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Chemical Properties of Tetragermaplatinacyclopentane. Insertion of an Alkyne into a Pt–Ge Bond and Silylation Caused by H_2SiPh_2

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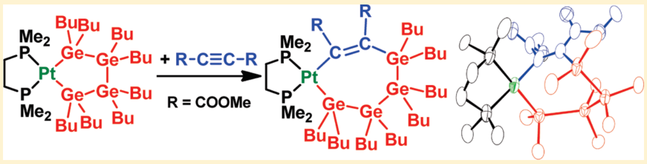
Supporting Information



ABSTRACT: A platinum complex having dibutylgermyl ligands, $[\mathrm{Pt(GeHBu_2)_2(dmpe)}]$ (dmpe = 1,2-bis(dimethylphosphino)ethane), reacted with excess H_2GeBu_2 at 90 °C to yield a five-membered tetragermaplatinacycle, $[\overline{\mathrm{Pt(GeBu_2GeBu_2GeBu_2Ge}}\mathrm{Bu_2)(dmpe)}]$ (**6**). The direct reaction of H_2GeBu_2 with $[\mathrm{Pt(dmpe)_2}]$ in 5:1 ratio also gave **6** in 67% yield. The reaction of dimethyl acetylenedicarboxylate with **6** caused insertion of a C≡C bond into a Pt–Ge bond to form a seven-membered germaplatinacycloheptene, which was characterized by X-ray crystallography. Complex **6** reacted with H_2GePh_2 and H_2SiPh_2 in 1:2 ratio to produce a mixture of tetragermane dihydride $\mathrm{H(GeBu_2)_4H}$ and bis(silyl)- or bis(germyl)platinum complexes $[\mathrm{Pt(EHPh_2)_2(dmpe)}]$ (E = Si, Ge).

INTRODUCTION

Persilylated and pergermylated metallacycles (Chart 1) are much less common than their carbon analogues, metallacycloalkanes, because of limitation in the preparation reactions.[1] Sila-[2] and germametallacycles[3] containing early transition metal complexes were reported to be obtained from metathesis reactions of dianionic oligosilanes or oligogermanes with dihalo complexes of these metals. The above metallacycles of late transition metals can be obtained by oxidative addition of two E–H (E = Si, Ge) bonds of oligosilanes or oligogermanes or E–E bond activation of the cyclic oligosilanes and oligogermanes to low-valent metal complexes. West reported that Pd-catalyzed reactions of cyclotetrasilane $(\mathrm{SiEt_2})_4$ with alkynes produced cyclotetrasilahexenes $\overline{\mathrm{SiEt_2SiEt_2SiEt_2SiEt_2CR{=}C}}\mathrm{R}$. They proposed the reaction mechanism that involved a persilylated palladacyclopentane intermediate, $[\overline{\mathrm{Pd(SiEt_2SiEt_2SiEt_2Si}}\mathrm{Et_2)(PPh_3)}_n]$, and its conversion into a seven-membered palladacycle, $[\overline{\mathrm{Pd(SiEt_2SiEt_2SiEt_2SiEt_2CR{=}C}}\mathrm{R)(PPh_3)}_n]$, via insertion of alkynes into the Pd–Si bond.[4] Mochida reported ring enlargement of cyclotetragermane $(\mathrm{Ge}^i\mathrm{Pr_2})_4$ with alkynes catalyzed by the Pd complexes and suggested via insertion of alkynes into the Pd–Ge bond of five-membered tetragermapalladacycle intermediates.[5] In these reactions, the postulated insertion of alkynes into the M–Ge bond was not demonstrated. Chemistry of persilylated and pergermylated metallacycles has become significant in recent years. Schram reported $[\overline{\mathrm{Pt(SiPh_2SiPh_2SiPh_2Si}}\mathrm{Ph_2)(PPh_3)_2}]$ as the first example of a transition metal *cyclo*-oligosilane complex.[6] Four- and five-membered platinacycles containing Si and Ge atoms $[\overline{\mathrm{Pt\{GePh_2(SiMe_2)_nGe}}\mathrm{Ph_2\}(PPh_3)_2}]$ (n = 1, 2) were prepared from the reaction of $\mathrm{HGePh_2(SiMe_2)_nPh_2GeH}$ with $[\mathrm{Pt}(\eta^2\text{-}\mathrm{C_2H_4})(\mathrm{PPh_3})_2]$.[7] Braddock-Wilking reported preparation of five-membered platinacycles $[\overline{\mathrm{Pt(ER_2ER_2ER_2E}}\mathrm{R_2)(dppe)}]$ ($\mathrm{ER_2} = \mathrm{SiC_{12}H_8}$ or $\mathrm{GeC_{12}H_8}$) from the reaction of $[\mathrm{PtMe_2(dppe)}]$ with excess sila- and germafluorenes.[8] We found conversion of bis(germyl)palladium and -platinum complexes $[\mathrm{M(GeHPh_2)_2(dmpe)}]$ (M = Pd, Pt (**1**)) to a four-membered platinum trigermane complex, $[\overline{\mathrm{Pt(GePh_2GePh_2Ge}}\mathrm{Ph_2)(dmpe)}]$ (**2**), and further to tetragermametallacyclopentanes $[\overline{\mathrm{M(GePh_2GePh_2GePh_2Ge}}\mathrm{Ph_2)(dmpe)}]$ (M = Pd,[9] Pt (**3**)[10]) upon their reactions with H_2GePh_2, as shown in Scheme 1. In this paper, we report the preparation of a new germaplatinacycle composed of dibutylgermylene groups as well as their new chemical properties.

RESULTS AND DISCUSSION

A platinum complex with dibutylgermyl ligands, $[\mathrm{Pt(GeHBu_2)_2(dmpe)}]$ (**4**), was obtained in 71% yield from the reaction of $[\mathrm{Pt(dmpe)_2}]$ with H_2GeBu_2 in 1:2 ratio at room temperature. Further reaction of **4** with excess H_2GeBu_2 at 90 °C for 230 h produced a tetragermaplatinacyclopentane, $[\overline{\mathrm{Pt(GeBu_2GeBu_2GeBu_2Ge}}\mathrm{Bu_2)(dmpe)}]$ (**6**), in 37% yield (Scheme 2). The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectra during the reaction indicated formation of a four-membered trigermaplatinum intermediate, $[\overline{\mathrm{Pt(GeBu_2GeBu_2Ge}}\mathrm{Bu_2)(dmpe)}]$ (**5**) (*vide infra*). Direct reaction of $[\mathrm{Pt(dmpe)_2}]$ with H_2GeBu_2 in 1:5 ratio on heating at 90 °C for 45 h produced **6** in 67% yield.

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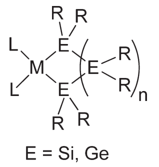
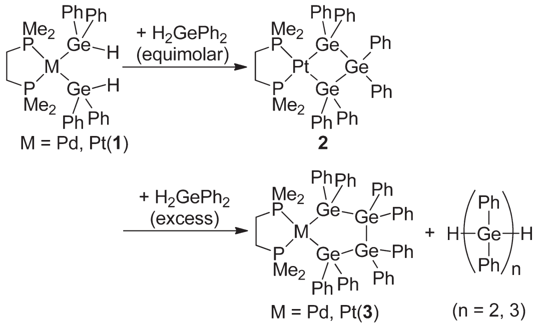
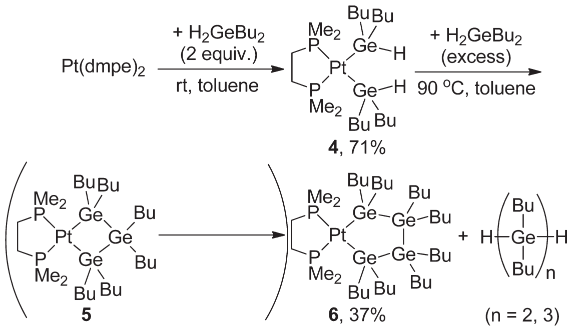
Chart 1



Scheme 1



Scheme 2



The ^1H NMR spectrum of the product mixture showed accompanying formation of oligogermane dihydrides, $H(GeBu_2)_nH$ (n = 2, 3; Ge−H signals at δ 4.09 and 4.13). Complexes **4** and **6** were air and thermally stable, and complex **6** was separated by silica gel column chromatography.

Figure 1 shows the molecular structure of **4** having Pt with a square-planar geometry. Table 1 compares their bond parameters with those of the $GePh_2$ analogue **1**. The Pt−Ge bonds of **4** (2.4454(5), 2.4380(5) Å) are within the range of the Pt−Ge bonds of *cis*-bis(germyl)platinum complexes with phosphine ligands (2.427(2)−2.499(1) Å).[7,8,10,11] The Pt−P bonds of **4** (2.267(1), 2.276(1) Å) are slightly shorter than those of **1** (M = Pt, 2.293(1), 2.295(2) Å).[10] The ^1H NMR spectrum of **4** exhibits a Ge−H hydrogen signal at δ 4.16 flanked with ^{195}Pt satellites ($^2J_{Pt-H}$ = 69 Hz). The peak is shifted downfield compared to H_2GeBu_2 (δ 3.86), similarly to the Ge−H signal of **1** (M = Pt: δ 5.82, H_2GePh_2: δ 5.15). The $^{13}C\{^1H\}$ NMR spectrum of **4** displays four signals of *n*-butyl carbons at δ 33.1, 27.5, 18.2, and 14.4. The α- and β-carbon signals (δ 18.2, 33.1) show coupling with ^{195}Pt nuclei (J_{Pt-C} = 55 and 23 Hz, respectively). The *n*-butyl carbon signals of **6** are observed as eight peaks, indicating the presence of two sets of $GeBu_2$ groups. The α-carbon signal at δ 19.6 with a large coupling constant (38 Hz) is assigned to the $GeBu_2$ groups bonded to the Pt atom, while the signal at δ 14.5 with a small $^3J_{Pt-C}$ value (16 Hz) is due to the α-carbon of internal $GeBu_2$ groups.

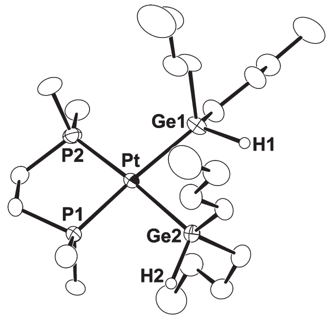


Figure 1. Thermal ellipsoids (50% probability) of **4**. Carbon-bound hydrogen atoms except for Ge−H hydrogens are omitted for simplicity.

Table 1. Selected Bond Distances (Å) and Angles (deg) of 4 and 1

	4	1[a]
Pt−Ge	2.4454(5), 2.4380(5)	2.4527(4), 2.4411(6)
Pt−P	2.267(1), 2.276(1)	2.293(1), 2.295(2)
Ge−H	1.70(6), 1.61(4)	1.57(4), 1.87(3)
Ge−Pt−Ge	86.04(2)	90.63(2)
P−Pt−P	86.29(4)	85.06(4)

[a] Data from ref 10.

Figure 2 shows the $^{31}P\{^1H\}$ NMR spectra during the 1:2 reaction of **4** and H_2GeBu_2 at 90 °C in toluene-d_8. After 14 h, the signal of **4** (δ 36.9, J_{Pt-P} = 1762 Hz) was decreased upon heating the reaction mixture, and a small signal of tetragermaplatinacyclopentane **6** at δ 33.7 (J_{Pt-P} = 1726 Hz) was observed (Figure 2a). A major signal at δ 36.3 (J_{Pt-P} = 1652 Hz) was assigned to trigermaplatinacyclobutane **5** because further heating of the solution caused a decrease of the peak of **4** and an increase of the signal due to **6** after 42 h of heating (Figure 2b). We reported the reaction of H_2GePh_2 with $[Pt(GeHPh_2)_2(dmpe)]$ to produce $[Pt(GePh_2GePh_2GePh_2)(dmpe)]$ (**2**, M = Pt), which was converted into $[Pt(GePh_2GePh_2GePh_2GePh_2)(dmpe)]$ (**3**, M = Pt), as well as the structures and spectroscopic data of the isolated complexes.[10] Complex **5** is not isolable from the reaction mixture, but it shows a smaller J_{Pt-P} value (1652 Hz) than **4** (1762 Hz) and **6** (1726 Hz), similarly to **2** (1819 Hz, **1** = 1895 Hz, **3** = 1851 Hz). Two small doublets with an AB pattern at δ 34.1 (J_{Pt-P} = 1810 Hz) and δ 34.7 (J_{Pt-P} = 1674 Hz) may be attributed to unsymmetrical Pt intermediates having two different Ge ligands ($-GeHBu_2$ and $-(GeBu_2)_2-GeHBu_2$, for example), formed during the reaction.

Germaplatinacycle **6** reacted with dimethyl acetylenedicarboxylate (DMAD) in 1:3 ratio at 90 °C for 46 h to afford a 4,5,6,7-tetragerma-3-platinacycloheptene, $[Pt\{C(COOMe){=}C(COOMe)GeBu_2GeBu_2GeBu_2GeBu_2\}(dmpe)]$ (**7**), in 82% yield (eq 1). The reaction involves

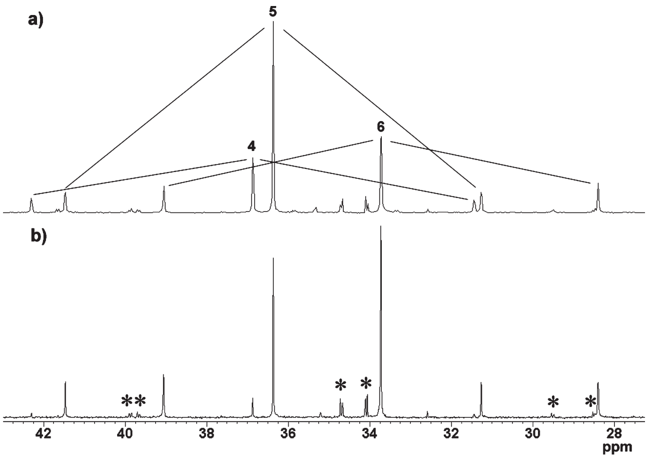


Figure 2. $^{31}P\{^1H\}$ NMR spectra during conversion of **4** into **6** in the presence of 2-fold H_2GeBu_2 at 90 °C in toluene-d_8 (a) after 14 h and (b) after 42 h. Two doublets at δ 34.1 (J_{Pt-P} = 1810 Hz) and 34.7 (J_{Pt-P} = 1674 Hz) labeled with an asterisk may be assigned as platinum intermediates with two different Ge ligands.

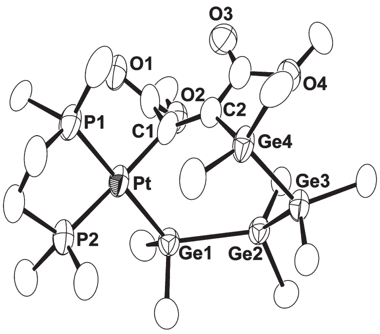
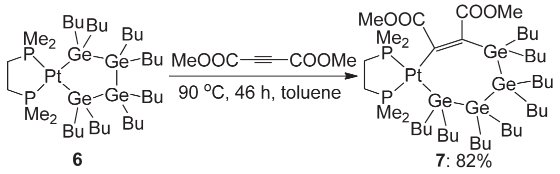


Figure 3. Thermal ellipsoids (50% probability) of **7**. All β-, γ-, and δ-carbons of n-Bu groups and carbon-bound hydrogen atoms are omitted for simplicity. Selected bond distances [Å] and angles [deg]: Pt−Ge1 2.497(1), Pt−P1 2.321(3), Pt−P2 2.310(4), Pt−C1 2.05(1), Ge1−Ge2 2.481(2), Ge2−Ge3 2.455(2), Ge3−Ge4 2.435(2), Ge4−C2 2.01(1), C1−C2 1.36(2), Ge1−Pt−P2 96.35(8), Ge1−Pt−C1 88.1(3), P1−Pt−P2 84.6(1), P1−Pt−C1 91.2(3), Pt−Ge1−Ge2, 119.80(5), Ge1−Ge2−Ge3 113.81(5), Ge2−Ge3−Ge4 103.90(5), Ge3−Ge4−C2 105.6(3), Pt−C1−C2 131.1(9), Ge4−C2−C1 124.3(9).

insertion of DMAD into a Pt−Ge bond.



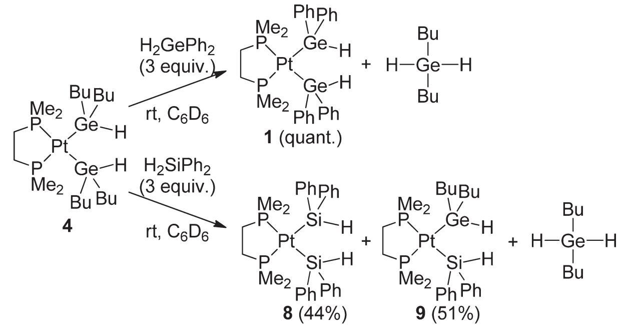
(1)

Figure 3 shows the molecular structure of **7**, which has a seven-membered ring with a boat conformation. Three n-butyl chains are disordered and the corresponding carbons are refined isotropically. The Pt−Ge bond of **7** (2.497(1) Å) is slightly longer than those of bis(germyl)platinum complex **4** (2.4454(5), 2.4380(5) Å) and germaplatinacycles **2** (2.451(1), 2.4542(9) Å) and **3** (2.4643(4), 2.4769(4) Å).[10] Three Ge−Ge bonds of **7** (2.481(2), 2.455(2), 2.435(2) Å) are longer than those of *cyclo*-$(GeMe_2)_6$ (2.409(2)−2.430(2) Å),[12] but shorter than that of $^tBu_3GeGe^tBu_3$ (2.705(1), 2.714(1) Å, the longest Ge−Ge bond).[13] The Pt−Ge1−Ge2 and Ge1−Ge2−Ge3 angles (119.80(5)°, 113.81(5)°) are larger than Ge2−Ge3−Ge4 and Ge3−Ge4−C2 angles (103.90(5)°, 105.6(3)°) to cause more severe deviation of Ge3 and Ge4 from the coordination plane than Ge1 and Ge2. The $^{31}P\{^1H\}$ NMR spectrum of **7** displays two signals at δ 31.9 and 16.6 coupled with the ^{195}Pt nuclei (J_{Pt-P} = 1696 and 2003 Hz, respectively). The former signal shows a similar coupling constant to that of **6** (J_{Pt-P} = 1726 Hz) and is assigned to the phosphorus *trans* to the coordinating Ge atom based on the larger *trans* influence of Ge than C. Two ^{13}C NMR signals of the vinyl carbons appear as a doublet of doublets at δ 181.0 (J_{P-C} = 106 and 12 Hz) and 138.0 (J_{P-C} = 9 and 3 Hz) and are flanked with ^{195}Pt satellite signals (J_{Pt-C} = 769 and 28 Hz, respectively). The aliphatic region of the $^{13}C\{^1H\}$ NMR spectrum contains 32 signals due to the carbons of eight n-butyl groups. This suggests a fixed conformation of the seven-membered chelate ring even in the solution.

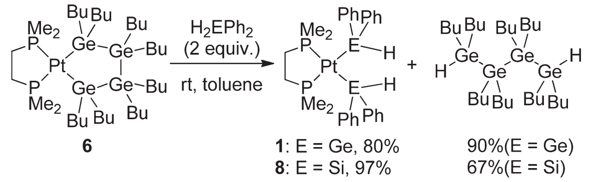
Thus, the tetragermaplatinacyclopentane **6** undergoes insertion of DMAD into a Pt−Ge bond, forming the seven-membered metallacycle. This is in contrast to the $GePh_2$ analogue **3**, which does not react with DMAD even under heating at 80 °C. Mochida proposed the formation of a tetragermapalladacyclopentane, insertion of an alkyne into a Pd−Ge bond, and reductive elimination of a six-membered-ring compound in the discussion of the mechanism of a Pd-catalyzed reaction.[5] Related C−Si bond forming reactions of the mononuclear silyl(alkyl)platinum complexes were reported to be enhanced by coordination of π-acidic compounds or phosphine ligands.[14] Reactions of the seven-membered platinacycle **7** with a 3-fold molar amount of DMAD, DMPE, H_2GeBu_2, and H_2GePh_2 at room temperature and even at 80 °C, however, did not afford any products via the reductive elimination.

Recently, preparation of discrete linear and branched oligogermanes was accomplished by stepwise Ge−Ge coupling reactions of R_3Ge-H with R'_3Ge-CH_2CN in the absence of transition metal complexes.[15] We reported that oligogermaplatinacycles **2** and **3** underwent the exchange of tri- and tetragermanediyl groups with H_3GePh, providing the oligogermane dihydrides $H(GePh_2)_nH$ (n = 3, 4) and unidentified germanium−platinum complexes.[10] The exchange reactions of H_2GePh_2 and H_2SiPh_2 with **6** were conducted with expectation of elimination of the oligogermane ligand. Addition of H_2GePh_2 to the solution of **6** in 2:1 ratio at room temperature produced a mixture of bis(germyl)platinum complex **1** and tetragermane $H(GeBu_2)_4H$ in 80% and 90% yields, respectively (eq 2). The analogous exchange reaction using H_2SiPh_2 also afforded bis(silyl)platinum complex $[Pt(SiHPh_2)_2(dmpe)]$ (**8**)[16] and $H(GeBu_2)_4H$ as a mixture (97% and 67%, respectively). The isolated $H(GeBu_2)_4H$ was characterized on the basis of the ^1H and $^{13}C\{^1H\}$ NMR spectroscopic data. In the ^1H NMR spectra, the Ge−H hydrogen signal displays a quintet at δ 4.10, which is shifted downfield from the position of H_2GeBu_2 (δ 3.86). These reactions proceed smoothly without byproduct at room temperature. The equimolar reaction of H_2SiPh_2 with **6** gives a mixture of the product **8** and

Scheme 3



unreacted **6** in equimolar ratio, and no other compounds were obtained in the reaction mixture.



(2)

These results were compared with a similar exchange using the bis(germyl)platinum complex **4**. The reaction of H_2GePh_2 with **4** in 3:1 ratio at room temperature for 46 h caused quantitative exchange of $GeBu_2H$ with $GePh_2H$ groups to form complex **1**, together with elimination of H_2GeBu_2, which were confirmed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy (Scheme 3). In contrast, treatment of a 3-fold molar amount of H_2SiPh_2 with **4** at room temperature for 46 h gave a mixture of bis(silyl)platinum complex **8** (44%) and a silyl(germyl)platinum intermediate, $[Pt(SiHPh_2)(GeHBu_2)(dmpe)]$ (**9**, 51%), as well as a small amount of unreacted compound **4** (5%). The ^{31}P NMR signals of **9** in the reaction mixture are observed as two doublets at δ 35.3 (J_{Pt-P} = 1766 Hz) and 39.2 (J_{Pt-P} = 1440 Hz) with equal J_{P-P} constant values (10 Hz). The J_{Pt-P} values are comparable to those of bis(germyl)platinum **4** (J_{Pt-P} = 1762 Hz) and of bis(silyl)platinum complex **8** (J_{Pt-P} = 1457 Hz).[16] These results suggest that exchange of Pt−$GeBu_2H$ with Pt−$SiPh_2H$ occurs more slowly than the reaction in eq 2, probably because the Ge−H bond activation of H_2GePh_2 is kinetically dominant over the Si−H bond activation of H_2SiPh_2.

In summary, we prepared a new tetragermaplatinacyclopentane composed of $GeBu_2$ groups. The insertion of DMAD into a Pt−Ge bond takes place similarly to the mechanism proposed for the Pd-catalyzed cycloaddition of tetrasilanes[4] or -germanes[5] to alkynes. The seven-membered germaplatinacycle is successfully isolated and fully characterized. Smooth and facile exchange reactions of the five-membered germaplatinacycle **6** occur due to strained energy of the metallacycle or formation of $H(GeBu_2)_4H$ having stable Ge−H bonds.

■ EXPERIMENTAL SECTION

General Procedures. All manipulations of the complexes were carried out using standard Schlenk techniques under an argon or nitrogen atmosphere or in a nitrogen-filled glovebox (Miwa MFG). Hexane and toluene were purified by using a solvent purification system (Glass Contour). The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on Varian Mercury 300 MHz and Bruker BioSpin Avance III 400 MHz NMR spectrometers. Chemical shifts in ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to the residual peaks of the solvents used. The peak position of the $^{31}P\{^1H\}$ NMR spectrum was referenced to external 85% H_3PO_4 (δ 0) in C_6D_6. IR absorption spectra were recorded on a Shimadzu FT/IR-8100 spectrometer. Elemental analysis was performed using a LECO CHNS-932 or Yanaco MT-5 CHN autorecorder at the Center for Advanced Materials Analysis, Technical Department, Tokyo Institute of Technology. Mass spectroscopic data were obtained on a Bruker Daltonics micrOTOF II (APCI) spectrometer. H_2GeBu_2 and H_2GePh_2 were synthesized from reduction of Cl_2GeBu_2 (Wako Pure Chemical Industries) and Cl_2GePh_2 (Sigma-Aldrich) by $LiAlH_4$. $[Pt(dmpe)_2]$ was prepared according to the literature procedure.[17] Dimethyl acetylenedicarboxylate (Tokyo Chemical Industry) was distilled by trap-to-trap under vacuum prior to use. H_2SiPh_2 (Wako Pure Chemical Industries) was used without further purification.

Preparation of $[Pt(GeHBu_2)_2(dmpe)]$ (4). In the glovebox, to a hexane solution (3 mL) of $[Pt(dmpe)_2]$ (201 mg, 0.41 mmol) was added 2-fold H_2GeBu_2 (153 mg, 0.81 mmol). The reaction mixture was stirred at room temperature for 18 h, and the solid in the mixture was removed by filtration. The solution was stored in a freezer overnight to produce **4** as colorless crystals suitable for X-ray crystallography (209 mg, 71%). Anal. Calcd for $C_{22}H_{54}Ge_2P_2Pt$: C, 36.65; H, 7.55. Found: C, 36.83; H, 7.35. ^1H NMR (400 MHz, C_6D_6, rt): δ 4.16 (m, 2H, Ge*H*, $^3J_{H-H}$ = 3.6 Hz, $^2J_{Pt-H}$ = 69 Hz), 1.80 (m, 8H, $GeCH_2CH_2$), 1.59 (m, 12H, $GeCH_2$, $GeCH_2CH_2CH_2$), 1.36 (m, 4H, $GeCH_2$), 1.17 (d, 12H, PCH_3, $^2J_{P-H}$ = 8.0 Hz, $^3J_{Pt-H}$ = 24 Hz), 1.03 (t, 12H, $GeCH_2CH_2CH_2CH_3$, $^3J_{H-H}$ = 8.0 Hz), 0.83 (m, 4H, PCH_2, *J* = 16.0 Hz). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, rt): δ 33.1 ($GeCH_2CH_2$, $^3J_{Pt-C}$ = 23 Hz), 30.0 (m, PCH_2), 27.5 ($GeCH_2CH_2CH_2$), 18.2 (vt, $GeCH_2$, $|^3J_{P-C} + ^3J_{P-C}|$ = 4.7 Hz, $^2J_{Pt-C}$ = 55 Hz), 14.4 ($GeCH_2CH_2CH_2CH_3$), 13.2 (m, PCH_3). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, rt): δ 36.7 (J_{Pt-P} = 1762 Hz). IR (KBr): 1865 (br, ν_{Ge-H}) cm^{-1}.

Preparation of $[\overline{Pt(GeBu_2GeBu_2GeBu_2GeBu_2})(dmpe)]$ (6). To a toluene solution (1 mL) of **4** (106 mg, 0.15 mmol) was added excess H_2GeBu_2 (140 mg, 0.74 mmol). The reaction mixture was stirred at 90 °C for 230 h, and the solution was removed under reduced pressure to get a yellow, oily residue. The crude product was purified by silica gel chromatography with ether/hexane (1:5) as eluent (R_f = 0.45) to obtain **6** as a white solid (60 mg, 37%). The ^1H NMR spectrum of the crude product displayed two quintets at δ 4.09 and 4.13 assigned to oligogermanes $H(GeBu_2)_nH$ (n = 2, 3). All signals of **6** in the ^1H and $^{13}C\{^1H\}$ NMR spectra were characterized by 2D NMR experiments. Anal. Calcd for $C_{38}H_{88}Ge_4P_2Pt$: C, 41.77; H, 8.12. Found: C, 41.92; H, 7.84. ^1H NMR (400 MHz, C_6D_6, rt): δ 1.80 (m, 8H, $GeCH_2CH_2$), 1.74 (m, 8H, $GeCH_2CH_2$), 1.65−1.39 (m, 32H, $GeCH_2$, $GeCH_2CH_2CH_2$), 1.23 (d, 12H, PCH_3), 1.09 (t, 12H, $GeCH_2CH_2CH_2CH_3$, $^3J_{H-H}$ = 7.4 Hz), 1.05 (t, 12H, $GeCH_2CH_2CH_2CH_3$, $^3J_{H-H}$ = 7.4 Hz), 0.76 (m, 4H, PCH_2, $^2J_{P-H}$ = 18 Hz). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, rt): δ 32.8 ($GeCH_2CH_2$, $^3J_{Pt-C}$ = 27 Hz), 31.8 ($GeCH_2CH_2$), 31.2 (m, PCH_2), 27.8 ($GeCH_2CH_2CH_2$), 27.4 ($GeCH_2CH_2CH_2$), 19.6 (vt, $GeCH_2$, $|^3J_{P-C} + ^3J_{P-C}|$ = 6 Hz, $^2J_{Pt-C}$ = 38 Hz), 15.3 (d, PCH_3, $^3J_{P-C}$ = 24 Hz, $^2J_{Pt-C}$ = 37 Hz), 14.5 ($GeCH_2$, $^3J_{Pt-C}$ = 16 Hz), 14.1 ($GeCH_2CH_2CH_2CH_3$), 13.9 ($GeCH_2CH_2CH_2CH_3$). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, rt): δ 33.6 (J_{Pt-P} = 1726 Hz). HRMS (APCI): calcd for $C_{38}H_{89}Ge_4P_2Pt$ $[M + H]^+$ 1098.2934, found m/z 1098.3054.

Direct Preparation of 6 from $[Pt(dmpe)_2]$. A mixture of $[Pt(dmpe)_2]$ (307 mg, 0.62 mmol) and H_2GeBu_2 (593 mg, 3.14 mmol) in 1:5 ratio in toluene (3 mL) was heated at 90 °C for 45 h. The purification was conducted similarly to give **6** (456 mg, 67%).

NMR Experiments during the Reaction Converting 4 and H_2GeBu_2 into 6. A toluene-d_8 solution (0.5 mL) of **4** (20 mg, 0.028 mmol) and H_2GeBu_2 (11 mg, 0.058 mmol) was heated at 90 °C in an NMR sample tube. The $^{31}P\{^1H\}$ NMR spectrum of the reaction solution displayed a mixture of **4** (δ 36.9, J_{Pt-P} = 1762 Hz), **5** (δ 36.3, J_{Pt-P} = 1652 Hz), and **6** (δ 33.7, J_{Pt-P} = 1726 Hz), together with two small doublets at δ 34.1 (J_{Pt-P} = 1810 Hz) and 34.7 (J_{Pt-P} = 1674 Hz) with the same J_{P-P} values (8.1 Hz). The ratio of **4**:**5**:**6** (20:45:35) after 14 h changed to 5:37:58 after 42 h based on the intensity of ^{31}P NMR signals.

Preparation of $[\overline{Pt\{C(COOMe)=C(COOMe)GeBu_2GeBu_2GeBu_2GeBu_2}\}(dmpe)]$ (7). To a toluene solution (4 mL) of **6** (213 mg, 0.19 mmol) was added DMAD (83.5 mg, 0.59 mmol). The reaction mixture was heated at 90 °C for 46 h. The solvent was pumped off to get a crude product. Separation by column chromatography with ether/hexane (2:1) as eluent (R_f = 0.29) gave complex **7** as a white solid (193 mg, 82%). Recrystallization from hexane at −20 °C afforded crystals of **7** suitable for X-ray crystallography. All signals of **7** in the ^1H and $^{13}C\{^1H\}$ NMR spectra were assigned by 2D NMR experiments. Anal. Calcd for $C_{44}H_{94}Ge_4O_4P_2Pt$: C, 42.80; H, 7.67. Found: C, 42.90; H, 7.67. ^1H NMR (400 MHz, C_6D_6, rt): δ 3.61 (s, 3H, $COOCH_3$), 3.57 (s, 3H, $COOCH_3$), 1.8−1.4 (48H, $GeCH_2$, $GeCH_2CH_2$, $GeCH_2CH_2CH_2$), 1.4−0.9 (40H, PCH_3, PCH_2, $GeCH_2CH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, rt): δ 181.0 (dd, PtC=, $^2J_{P-C}$ = 12, 106 Hz, J_{Pt-C} = 769 Hz), 177.0 (m, PtC=CC=O, $^3J_{Pt-C}$ = 17 Hz), 171.0 (dd, PtCC=O, $^3J_{P-C}$ = 2.8, 14 Hz, $^2J_{Pt-C}$ = 111 Hz), 138.0 (dd, PtC=C, $^3J_{P-C}$ = 3.0, 9.1 Hz, $^2J_{Pt-C}$ = 28 Hz), 50.7, 50.5 ($COOCH_3$), 32.7 ($GeCH_2CH_2$, $^3J_{Pt-C}$ = 25 Hz), 31.9 ($GeCH_2CH_2$, $^3J_{Pt-C}$ = 14 Hz), 31.4, 31.3, 31.0, 30.9 ($GeCH_2CH_2$), 30.2 (dd, PCH_2, $^2J_{Pt-C}$ = 19, 34 Hz), 29.5, 29.3 ($GeCH_2CH_2$), 28.6 (dd, PCH_2, $^2J_{P-C}$ = 13, 30 Hz), 28.3, 28.2, 27.9, 27.8, 27.8, 27.7, 27.6, 27.1 ($GeCH_2CH_2CH_2$), 19.7 (vt, $GeCH_2$, $|^3J_{P-C} + {}^3J_{P-C}|$ = 8.7 Hz, $^2J_{Pt-C}$ = 21 Hz), 19.5 (d, $GeCH_2$, $^3J_{P-C}$ = 4.4 Hz, $^2J_{Pt-C}$ = 40 Hz), 16.9 ($GeCH_2$, J_{Pt-C} = 24 Hz), 16.2 (2C), 15.8, 15.5, 14.8 ($GeCH_2$), 14.5, 14.5, 14.3, 14.3, 14.2, 14.1 (2C), 14.1 ($GeCH_2CH_2CH_2CH_3$). 12.7 (d, PCH_3, J_{P-C} = 26 Hz, $^2J_{Pt-C}$ = 30 Hz), 10.6 (dd, PCH_3, J_{P-C} = 3.0, 26 Hz, $^2J_{Pt-C}$ = 34 Hz). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, rt): δ 31.9 ($P_{trans\ \mathrm{to\ Ge}}$, J_{Pt-P} = 1696 Hz), 16.6 ($P_{trans\ \mathrm{to\ C}}$, J_{Pt-P} = 2003 Hz). IR (KBr): 1688 ($\nu_{C=O}$), 1198 (ν_{C-O}) cm^{-1}.

Reaction of H_2GePh_2 with 6. To a toluene solution (2 mL) of **6** (102 mg, 0.093 mmol) was added 2-fold H_2GePh_2 (43 mg, 0.19 mmol), and then the resulting mixture was stirred at room temperature for 23 h. The solvent and volatile materials were evaporated under reduced pressure. The oily residue was separated with hexane (3 mL), washed with hexane (3 mL) three times, and dried *in vacuo* to give bis(germyl)platinum complex **1** (60 mg, 80%). The crude product in hexane solution was purified by column chromatography with hexane eluent (R_f = 0.95) to yield $H(GeBu_2)_4H$ as a colorless oil (63 mg, 90%). Data for $H(GeBu_2)_4H$: Anal. Calcd for $C_{32}H_{74}Ge_4$: C, 51.28; H, 9.95. Found: C, 50.47; H, 10.19. ^1H NMR (400 MHz, C_6D_6, rt): δ 4.10 (quin, 2H, Ge*H*, J_{H-H} = 3.4 Hz), 1.37−1.68 (m, 16H, $GeCH_2CH_2$), 1.39−1.50 (m, 16H, $GeCH_2CH_2CH_2$), 1.29−1.33 (m, 16H, $GeCH_2$), 0.98 (t, 12H, $GeCH_2CH_2CH_2CH_3$, $^3J_{H-H}$ = 7.2 Hz), 0.96 (t, 12H, $GeCH_2CH_2CH_2CH_3$, $^3J_{H-H}$ = 7.2 Hz). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, rt): δ 31.0, 30.9 ($GeCH_2CH_2$), 27.2, 26.7, ($GeCH_2CH_2CH_2$), 15.2 ($GeCH_2$), 14.4, 14.0 ($GeCH_2CH_2CH_2CH_3$), 13.6 ($GeCH_2$). IR (neat): 1983 (ν_{Ge-H}) cm^{-1}. HRMS (APCI): calcd for $C_{32}H_{73}Ge_4$ $[M - H]^+$ 753.2559, found *m*/*z* 753.2542.

Reaction of H_2SiPh_2 with 6. The procedure was similar to the reaction with H_2GePh_2. To a toluene solution (4 mL) of **6** (103 mg, 0.094 mmol) was added 2-fold H_2SiPh_2 (35 mg, 0.19 mmol), and then the reaction mixture was stirred at room temperature for 37 h. After purification of the crude product, $[Pt(SiHPh_2)_2(dmpe)]^{16}$ (**8**) (65 mg, 97%) and $H(GeBu_2)_4H$ (47 mg, 67%) were isolated.

Equimolar Reaction of H_2SiPh_2 with 6. To a C_6D_6 solution (0.6 mL) of **6** (70 mg, 0.064 mmol) in an NMR sample tube was added equimolar H_2SiPh_2 (12 mg, 0.065 mmol). The ^1H and $^{31}P\{^1H\}$ NMR spectra of the reaction mixture after 22 h at room temperature displayed a mixture of **6** and **8** in 1:1 ratio.

Table 2. Crystallographic Data and Details of Refinement of 4 and 7

	4	7
formula	$C_{22}H_{54}Ge_2P_2Pt$	$C_{44}H_{94}Ge_4O_4P_2Pt$
fw	720.89	1234.62
cryst size/mm	0.20 × 0.25 × 0.30	0.16 × 0.22 × 0.24
cryst syst	monoclinic	tetragonal
cryst color	colorless	colorless
space group	$P2_1/c$ (No. 14)	$I4_1/a$ (No. 88)
a/Å	9.025(1)	20.392(2)
b/Å	17.619(3)	
c/Å	19.008(3)	54.171(6)
α/deg		
β/deg	93.872(2)	
γ/deg		
V/Å^3	3015.5(8)	22526(4)
Z	4	16
D_{calcd}/g cm^{-3}	1.588	1.456
$F(000)$	1432	10016
μ/mm^{-1}	6.7012	4.6652
no. of reflns meads	24 236	104 074
no. of unique reflns	6741	12 886
R_{int}	0.032	0.0996
no. of obsd reflns ($I > 2\sigma(I)$)	5739	9495
no. of variables	260	497
R, R_w ($I > 2\sigma(I)$)	0.0293, 0.0755	0.0829, 0.2229
R, R_w (all data)	0.0339, 0.0783	0.1039, 0.2468
GOF on F^2	0.999	1.046

Reaction of 4 with H_2GePh_2. To a C_6D_6 solution (0.5 mL) of **4** (20 mg, 0.028 mmol) and dibenzyl as an internal standard (8.3 mg, 0.046 mmol) in an NMR sample tube was added 3-fold H_2GePh_2 (20 mg, 0.087 mmol). The ^1H and $^{31}P\{^1H\}$ NMR spectra of the reaction mixture after 46 h at room temperature exhibited complete conversion to afford complex **1** and H_2GeBu_2.

Reaction of 4 with H_2SiPh_2. To a C_6D_6 solution (0.5 mL) of **4** (22 mg, 0.031 mmol) and dibenzyl as an internal standard (8.5 mg, 0.047 mmol) in an NMR sample tube was added 3-fold H_2SiPh_2 (17 mg, 0.092 mmol) at room temperature. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture after 46 h exhibited two doublets at δ 35.3 (J_{Pt-P} = 1766 Hz) and 39.2 (J_{Pt-P} = 1440 Hz) with the same J_{P-P} values (10 Hz), which were assigned to the Pt intermediate $[Pt(GeHBu_2)(SiHPh_2)(dmpe)]$ (**9**). Resonances were also observed for the bis(silyl)platinum complex **8** (δ 37.0, J_{Pt-P} = 1457 Hz) and the starting material **4** (δ 36.7, J_{Pt-P} = 1762 Hz). The ratio of **4**:**8**:**9** was estimated as 5:44:51 on the basis of the intensity of ^{31}P NMR signals. In the ^1H NMR spectrum, the Ge−H hydrogen signal of free Bu_2GeH_2 was observed also at δ 3.86.

X-ray Crystallography. Crystals of **4** and **7** suitable for an X-ray diffraction study were mounted on MicroMounts (MiTeGen). The crystallographic data of **4** and **7** were collected on a Rigaku Saturn CCD area detector equipped with monochromated Mo Kα radiation (λ = 0.71073 Å) at 150 K. Calculations were carried out using the program package Crystal Structure, version 4.0, for Windows. The positional and thermal parameters of non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares method using SHELXL-97.[18] Hydrogen atoms, except for the Ge—H hydrogens of **4**, were placed at calculated positions and refined with a riding mode on their corresponding carbon atoms. Disordered carbon atoms of the *n*-Bu group on Ge3 and at the terminal position on Ge1 and Ge4 were calculated isotropically. Crystallographic data and details of refinement of **4** and **7** are summarized in Table 2.

ASSOCIATED CONTENT

Supporting Information. Crystallographic data for **4** and **7** as a CIF file. Spectroscopic data of $H(GeBu_2)_4H$. These materials are available free of charge via the Internet at http://pubs.acs.org.

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