

# Syntheses of Di- and Trinuclear Platinum Complexes with Multibridged Germanium Centers Derived from Unsymmetrical Digermanes

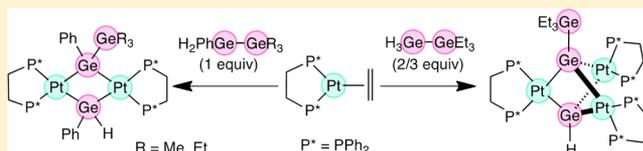
Hidekazu Arai, Rei Hashimoto, Kunio Mochida,\* and Takayuki Kawashima

Department of Chemistry, Gakushuin University, 1-5-1 Mejiro, Toshima-ku, Tokyo 171-8588, Japan

## S Supporting Information

**ABSTRACT:** A trigonal-bipyramidal  $\text{Pt}_3\text{Ge}_2$  cluster was synthesized by the reaction of the zerovalent platinum complex  $[\text{Pt}(\text{dppe})(\eta^2\text{-C}_2\text{H}_4)]$  ( $\text{dppe}$  = 1,2-bis(diphenylphosphino)ethane) with the unsymmetrical digermane  $\text{H}_3\text{GeGeEt}_3$  at a 3/2 molar ratio. The platinum centers formed a triangular plane bridged by two germylene ligands, one of which maintained the Ge–Ge bond.

To investigate the  $\text{Pt}_3\text{Ge}_2$  cluster formation process, the phenyl-substituted digermanes  $\text{HPh}_2\text{GeGeMe}_3$  and  $\text{H}_2\text{PhGeGeR}_3$  ( $\text{R} = \text{Me}, \text{Et}$ ), in which two hydrogen atoms and one hydrogen atoms of the reactive  $\text{GeH}_3$  moiety were replaced by the bulkier phenyl group(s) together with the substitution of the  $\text{GeEt}_3$  group by a  $\text{GeMe}_3$  group, respectively, were used to simplify the reaction system. They provided the digermylplatinum hydride  $[\text{Pt}(\text{dppe})(\text{H})(\text{GePh}_2\text{GeMe}_3)]$  (**2**) and the bis( $\mu$ -germylene)diplatinum complexes  $[\text{Pt}_2(\text{dppe})_2(\mu\text{-GeHPh})(\mu\text{-Ge}(\text{Ph})\text{GeR}_3)]$  (**3**,  $\text{R} = \text{Me}$ ; **4**,  $\text{R} = \text{Et}$ ) in moderate yields, respectively. For **3** and **4**, the first-formed digermylplatinum hydride **I-1** underwent dissociation of one of the phosphorus donors followed by 1,2-germyl migration to give the corresponding bis(germyl)platinum complex **I-2**, as observed in the previously reported silicon system. On the one hand, the germly migration did not take place in the case of **2**, owing the Ge–Ge bond being less reactive than the Si–Si bond. Intermediates **I-1** and **I-2** coupled to each other to afford the germylene-bridged diplatinum complexes **3** and **4** accompanied by extrusion of  $\text{H}_2$  and  $\text{R}_3\text{GeH}$ . In the case of  $\text{H}_3\text{GeGeEt}_3$ , the corresponding bis( $\mu$ -germylene)diplatinum complex reacted with  $[\text{Pt}(\text{dppe})(\eta^2\text{-C}_2\text{H}_4)]$ , resulting in the formation of the desired  $\text{Pt}_3\text{Ge}_2$  cluster. The spiro-type  $\text{Pt}_4\text{Ge}$  complex was obtained only by changing mole equivalents of  $[\text{Pt}(\text{dppe})(\eta^2\text{-C}_2\text{H}_4)]$ , demonstrating the usefulness of the present method using  $\text{H}_3\text{GeGeEt}_3$ , which can readily regulate the molar ratio.



## INTRODUCTION

Transition-metal clusters containing main-group elements play an important role in catalyzing various reactions in artificial systems as well as in the active site of metalloproteins.<sup>1,2</sup> A metal–metal bond and a metal–metal interaction through a main-group element in clusters function differently from those of mononuclear transition-metal species. Transition-metal clusters that consist of a heavier main-group element are classified as heterobimetallic clusters and are expected to have unique physiological properties.<sup>3</sup> Among the heavier group 14 elements, germanium and tin are well-known as modifiers of heterogeneous catalytic systems, and transition-metal clusters containing these elements have been synthesized and have been shown to possess catalytic activity.<sup>4</sup> Adams and co-workers have reported that the ruthenium–tin cluster  $[\text{Ru}_4(\mu_4\text{-SnPh})_2(\text{CO})_{12}]$  fixed on mesoporous silica catalyzes the hydrogenation of olefins.<sup>5</sup>

Transition-metal–germanium clusters have been achieved by the reaction of a low-valent transition-metal complex with a monogermane ( $\text{R}_{3-n}\text{GeH}_n$ ;  $n = 1\text{--}3$ )<sup>6,7</sup> or a digermane, ( $\text{C}_5\text{Me}_4\text{H}$ ) $\text{Me}_2\text{GeGeMe}_2(\text{C}_5\text{Me}_4\text{H})$ .<sup>8</sup> Since the reaction requires the scission of inactive Ge–C bonds, the transition-metal center is restricted to elements from groups 8 and 9, which have the high bond activation abilities necessary for oxidative addition to the Ge–C bond. Use of the germane gas  $\text{GeH}_4$

without a Ge–C bond is impractical, as it is difficult to regulate the stoichiometry upon oxidative addition to a transition metal. Clusters consisting of group 10 transition metals and germanium atoms are limited to the planar trinuclear palladium cluster  $[\text{Pd}_4(\text{dmpe})_3(\mu\text{-GePh}_2)_3]$  ( $\text{dmpe}$  = 1,2-bis(dimethylphosphino)ethane),<sup>9</sup> in contrast with the silicon derivatives,<sup>10–12</sup> which are attributed to poor methods of introducing a bridged-germanium donor into metal clusters. Recently, we have developed a procedure to synthesize platinum clusters containing silylyne ligands by using unsymmetrical disilanes.<sup>13</sup> The formation process is described as follows: (i) oxidative addition of Si–H in disilane, (ii) 1,2-silyl migration on the platinum center, (iii) dimerization of the bis(silyl)platinum complex and subsequent reductive elimination of trialkylsilane, and (iv) addition of another platinum species. Application of this method to germanium analogues may induce the production of germanium-containing clusters.

In this study, we prepared a platinum–germanium cluster and investigated the reaction of the zerovalent platinum complex  $[\text{Pt}(\text{dppe})(\text{C}_2\text{H}_4)]$  (**1**;  $\text{dppe}$  = 1,2-bis(diphenylphosphino)ethane) with the unsymmetrical digermanes  $\text{H}_n\text{Ph}_{3-n}\text{GeGeR}_3$  ( $\text{R} = \text{Me}, \text{Et}$ ;  $n = 1\text{--}3$ ). Moreover, the

Received: July 27, 2012

Published: September 10, 2012

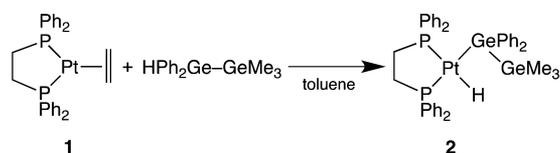
process of the unusual dephenylation of  $\text{H}_2\text{PhGeGeEt}_3$  with trifluoroacetic acid ( $\text{CF}_3\text{CO}_2\text{H}$ ) was studied.

## RESULTS AND DISCUSSION

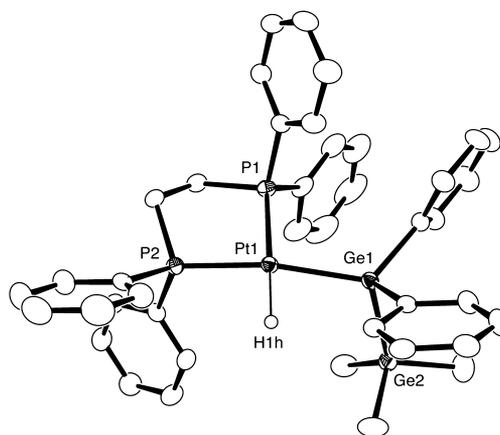
**Preparation of  $\text{H}_3\text{GeGeEt}_3$ .** The dephenylation of a phenyl-substituted germane using a common strong Bronsted acid is one of the most popular methods to obtain a precursor that can be converted to the corresponding hydrogermane by hydrogenation.<sup>14</sup> The  $\text{HCl}/\text{AlCl}_3$  system cannot control the number of eliminated phenyl groups, affording a mixture of the starting material and several dephenylated products. As an alternative method, a relatively weak organic acid such as  $\text{CX}_3\text{CO}_2\text{H}$  ( $X = \text{F}, \text{Cl}$ ) provides stoichiometric dephenylation of the germanium atom.<sup>15</sup> During the exploration of a reaction system suitable for dephenylation of  $\text{H}_2\text{PhGeGeEt}_3$  to obtain  $\text{H}_3\text{GeGeEt}_3$ , we unexpectedly noticed that treatment of  $\text{H}_2\text{PhGeGeEt}_3$  with  $\text{CF}_3\text{CO}_2\text{H}$  in  $\text{CH}_2\text{Cl}_2$  directly generated the desired product  $\text{H}_3\text{GeGeEt}_3$  in 18% yield without a hydride source such as  $\text{LiAlH}_4$ . A combination of other acids ( $\text{CF}_3\text{SO}_3\text{H}$  and *p*-toluenesulfonic acid) and solvents (toluene and  $\text{CHCl}_3$ ) led to recovery of the starting material or formation of a complicated mixture of several compounds. By monitoring the dephenylation with  $^1\text{H}$  NMR spectroscopy, no conversion of the starting material was observed after addition of the first dose of  $\text{CF}_3\text{CO}_2\text{H}$ . After the second dose of  $\text{CF}_3\text{CO}_2\text{H}$  was added, the  $^1\text{H}$  NMR spectrum of the reaction mixture exhibited  $\text{H}_3\text{GeGeEt}_3$  formation accompanied by an unidentified product with a broad signal around 1.0–1.2 ppm, which disappeared upon  $\text{LiAlH}_4$  treatment followed by concentration.<sup>16</sup> Use of  $\text{CF}_3\text{CO}_2\text{D}$  in  $\text{CD}_2\text{Cl}_2$  produced deuterated benzene and undeuterated product  $\text{H}_3\text{GeGeEt}_3$ , indicating that the hydrogen atom of  $\text{H}_3\text{GeGeEt}_3$  did not originate from the acid or the solvent. We presume that dephenylation of  $\text{H}_2\text{PhGeGeEt}_3$ , giving  $\text{H}_2(\text{CF}_3\text{COO})\text{GeGeEt}_3$ , followed by its disproportionation results in the formation of  $\text{H}_3\text{GeGeEt}_3$  and  $\text{H}(\text{CF}_3\text{CO}_2)_2\text{GeGeEt}_3$ , the latter of which seems to decompose rapidly, because  $\text{LiAlH}_4$  treatment did not increase the yield of  $\text{H}_3\text{GeGeEt}_3$  after the second dose of  $\text{CF}_3\text{CO}_2\text{H}$ .<sup>16</sup> For the scope of substrates, however, this method could not be applied to the direct hydrogenation of other phenyl-substituted monogermans ( $\text{Ph}_3\text{GeH}$ ,  $\text{Ph}_2\text{GeH}_2$ ) and digermans ( $\text{HPh}_2\text{GeGeEt}_3$ ,  $\text{Ph}_3\text{GeGeEt}_3$ ).

**Reaction with  $\text{HPh}_2\text{GeGeMe}_3$ .** The reaction of **1** with  $\text{HPh}_2\text{GeGeMe}_3$  in toluene at room temperature afforded the digermylplatinum hydride  $[\text{Pt}(\text{dppe})(\text{H})(\text{GePh}_2\text{GeMe}_3)]$  (**2**) in 39% yield by the oxidative addition of the Ge–H bond to the platinum center (Scheme 1). Using X-ray diffraction analysis

**Scheme 1.** Reaction of **1** with  $\text{HPh}_2\text{GeGeMe}_3$



(XRD), it was determined that the platinum center in **2** had four-coordinate square-planar geometry with a  $\text{GeP}_2\text{H}$  donor set (Figure 1), and the two Pt–P and Pt–Ge bond lengths were similar to those reported previously.<sup>17</sup> The similarity of the two Pt–P bond lengths means that the trans influence of a digermyl ligand was close to that of a hydride. The Ge–Ge



**Figure 1.** Crystal structure of **2**, showing 50% probability thermal ellipsoids. The hydrogen atoms except for H(1h) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt(1)–P(1) = 2.2881(6), Pt(1)–P(2) = 2.2785(7), Pt(1)–Ge(1) = 2.4325(3), Pt(1)–H(1h) = 1.63(3), Ge(1)–Ge(2) = 2.4386(4); P(1)–Pt(1)–P(2) = 86.17(2), P(1)–Pt(1)–Ge(1) = 100.740(18), P(1)–Pt(1)–H(1h) = 179.2(10), P(2)–Pt(1)–Ge(1) = 169.711(17), P(2)–Pt(1)–H(1h) = 93.1(9), Ge(1)–Pt(1)–H(1h) = 80.0(9).

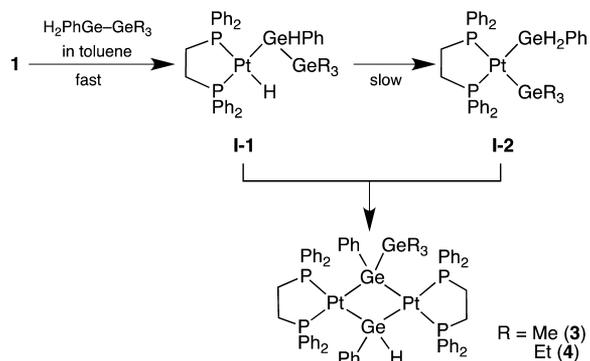
bond alignment was perpendicular to the platinum coordination plane to prevent steric repulsion between the trimethylgermyl group and one of the diphenylphosphino donors. The  $^1\text{H}$  NMR spectrum of **2** in  $\text{C}_6\text{D}_6$  showed the Pt–H signal as a doublet of doublets at  $-0.21$  ppm, diagnostic of platinum hydride bearing the supporting ligand dppe,<sup>18</sup> although it resonated at a magnetic field lower than the typical Pt–H region ( $-5$  to  $-1$  ppm).<sup>17b,19</sup> The  $^{31}\text{P}$  NMR spectrum exhibited two resonances at 55.4 ( $^1J_{\text{PtP}} = 2033$  Hz) and 59.3 ppm ( $^1J_{\text{PtP}} = 1996$  Hz) flanked with  $^{195}\text{Pt}$  satellites assignable to the two inequivalent phosphorus atoms trans to the digermyl ligand and the hydride, respectively. The two near  $^1J_{\text{PtP}}$  values correlated with the Pt–P bond length results. In comparison with silicon analogues,<sup>20</sup> the larger coupling constant  $^1J_{\text{PtP}}$  and the shorter Pt–P bond length associated with the germanium donor illustrated, as expected, the weaker trans influence of the digermyl ligand.

Complex **2** did not change even at  $110$  °C in toluene- $d_8$ , because of its high thermal stability. In fact, the trimethylgermyl group behaved as an inert substituent. The secondary germane  $\text{Mes}_2\text{GeH}_2$  ( $\text{Mes} = 2,4,6$ -trimethylphenyl)<sup>17b</sup> and the sterically encumbered primary germane  $\text{TripGeH}_3$  ( $\text{Trip} = 9$ -triptycyl)<sup>17d</sup> were reacted with the zerovalent platinum complex  $[\text{Pt}(\text{PPh}_3)_2(\eta^2\text{-C}_2\text{H}_4)]$  to afford the corresponding germlylplatinum hydrides stable at room temperature. Meanwhile, use of the sterically less hindered  $\text{Ph}_2\text{GeH}_2$ <sup>21</sup> and  $\text{MesGeH}_3$ <sup>17c</sup> generated the germlyl-bridged diplatinum complexes in the presence of the same platinum complex  $[\text{Pt}(\text{PPh}_3)_2(\eta^2\text{-C}_2\text{H}_4)]$ . Digermane  $\text{HPh}_2\text{GeGeMe}_3$  was employed like a bulky tertiary germane because the trimethylgermyl group did not migrate to the platinum center, in contrast to the disilane system.<sup>17</sup> These insights suggest that the sterically less hindered digermans  $\text{H}_2\text{PhGeGeR}_3$  ( $R = \text{Me}, \text{Et}$ ) and  $\text{H}_3\text{GeGeEt}_3$ , due to the decreased number of phenyl groups on the germanium atom, were required to prepare a multinuclear platinum–germyl cluster.

**Reaction with  $\text{H}_2\text{PhGeGeR}_3$ .** The reactions of **1** with  $\text{H}_2\text{PhGeGeR}_3$  in toluene at room temperature afforded the bis( $\mu$ -germylene)diplatinum complexes  $[\text{Pt}_2(\text{dppe})_2(\mu$ -

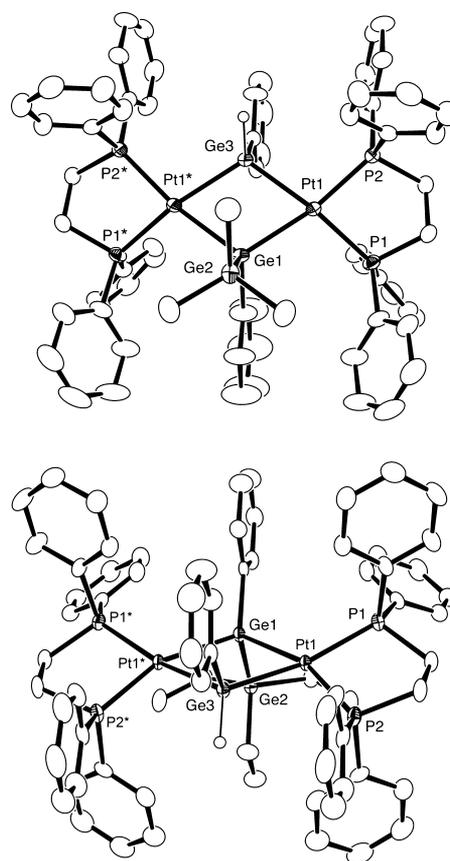
GeHPh)( $\mu$ -Ge(Ph)GeR<sub>3</sub>)] (R = Me (3), Et (4)) in 42% and 29% yields, respectively (Scheme 2), accompanied by extrusion

**Scheme 2. Reaction of 1 with H<sub>2</sub>PhGeGeR<sub>3</sub>**



of H<sub>2</sub> and R<sub>3</sub>GeH detected by <sup>1</sup>H NMR experiments.<sup>22</sup> The crystal structures of 3 and 4 showed a Pt<sub>2</sub>Ge<sub>2</sub> core with a rhombus framework in which a mirror plane existed on the Ge–Ge alignment. No differences between 3 and 4 were observed. These complexes revealed that the two platinum centers had a four-coordinate square-planar geometry with a Ge<sub>2</sub>P<sub>2</sub> donor set and were bridged by different germynes: that is, a germlyphenylgermylene and hydrophenylgermylene (Figure 2). The coordination plane of the platinum atom was disordered, as shown by the slightly large dihedral angle of 16.06(2)° for 3 and 22.10(2)° for 4, as defined by the P–Pt–P and the Ge–Pt–Ge planes, since one of the diphenylphosphino groups in dppe prevented steric repulsion to the trialkylgermyl group on the Ge(Ph)GeR<sub>3</sub> ligand. The Pt–Ge and Pt–P bond lengths were within the typical range of the corresponding single bonds. The Pt(1)⋯Pt(1)\* and Ge(1)⋯Ge(3) atomic distances were much longer than the diagnostic Pt–Pt and Ge–Ge single bonds,<sup>23</sup> respectively, indicating much weaker interaction between the atoms. By the DFT calculation reported by Sakaki et al., the model complex [Pt<sub>2</sub>(dipe)<sub>2</sub>(Ge<sub>2</sub>H<sub>4</sub>)] (dipe = 1,2-diphosphinoethane) represented a completely cleavage of the Ge–Ge bond and a formation of the Pt–Ge covalent bond to be characterized a bis( $\mu$ -germylene)diplatinum complex.<sup>24</sup> In addition, it was found that the two phenyl groups on the germylene ligands were oriented cis to each other.

Complexes 3 and 4 are rare examples of metal centers bridged by two different germynes as well as a bis( $\mu$ -germylene)platinum species, in contrast with many reports of analogous bis( $\mu$ -silylene)diplatinum complexes, which have been synthesized by dimerization of a monomeric bis(silyl)platinum or silyl platinum hydride.<sup>25,26</sup> In contrast, the monomeric bis(germyl)platinum complex bearing the bis(diphenylphosphino)ethane (dppe) ligand involves Ge–Ge bond formation by 1,2-germyl migration on the platinum center to convert to the digermylplatinum hydride reported by Ishii and co-workers.<sup>17d</sup> The Braddock-Wilking and Osakada groups, independently, have reported secondary germane oligomerization on the platinum center to afford the platinumgermacycle consisting of the formed tetragermane.<sup>26</sup> The behavior suggests that 1,2-germyl migration for Ge–Ge bond activation is not thermodynamically favored and depends on the coordination sphere of the platinum center. Therefore, the formation of 3 and 4 was interpreted as follows: the digermylplatinum hydride I-1 afforded by the Ge–H oxidative



**Figure 2.** Crystal structures of 3 (top) and 4 (bottom), showing 50% probability thermal ellipsoids. The hydrogen atoms, except for that on Ge(3), are omitted for clarity. Selected bond lengths (Å) and angles (deg) for 3: Pt(1)–P(1) = 2.2939(10), Pt(1)–P(2) = 2.2859(10), Pt(1)–Ge(1) = 2.4786(4), Pt(1)–Ge(3) = 2.4612(4); P(1)–Pt(1)–P(2) = 85.95(4), Ge(1)–Pt(1)–Ge(3) = 69.744(17), Pt(1)–Ge(1)–Pt(1)\* = 109.61(2), Pt(1)–Ge(3)–Pt(1)\* = 110.76(2). Selected bond lengths (Å) and angles (deg) for 4: Pt(1)–P(1) = 2.3092(9), Pt(1)–P(2) = 2.2700(9), Pt(1)–Ge(1) = 2.4875(4), Pt(1)–Ge(3) = 2.4486(4); P(1)–Pt(1)–P(2) = 85.83(4), Ge(1)–Pt(1)–Ge(3) = 69.188(16), Pt(1)–Ge(1)–Pt(1)\* = 109.50(2), Pt(1)–Ge(3)–Pt(1)\* = 112.12(2).

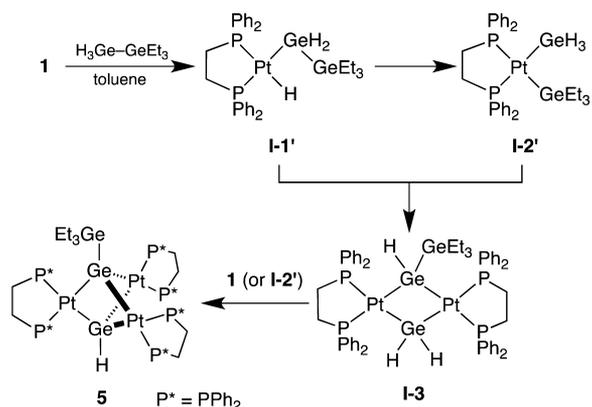
addition of H<sub>2</sub>PhGeGeR<sub>3</sub> to the platinum atom in 1 was converted to the bis(germyl)platinum intermediate I-2 by slow 1,2-germyl migration; the intermediates I-1 and I-2 coupled to each other to afford the diplatinum complexes bridged by the germylene ligand, which maintains a Ge–Ge bond.<sup>28</sup>

The <sup>1</sup>H NMR spectra of 3 and 4 in C<sub>6</sub>D<sub>6</sub> exhibited the unsymmetrical ethylene linker and phenyl groups in dppe, and the signals assignable to Ge–H were observed as multiplets at 3.7–4.0 and 3.5–3.8 ppm, respectively, which were shifted to a higher magnetic field relative to that of H<sub>2</sub>PhGeGeR<sub>3</sub> (R = Me, 4.40 ppm; R = Et, 4.42 ppm). The <sup>31</sup>P NMR spectra of 3 and 4 in C<sub>6</sub>D<sub>6</sub> showed two inequivalent phosphorus atoms as a doublet of doublets flanked with <sup>195</sup>Pt satellites at 56.7/58.0 and 55.2/57.6 ppm, respectively. The other phosphorus resonance was also observed as a singlet at 57.1 ppm, despite the use of a recrystallized sample of 3,<sup>29</sup> which was associated with the bis( $\mu$ -germylene)diplatinum complex [Pt(dppe)( $\mu$ -GeHPh)]<sub>2</sub> bridged by the same two germylene ligands. The trimethylgermyl group in I-1 (R = Me) took advantage of the 1,2-germyl migration, which enhanced the formation of I-2 followed by homodimerization to produce [Pt(dppe)( $\mu$ -

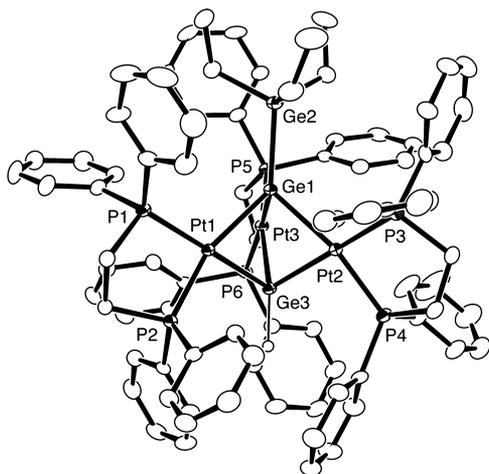
GeHPh)]<sub>2</sub>. Unfortunately, complexes **3** and **4** did not transform into a higher dimensional cluster, regardless of the addition of **1**.

**Reaction with H<sub>3</sub>GeGeEt<sub>3</sub>.** The isolated digermene H<sub>3</sub>GeGeEt<sub>3</sub> is a liquid at room temperature; therefore, it is suitable to use for a stoichiometric reaction, in sharp contrast with GeH<sub>4</sub> and MeGeH<sub>3</sub>, which are gases at room temperature. We tried to synthesize H<sub>3</sub>GeGeMe<sub>3</sub>, but we failed to isolate it. Treatment of **1** with H<sub>3</sub>GeGeEt<sub>3</sub> at a 3/2 molar ratio in toluene afforded the bis(μ<sub>3</sub>-germylyne)triplatinum complex [Pt<sub>3</sub>(dppe)<sub>3</sub>(μ<sub>3</sub>-GeH)(μ<sub>3</sub>-GeGeEt<sub>3</sub>)] (**5**) in 9.5% yield (Scheme 3). The reaction was accompanied by the extrusion

**Scheme 3. Formation Process of 5 in the Reaction of 1 with H<sub>3</sub>GeGeEt<sub>3</sub>**



of Et<sub>3</sub>GeH, which was detected by <sup>1</sup>H NMR spectroscopy. The crystal structure of **5** (Figure 3, Table 1) showed that the



**Figure 3.** Crystal structure of **5**, showing 50% probability thermal ellipsoids. The hydrogen atoms, except for that on Ge(3), are omitted for clarity.

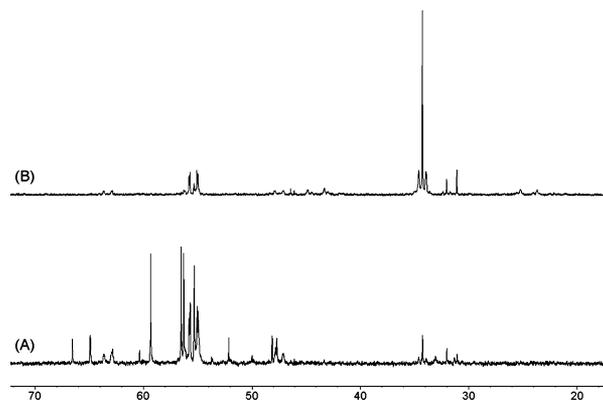
complex contained a trigonal-bipyramidal core consisting of three platinum atoms on the equatorial plane and two germanium atoms in the apical positions. One of the two μ<sub>3</sub>-bridged germylynes maintained the Ge–Ge bond, which was the same as in the cases of **3** and **4**. The platinum centers had four-coordinated distorted-square-planar geometry, and the Pt–Ge bond length (ca. 2.49 Å) associated with μ<sub>3</sub>-Ge(GeEt<sub>3</sub>) was longer than that of μ<sub>3</sub>-GeH (ca. 2.42 Å), which was attributed to minimizing the steric repulsion between the

**Table 1. Selected Bond Lengths (Å) and Angles (deg) of 5**

Bond Lengths (Å)			
Pt(1)–P(1)	2.2512(12)	Pt(2)–Ge(3)	2.4183(6)
Pt(1)–P(2)	2.2414(12)	Pt(3)–P(5)	2.2503(13)
Pt(1)–Ge(1)	2.4897(6)	Pt(3)–P(6)	2.2487(12)
Pt(1)–Ge(3)	2.4220(6)	Pt(3)–Ge(1)	2.4902(6)
Pt(2)–P(3)	2.2577(13)	Pt(3)–Ge(2)	2.4226(6)
Pt(2)–P(4)	2.2400(13)	Ge(1)–Ge(2)	2.4307(7)
Pt(2)–Ge(1)	2.4918(5)	Ge(1)–Ge(3)	2.8172(7)
Bond Angles (deg)			
P(1)–Pt(1)–P(2)	87.37(5)	Pt(1)–Ge(1)–Pt(2)	88.751(18)
Ge(1)–Pt(1)–Ge(3)	69.984(17)	Pt(1)–Ge(1)–Pt(3)	86.914(16)
P(3)–Pt(2)–P(4)	87.13(5)	Pt(2)–Ge(1)–Pt(3)	90.484(18)
Ge(1)–Pt(2)–Ge(3)	70.007(18)	Pt(1)–Ge(3)–Pt(2)	92.070(18)
P(5)–Pt(3)–P(6)	87.26(5)	Pt(1)–Ge(3)–Pt(3)	89.985(17)
Ge(1)–Pt(3)–Ge(3)	69.966(17)	Pt(2)–Ge(3)–Pt(3)	93.905(19)

diphenylphosphino group and the triethylgermyl one. The Pt···Pt interatomic distances of 3.42–3.54 Å were similar to those of the bis(μ<sub>3</sub>-silylyne)triplatinum complex [Pt<sub>3</sub>(dppe)<sub>3</sub>(μ<sub>3</sub>-SiR)<sub>2</sub>] (R = H, Me) with a Pt<sub>3</sub>Si<sub>2</sub> core,<sup>13</sup> despite the substitution of main-group elements. The other M<sub>3</sub>Ge<sub>2</sub> clusters had the following M–M single-bond lengths: [Fe<sub>3</sub>(CO)<sub>9</sub>(μ<sub>3</sub>-GeEt)<sub>2</sub>], 2.73 Å;<sup>6c</sup> [Fe<sub>3</sub>(CO)<sub>9</sub>(μ<sub>3</sub>-Ge{Fe(CO)<sub>2</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)}<sub>2</sub>)], 2.72 Å;<sup>6c</sup> [Ru<sub>3</sub>(CO)<sub>9</sub>(μ<sub>3</sub>-Ge{Ru(CO)<sub>2</sub>(η<sup>5</sup>-C<sub>5</sub>Me<sub>4</sub>H)}<sub>2</sub>)], 2.90 Å.<sup>8</sup> For the <sup>1</sup>H NMR spectrum of **5** in C<sub>6</sub>D<sub>6</sub>, the Ge–H peak was observed as a broad signal at 3.0–3.4 ppm due to coupling with six <sup>31</sup>P and three <sup>195</sup>Pt nuclei. The relatively simple spectral pattern was attributed to the 3-fold rotation axis along the Ge–Ge alignment, which agreed with the two near phosphorus resonances at 34.26 and 34.35 ppm in the <sup>31</sup>P NMR spectrum of **5**.

To investigate the formation process of **5**, a <sup>31</sup>P NMR experiment was performed with a molar ratio of [**1**] to [H<sub>3</sub>GeGeEt<sub>3</sub>] of 1/1, because the reaction rate is too fast to detect the reaction intermediates under stoichiometric conditions (Figure 4). The <sup>31</sup>P NMR spectrum at room



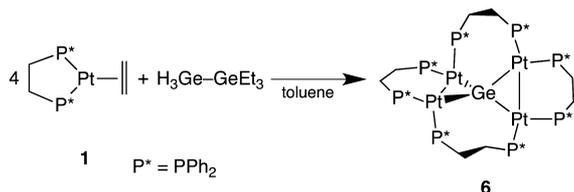
**Figure 4.** <sup>31</sup>P NMR spectra for the reaction of **1** with H<sub>3</sub>GeGeEt<sub>3</sub> at a molar ratio of 1/1 in toluene-*d*<sub>8</sub> at room temperature (A) and at 80 °C for 24 h (B).

temperature showed two sets of two singlets (δ 56.6 (<sup>1</sup>J<sub>PtP</sub> = 2040 Hz)/59.4 (<sup>1</sup>J<sub>PtP</sub> = 1752 Hz) and 55.3 (<sup>1</sup>J<sub>PtP</sub> = 1824 Hz)/56.3 (<sup>1</sup>J<sub>PtP</sub> = 2086 Hz)), and two doublets of doublets (δ 55.0 (<sup>1</sup>J<sub>PtP</sub> = 1917 Hz, <sup>2</sup>J<sub>PP</sub> = 8.1 Hz, <sup>4</sup>J<sub>PP</sub> = 6.2 Hz)/55.8 (<sup>1</sup>J<sub>PtP</sub> = 1920 Hz, <sup>3</sup>J<sub>PtP</sub> = 103 Hz, <sup>2</sup>J<sub>PP</sub> = 8.0 Hz, <sup>4</sup>J<sub>PP</sub> = 6.2 Hz)) with <sup>195</sup>Pt satellites assignable to the digermylplatinum hydride (I-

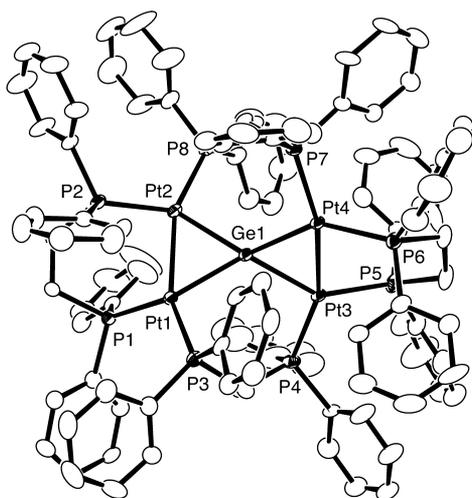
1'), the bis(germyl)platinum complex (I-2'), and the bis( $\mu$ -germylene)diplatinum complex (I-3), respectively. The two doublets of doublets of I-3 were similar to those of 3 and 4, indicating that the two different germylene ligands were bridged between two platinum centers. Incubation at 80 °C for 24 h allowed the consumption of monomer intermediates (I-1', I-2') and the simultaneous appearance of 5, with the remaining diplatinum complex I-3. The spectral data suggested that the sterically less hindered germylene ligands in I-3, generated from I-1' with I-2', might induce the addition of I-2' followed by the formal reductive elimination of GeH<sub>4</sub> and Et<sub>3</sub>GeH to afford 5. The reaction of I-3 with 1 is considered to proceed more rapidly than that with I-2', because the reaction took place under conditions using 1.5 mol equiv of 1 relative to H<sub>3</sub>GeGeEt<sub>3</sub>.

On the other hand, a change of the molar ratio of 1 to H<sub>3</sub>GeGeEt<sub>3</sub> to 4/1 resulted in the formation of the spiro-type tetraplatinum complex [Pt<sub>4</sub>(dpppe)<sub>4</sub>( $\mu_4$ -Ge)] (6) in 36% yield (Scheme 4). The <sup>1</sup>H NMR spectrum during the formation of 6

**Scheme 4. Formation of Spiro-Pt<sub>4</sub>Ge Cluster 6 for the Reaction of 1 with H<sub>3</sub>GeGeEt<sub>3</sub>**



was so complex that the observed species could not be assigned, which is not apparent for the formation process of 6. X-ray diffraction analysis of 6 (Figure 5) showed that the germanium atom had a tetragonal geometry with a Pt<sub>4</sub> donor set, of which the two diplatinum units {Pt<sub>2</sub>(dpppe)} with a Pt–Pt single bond were bridged by two dppe ligands. The Pt–Ge bond lengths were 2.42–2.45 Å, diagnostic of a typical Pt–Ge bond length, and the Pt–Ge–Pt bond angles were similar to



**Figure 5.** Crystal structure of 6, showing 50% probability thermal ellipsoids. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt(1)–Pt(2) = 2.6395(4), Pt(3)–Pt(4) = 2.6788(5), Pt(1)–Ge(1) = 2.4382(8), Pt(2)–Ge(1) = 2.4506(9), Pt(3)–Ge(1) = 2.4436(9), Pt(4)–Ge(1) = 2.4236(9); Pt(1)–Ge(1)–Pt(2) = 65.36(2), Pt(3)–Ge(1)–Pt(4) = 66.78(2).

those of the silicon analogue [Pt<sub>4</sub>(dpppe)<sub>4</sub>( $\mu_4$ -Si)] and other complexes including the spiro-M<sub>4</sub>Ge fragment.<sup>30</sup> Although the formation of the M<sub>4</sub>E (E = Si, Ge) fragment was achieved by treatment of SiH<sub>4</sub> and GeH<sub>4</sub>, our method mentioned so far using the unsymmetrical digermane H<sub>3</sub>GeGeEt<sub>3</sub> as well as disilane H<sub>3</sub>SiSiMe<sub>2</sub><sup>t</sup>Bu is a safe and convenient procedure to regulate the molar ratio to metal sources.

## CONCLUSION

We prepared the 1,1,1-triethylidigermane H<sub>3</sub>GeGeEt<sub>3</sub> by a formally direct hydrogenation from H<sub>2</sub>PhGeGeEt<sub>3</sub> in the presence of CF<sub>3</sub>CO<sub>2</sub>H and studied the reaction of the zerovalent platinum complex [Pt(dpppe)( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)] (1) with unsymmetrical digermanes to afford polyhedral platinum–germanium clusters. The sterically bulky substituents on the digermanes involved multinucleation of product, that is, the digermylplatinum hydride 2 from HPh<sub>2</sub>GeGeMe<sub>3</sub> and the bis(digermylene)diplatinum complexes 3 and 4 from H<sub>2</sub>PhGeGeR<sub>3</sub>, and the desired bis(digermylene)triplatinum complex 5 provided a trigonal-bipyramidal skeleton from H<sub>3</sub>GeGeEt<sub>3</sub>. In contrast with the silicon system, the Ge–Ge bond was relatively inert during the formation process and remained in one of the two bridging germylene or germylene ligands. These results are consistent with the fact that Ge–Ge bond formation on the platinum center often occurs.

## EXPERIMENTAL SECTION

**General Procedure.** All experiments were carried out using standard vacuum line and Schlenk techniques in an Ar atmosphere or drybox. All the reagents were of the highest grade available and were used without further purification. All solvents used for the syntheses were distilled according to the general procedure. Benzene-*d*<sub>6</sub> and toluene-*d*<sub>8</sub> were distilled from potassium metal under an Ar atmosphere. HPh<sub>2</sub>GeGeMe<sub>3</sub> and [Pt(dpppe)(C<sub>2</sub>H<sub>4</sub>)] (1) were synthesized according to the previously reported methods.<sup>31,32</sup> The NMR spectral measurements were performed on a JEOL AL-300 NMR spectrometer at 300 MHz for <sup>1</sup>H and 122 MHz for <sup>31</sup>P. The <sup>1</sup>H chemical shifts were corrected relative to the residual protonated solvent according to the literature.<sup>33</sup> The <sup>31</sup>P chemical shift is corrected relative to external H<sub>3</sub>PO<sub>4</sub> (0 ppm). Elemental analysis was performed on a Thermo Scientific FLASH 2000 corrected by acetoanilide.

**Synthesis of H<sub>2</sub>PhGeGeMe<sub>3</sub>.** To PhGeH<sub>3</sub> (0.820 g, 5.40 mmol) in THF (10 mL) was added a pentane solution of <sup>t</sup>BuLi (3.4 mL, 5.4 mmol) at –80 °C, and the solution was stirred and gradually warmed to –60 °C. Me<sub>3</sub>GeCl (0.820 g, 5.40 mmol) was added to the resulting solution and cooled to –80 °C. After continuous stirring at room temperature, the organic layer was washed with water and dried by anhydrous sodium sulfate. The reaction solution was filtered, and volatiles were removed from the filtrate under reduced pressure carefully. Purification by trap-to-trap distillation afforded H<sub>2</sub>PhGeGeMe<sub>3</sub> as a colorless oil. Yield: 0.43 g (30%). <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>):  $\delta$  7.5–7.4 (m, 2H, Ph), 7.2–7.1 (m, 3H, Ph), 4.40 (s, 2H, GeH), 0.28 (s, 9H, CH<sub>3</sub>). <sup>13</sup>C NMR (benzene-*d*<sub>6</sub>):  $\delta$  135.8 (Ph), 134.5 (Ph *ipso*), 128.6 (Ph), 128.5 (Ph), –0.9 (Me). EI-MS: *m/z* (% relative intensity) 270 (M<sup>+</sup>, 10), 253 (M<sup>+</sup> – H<sub>2</sub> – Me, 9), 151 (M<sup>+</sup> – H<sub>2</sub> – GeMe<sub>3</sub>, 42), 119 (M<sup>+</sup> – GePhH<sub>2</sub>, 100).

**Synthesis of H<sub>2</sub>PhGeGeEt<sub>3</sub>.** H<sub>2</sub>PhGeGeEt<sub>3</sub> was synthesized by the same method as for H<sub>2</sub>PhGeGeMe<sub>3</sub>, except for use of Et<sub>3</sub>GeCl instead of Me<sub>3</sub>GeCl and scaling up to 38.0 mmol for all reagents. Yield: 6.70 g (57%). <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>):  $\delta$  7.6–7.5 (m, 2H, Ph), 7.2–7.1 (m, 3H, Ph), 4.42 (s, 2H, GeH), 1.03 (t, 9H, J = 7.8 Hz, CH<sub>2</sub>CH<sub>3</sub>), 0.87 (q, 6H, J = 8.1 Hz, CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (benzene-*d*<sub>6</sub>):  $\delta$  135.9 (Ph), 134.6 (Ph *ipso*), 128.5 (Ph), 128.4 (Ph), 10.1 (CH<sub>2</sub>CH<sub>3</sub>), 6.0 (CH<sub>2</sub>CH<sub>3</sub>). Anal. Calcd for H<sub>2</sub>PhGeGeEt<sub>3</sub> (C<sub>12</sub>H<sub>22</sub>Ge<sub>2</sub>): C, 46.26; H, 7.12. Found: C, 46.49; H, 7.26. EI-MS:

$m/z$  (% relative intensity) 312 ( $M^+$ , 7), 283 ( $M^+ - Et$ , 10), 255 ( $M^+ + H - Et_2$ , 16), 225 ( $M^+ - Et_3$ , 22), 151 ( $M^+ - H_2 - GeMe_3$ , 37), 161 ( $M^+ - GePhH_2$ , 100), 151 ( $M^+ - H_2 - GeEt_3$ , 91).

**Synthesis of  $H_3GeGeEt_3$ .**  $CF_3COOH$  (1.80 g, 16.0 mmol) was added to a  $CH_2Cl_2$  solution (45 mL) of  $H_2PhGeGeEt_3$  (5.00 g, 16.0 mmol) at  $-50^\circ C$ , and the solution was stirred overnight at  $0^\circ C$ . After removal of all volatiles under reduced pressure,  $CH_2Cl_2$  (45 mL) and  $CF_3COOH$  (1.80 g, 16.0 mmol) were added to the residue at  $-50^\circ C$ . The solution was stirred for 3 days at room temperature and then was evaporated under reduced pressure. The residue was dissolved in  $Et_2O$  (40 mL), the ether solution was added dropwise to a suspension of  $LiAlH_4$  (0.61 g, 16.0 mmol) in  $Et_2O$  (30 mL) on ice bath, and the suspension was stirred for 24 h.<sup>16</sup> The reaction mixture was quenched by the addition of  $H_2O$  and filtered, and the solvent was removed from the filtrate by careful distillation. Purification by trap-to-trap distillation afforded  $H_3GeGeEt_3$  as a colorless oil. Yield: 0.69 g (18%).  $^1H$  NMR (benzene- $d_6$ ):  $\delta$  3.15 (s, 3H,  $GeH_3$ ), 1.01 (t, 9H,  $CH_2CH_3$ ), 0.79 (q, 6H,  $J = 8.8$  Hz,  $CH_2CH_3$ ).  $^{13}C$  NMR (benzene- $d_6$ ):  $\delta$  7.0 ( $CH_2CH_3$ ), 6.1 ( $CH_2CH_3$ ). EI-MS:  $m/z$  (% relative intensity) 236 ( $M^+$ , 7), 207 ( $M^+ - Et$ , 20), 179 ( $M^+ + H - Et_2$ , 37), 161 ( $M^+ - GePhH_2$ , 100).

**Preparation of Platinum Complexes.  $[Pt(dppe)(H)(GePh_2GeMe_3)]$  (2).** To  $HPh_2GeGeMe_3$  (28 mg, 80.4  $\mu$ mol) in toluene (1 mL) was added a toluene solution (1 mL) of **1** (50.0 mg, 80.4  $\mu$ mol) at room temperature, and hexane (2 mL) was added to the resulting solution. The solution was allowed to stand for 2 days to afford colorless crystals. Yield: 29.6 mg (39%).  $^1H$  NMR (benzene- $d_6$ ):  $\delta$  7.82 (d, 8H,  $J = 6.9$  Hz, Ph), 7.27 (t, 4H,  $J = 8.4$  Hz, Ph), 7.1–6.8 (m, 18H, Ph), 2.0–1.6 (m, 4H,  $PCH_2$ ), 0.59 (s, 9H,  $GeMe_3$ ), -0.21 (dd, 1H,  $^1J_{PtH} = 1019$  Hz,  $^2J_{PtH} = 175$  Hz (trans),  $^2J_{PtH} = 11$  Hz (cis), PtH).  $^{31}P\{^1H\}$  NMR (benzene- $d_6$ ):  $\delta$  59.3 (s,  $^1J_{PtP} = 1996$  Hz), 55.4 (s,  $^1J_{PtP} = 2033$  Hz). Anal. Calcd for  $2 \cdot 0.2$  (toluene) ( $C_{42.4}H_{45.6}Ge_2P_2Pt$ ): C, 53.18; H, 4.80. Found: C, 53.11; H, 4.76.<sup>34</sup>

**$[Pt_2(dppe)_2(\mu-GeHPh)(\mu-Ge(Ph)GeMe_3)]$  (3).** To  $H_2PhGeGeMe_3$  (22 mg, 82  $\mu$ mol) in toluene (1 mL) was added a toluene solution (2 mL) of **1** (50.0 mg, 80.4  $\mu$ mol) at  $-30^\circ C$ , and the resulting solution was allowed to stand for 24 h. Hexane (1 mL) was added to the resulting solution. The solution was allowed to stand for 2 days to afford yellow crystals. Yield: 27.8 mg (42%).  $^1H$  NMR (benzene- $d_6$ ):  $\delta$  7.99 (t, 4H,  $J = 8.4$  Hz, Ph), 7.75 (t, 4H,  $J = 7.2$  Hz, Ph), 7.6–7.4 (m, 4H, Ph), 7.2–6.6 (m, 48H, Ph), 4.0–3.7 (m, 1H, GeH), 2.1–1.2 (m, 8H,  $CH_2P$ ), 0.47 (s, 9H,  $GeMe_3$ ).  $^{31}P\{^1H\}$  NMR (benzene- $d_6$ ):  $\delta$  58.0 (d,  $^1J_{PtP} = 1831$  Hz,  $^3J_{PtP} = 175$  Hz,  $^2J_{PtP} = 20$  Hz,  $^4J_{PtP} = 9.4$  Hz), 56.7 (d,  $^1J_{PtP} = 1863$  Hz,  $^3J_{PtP} = 265$  Hz,  $^2J_{PtP} = 20$  Hz,  $^4J_{PtP} = 9.4$  Hz) ( $[Pt(dppe)(\mu-GeHPh)]_2$ : 57.1 (s,  $^1J_{PtP} = 1792$  Hz,  $^3J_{PtP} = 336$  Hz)). IR (KBr,  $cm^{-1}$ ):  $\nu(Ge-H)$  1982 m, 1905 m. Anal. Calcd for  $(3)_{0.9} \cdot ([Pt(dppe)(\mu-GeHPh)]_2)_{0.1}$  ( $C_{66.7}H_{67.2}Ge_{2.9}P_4Pt_2$ ): C, 50.27; H, 4.25. Found: C, 49.83; H, 4.00.

**$[Pt_2(dppe)_2(\mu-GeHPh)(\mu-Ge(Ph)GeEt_3)]$  (4).** To  $H_2PhGeGeEt_3$  (12.6 mg, 53.6  $\mu$ mol) in toluene (1 mL) was added a toluene solution (1 mL) of **1** (50.0 mg, 80.4  $\mu$ mol) at room temperature, and the resulting solution was stirred at  $80^\circ C$  for 24 h. Hexane (1 mL) was added to the resulting solution. The solution was allowed to stand for 2 days to afford yellow crystals. Yield: 19.4 mg (29%).  $^1H$  NMR (benzene- $d_6$ ):  $\delta$  7.98 (t, 4H,  $J = 8.4$  Hz, Ph), 7.85 (t, 4H,  $J = 8.1$  Hz, Ph), 7.6–7.4 (m, 2H, Ph), 7.3–6.7 (m, 50H, Ph), 3.8–3.5 (m, 1H, GeH), 2.2–1.5 (m, 8H,  $CH_2P$ ), 1.19 (t, 9H,  $J = 7.7$  Hz,  $CH_2CH_3$ ), 0.89 (q, 6H,  $J = 7.7$  Hz,  $CH_2CH_3$ ).  $^{31}P\{^1H\}$  NMR (benzene- $d_6$ ):  $\delta$  57.6 (d,  $^1J_{PtP} = 1810$  Hz,  $^3J_{PtP} = 185$  Hz,  $^2J_{PtP} = 23$  Hz,  $^4J_{PtP} = 9.4$  Hz), 55.2 (d,  $^1J_{PtP} = 1888$  Hz,  $^3J_{PtP} = 283$  Hz,  $^2J_{PtP} = 23$  Hz,  $^4J_{PtP} = 9.4$  Hz). IR (KBr,  $cm^{-1}$ ):  $\nu(Ge-H)$  1874 m. Anal. Calcd for  $4$  ( $C_{70}H_{74}Ge_3P_4Pt_2$ ): C, 51.04; H, 4.53. Found: C, 51.25; H, 4.49.

**$[Pt_3(dppe)_3(\mu_3-GeH)(\mu_3-GeGeEt_3)]$  (5).** To  $H_3GeGeEt_3$  (12.6 mg, 53.5  $\mu$ mol) in benzene (2 mL) was added a benzene solution (2 mL) of **1** (50.0 mg, 80.4  $\mu$ mol) at room temperature, and the resulting solution was stirred at  $80^\circ C$  for 2 days. Hexane (6 mL) was added to the resulting solution. The solution was allowed to stand for 2 days to afford orange crystals. Yield: 5.3 mg (9.5%).  $^1H$  NMR (benzene- $d_6$ ):  $\delta$  8.3–8.2 (m, 12H, Ph), 7.30 (t, 18H,  $J = 7.2$  Hz, Ph), 7.2–7.1 (m, 12H, Ph), 6.98 (t, 6H,  $J = 6.9$  Hz, Ph), 6.84 (t, 12H,  $J = 6.9$  Hz, Ph), 3.4–3.0 (br, 1H, GeH), 2.1–1.7 (m, 12H,  $CH_2P$ ), 0.59 (t, 9H,  $J = 7.8$  Hz,

$CH_2CH_3$ ), 0.33 (q, 6H,  $J = 7.6$  Hz,  $CH_2CH_3$ ).  $^{31}P\{^1H\}$  NMR (benzene- $d_6$ ):  $\delta$  34.35 (s,  $^1J_{PtP} = 2197$  Hz,  $^3J_{PtP} = 83$  Hz), 34.26 (s,  $^1J_{PtP} = 2572$  Hz,  $^3J_{PtP} = 83$  Hz). IR (KBr,  $cm^{-1}$ ):  $\nu(Ge-H)$  1959 m. Anal. Calcd for  $5 \cdot C_6H_6$  ( $C_{90}H_{94}Ge_3P_6Pt_3$ ): C, 49.94; H, 4.38. Found: C, 50.21; H, 4.01.

**$[Pt_4(dppe)_4(\mu_4-Ge)]$  (6).** To a toluene solution (2 mL) of **1** (20 mg, 32  $\mu$ mol) was added a toluene solution (1 mL) of  $H_3GeGeEt_3$  (1.9 mg, 8.1  $\mu$ mol) at  $-30^\circ C$ , and the resulting solution was allowed to stand for 3 weeks at room temperature. Hexane (2 mL) was added, and the solution was allowed to stand for 1 week to afford dark brown crystals. Yield: 7.0 mg (36%).  $^1H$  NMR (benzene- $d_6$ ):  $\delta$  7.74 (br s, 4H, Ph), 7.5–7.3 (br, 4H, Ph), 7.27 (br s, 4H, Ph), 7.1–6.7 (m, 20H, Ph), 6.73 (t, 4H,  $J = 7.5$  Hz, Ph), 6.65 (t, 4H,  $J = 7.5$  Hz, Ph), 4.2–3.9 (br, 4H,  $CH_2P$ ), 3.1–2.8 (br, 4H,  $CH_2P$ ), 2.47 (br s, 8H,  $CH_2P$ ). Anal. Calcd for  $6 \cdot 2.5$  (toluene) ( $C_{121.5}H_{116}Ge_8Pt_4$ ): C, 54.51; H, 4.37. Found: C, 54.41; H, 4.08.

**X-ray Crystallography.** Single crystals suitable for XRD analyses were obtained from toluene/hexane solutions for **2–4** and benzene/hexane solutions for **5** and **6**. Each crystal was mounted on a glass fiber, and the diffraction data were collected on a Bruker APEX II CCD detector using graphite-monochromated Mo  $K\alpha$  radiation at 123 K (Table S1).

All the structures were solved by a combination of direct methods and Fourier techniques, and all the non-hydrogen atoms were anisotropically refined by full-matrix least-squares calculations. The atomic scattering factors and anomalous dispersion terms were obtained from ref 35. The refinement of all structures was carried out by full-matrix least-squares methods of SHELXL-97.<sup>36</sup>

## ■ ASSOCIATED CONTENT

### Supporting Information

A figure giving selected  $^{31}P$  NMR spectra for the reaction of **1** with  $H_2PhGeGeEt_3$  and a table and CIF files giving crystallographic data for the platinum–germanium complexes **2–6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*Tel: +81-3-3986-0221. Fax: +81-3-5992-1029. E-mail: kunio.mochida@gakushuin.ac.jp.

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was financially supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 21550066) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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