 136.2 (C_6H_5 ortho), 127.1 (C_6H_5 meta), 126.5 (C_6H_5 meta or para), 125.9 (C_6H_5 meta or para), 124.6 (C_6H_5 para), 30.4 (m, PCH_2), 29.3 (m, PCH_2), 13.9 (apparent triplet, PCH_3 , $J_{P-H} = 7.2$ Hz), 13.0 (apparent doublet, PCH_3 , $J_{P-H} = 13$ Hz). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6 , room temperature): δ 14.2 (dd, PCH_3 , $^2J_{P-P} = 11.7$, 7.8 Hz), 15.2 (dd, PCH_3 , $^2J_{P-P} = 11.7$, 7.8 Hz). Complex **3** was prepared also by a direct method from the reaction of $[PdMe_2(dmpe)]$ (529 mg, 1.85 mmol) with twice the molar amount of H_2GePh_2 (845 mg, 3.69 mmol) in toluene (3 mL) at room temperature for 4 days. Complex **3** was obtained as a yellow solid in 45% yield.

Preparation of $[Pd(GePh_2GePh_2GePh_2GePh_2)(dmpe)]$ (4**).** A mixture of **2** (200 mg, 0.28 mmol) and excess H_2GePh_2 (322 mg, 1.4 mmol) in toluene (3 mL) was heated at 90 °C for 30 h. The solvent was evaporated to give a solid, which was washed with 3 mL of hexane three times and dried *in vacuo* to afford complex **4** as a yellow powder (135 mg, 41%). Anal. Calcd for $C_{54}H_{56}Ge_4P_2Pd$: C, 55.72; H, 4.85. Found: C, 55.21; H, 4.87. 1H NMR (300 MHz, C_6D_6 , room temperature): δ 7.71 (m, 8H, C_6H_5 ortho), 7.47 (m, 8H, C_6H_5 ortho), 7.08–6.94 (m, 24H, C_6H_5 meta and para), 0.72 (d, 4H, PCH_2 , $^2J_{P-H} = 18$ Hz), 0.60 (d, 12H, PCH_3 , $^2J_{P-H} = 8.7$ Hz). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6 , room temperature): δ 148.2 (t, C_6H_5 ipso, $^3J_{P-C} = 6.9$ Hz), 141.5 (C_6H_5 ipso), 137.7 (C_6H_5 ortho), 137.2 (C_6H_5 ortho), 127.8 (C_6H_5 meta), 127.5 (C_6H_5 meta or para), 127.3 (C_6H_5 meta or para), 127.0 (C_6H_5 para), 29.2 (t, PCH_2 , $J_{P-C} = 22.5$ Hz), 12.9 (m, PCH_3). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6 , room temperature): δ 21.8.

Thermal Reaction of **2.** A solution of **2** (21 mg, 0.029 mmol) and 4,4'-dimethylbiphenyl (14 mg 0.077 mmol) as an internal standard in C_6D_6 (0.6 mL) was heated at 70 °C in an NMR sample tube. The reaction mixture was monitored at 70 °C for 5 h. The concentrations of **2** (δ 7.80), **3** (δ 7.93), and **4** (δ 7.71) were estimated from the intensity of the C_6H_5 ortho signals in the 1H NMR spectra. Heating of the solution of **2** for 5 h converted into a mixture of **2** (2.7 mM), **3** (22.6 mM), and **4** (1.8 mM).

Thermal Reaction of **2 in the Presence of H_2GePh_2 .** A solution of **2** (20 mg, 0.028 mmol), H_2GePh_2 (64 mg, 0.28 mmol), and dibenzyl (7.7 mg 0.042 mmol) as an internal standard in C_6D_6 (0.6 mL) was heated at 70 °C in an NMR sample tube. After 5 h, the 1H NMR spectrum of the solution was observed as a mixture of **2** (14.8 mM), **3** (1.1 mM), and **4** (25.5 mM). The reaction was complete after 44 h to give complex **4** as the final product.

Reaction of **3 with Excess H_2GePh_2 .** To a C_6D_6 solution (0.6 mL) of **3** (22 mg, 0.019 mmol) in an NMR sample tube was added excess H_2GePh_2 (45 mg, 0.20 mmol). The $^{31}P\{^1H\}$ NMR spectrum after 3 h at 80 °C exhibited three signals assigned as **2** (δ 19.9), **3** (δ 15.2, 14.2), and **4** (δ 21.8), and a small peak attributed to possible intermediate **D** or **F** (δ 19.3, 18.4), as mentioned in Scheme 4. After 47 h, the conversion into **4** and disappearance of **2** and **3**

Table 1. Crystallographic Data and Details of Refinement of **2, **3**, and **4****

	2	3	4
formula	$C_{30}H_{38}Ge_2P_2Pd$	$C_{48}H_{62}P_4Pd_2Ge_3$	$C_{54}H_{56}Ge_4P_2Pd$
fw	712.16	1193.48	1163.79
cryst size/mm	0.15 × 0.20 × 0.35	0.18 × 0.22 × 0.35	0.05 × 0.18 × 0.21
cryst syst	monoclinic	monoclinic	monoclinic
cryst color	colorless	yellow	yellow
space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/a$ (No. 14)
<i>a</i> /Å	12.063(3)	16.287(2)	22.863(4)
<i>b</i> /Å	19.635(4)	16.178(2)	21.865(3)
<i>c</i> /Å	13.470(3)	18.868(2)	30.131(5)
β /deg	105.616(3)	93.813(2)	101.893(2)
<i>V</i> /Å ³	3072(1)	4960.6(9)	14739(4)
<i>Z</i>	4	4	12
<i>D</i> _{calc} /g cm ⁻³	1.539	1.598	1.573
<i>F</i> (000)	1432	2392	7008
μ /mm ⁻¹	2.6431	2.6679	2.8777
no. of reflns measd	22 547	35 463	110 880
no. of unique reflns	7000	11 042	33 623
<i>R</i> _{int}	0.023	0.037	0.052
no. of obsd reflns (<i>I</i> > 2.00 σ (<i>I</i>))	6017	8732	15 678
no. of variables	360	576	1816
<i>R1</i> (<i>I</i> > 2.00 σ (<i>I</i>))	0.0309	0.0287	0.0562
<i>wR2</i> (<i>I</i> > 2.00 σ (<i>I</i>))	0.0850	0.0559	0.1320
GOF	1.004	1.084	0.957

were confirmed by 1H and $^{31}P\{^1H\}$ NMR spectroscopy. Thermolysis of **3** in the absence of H_2GePh_2 in toluene-*d*₈ at 80 °C did not change the 1H NMR spectra of the reaction mixture at all for 48 h.

X-ray Crystallography. Crystals of **2**, **3**, and **4** suitable for an X-ray diffraction study were mounted on a glass capillary tube. The data were collected to a maximum 2θ value of 55.0°. A total of 720 oscillation images were collected on a Rigaku Saturn CCD area detector equipped with monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) at -160 °C. Hydrogen atoms, except for the GeH hydrogens of **2**, were located by assuming the ideal geometry and were included in the structure calculation without further refinement of the parameters. Crystallographic data and details of refinement are summarized in Table 1.

Acknowledgment. This work was financially supported by grants-in-aid for Scientific Research for Young Chemists (No. 19750043), for Scientific Research (No. 1925008), and for Scientific Research on Priority Areas (No. 19027018), from the Ministry of Education, Culture, Sport, Science, and Technology, Japan. We thank Dr. N. Nakata (Saitama University) for helpful discussions.

Note Added in Proof. The Ge–Ge bond forming reaction of a bis(germyl)platinum complex $[Pt\{GeH_2(C_6H_2Me_3-2,4,6)\}_2(PPh_3)_2]$ similarly to Scheme 1(i) has recently been reported: Arii, H.; Nanjo, M.; Mochida, K. *Organometallics* **2008**, *27*, 4147–4151.

Supporting Information Available: Crystallographic data for **2**, **3**, and **4** as a CIF file. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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