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Characterization of Mononuclear and Dinuclear Germylplatinum Complexes and Ge−Ge Bond Formation at the Platinum Center

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The reaction of the zerovalent platinum complex [$Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)$] (**1**) with the germanium trihydride GeH_3Mes (Mes = 2,4,6-trimethylphenyl) produced various germylplatinum complexes by control of the molar ratio. When complex **1** reacted with GeH_3Mes in a molar ratio of 1:1, dimerization of the platinum unit occurred at −30 °C to afford the unsymmetrical diplatinum complex [$Pt_2(PPh_3)_3(\mu\text{-}GeH_2Mes)_2$] (**2**) and the symmetrical diplatinum complex [$Pt(PPh_3)(\mu\text{-}GeH_2Mes)]_2$ (**3**), for which the ^1H NMR spectrum indicated a mixture of *cis*/*trans*-isomers in a ratio of 2:3. When a toluene solution of **2** increased in temperature from −20 °C to room temperature, liberation of a PPh_3 group occurred at the $Pt(PPh_3)_2$ site, followed by rotation of the bridging germyl group to form a mixture of *cis*/*trans*-**3**. Otherwise, treatment of **1** with GeH_3Mes at a molar ratio of 1:2 afforded the bis(germyl)platinum complex [$Pt(PPh_3)_2(GeH_2Mes)_2$] (**4**) at −30 °C, and then **4** converted to the digermanylplatinum hydride [$Pt(PPh_3)_2(H)(GeHMesGeH_2Mes)$] (**5**) at room temperature in toluene. The conversion rate obeyed a first-order rate law, and the activation parameters $\Delta H^‡$ and $\Delta S^‡$ were calculated at 20(2) kcal mol^{-1} and −7(8) cal K^{-1} mol^{-1}, respectively. These results suggest that in later transition metal platinum complexes, Ge−Ge bond formation is carried out by intramolecular germyl migration.

Introduction

Low-valent transition metal complexes have been used as the catalyst in insertion reactions of unsaturated hydrocarbons into an E−E bond (E = Si, Ge, Sn) or in the polymerization of compounds with E−H bonds.[1,2] An ME_2 species is considered to be an intermediate in these reactions and has attracted attention due to its role in the synthesis and characterization of the complexes containing M−E bonds. Group 10 metal complexes are one of the most well-known types of M−E complexes; in particular, many silylplatinum complexes have been synthesized by using methods such as oxidative addition of an Si−H bond to a Pt(0) complex, the dehydrocoupling reaction of a platinum hydride complex with hydrosilane, or the salt elimination of a platinum chloride complex with silyllithium.[3,4] A silyl compound with multiple Si−H bonds induces formation of a multinuclear complex through the oxidative addition of Si−H bonds and/or the elimination of dihydrogen.[5] Platinum complexes containing the heavy group 14 element Ge have also been synthesized by a similar method to obtain germylplatinum complexes,[6] although the number of germylplatinum complexes is less than that of silylplatinum species. Recently, Braddock-Wilking and co-workers have reported that the treatment of [$Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)$] with secondary germane GeH_2Ph_2 affords a germylplatinum hydride at −80 °C and a symmetrical diplatinum complex bridged by the $GeHPh_2$ groups between the two platinum centers at room temperature (Scheme 1).[7] In addition, E−E bond formation at the transition metal center is the most important step in the synthesis of polymers with an extended backbone of heavy group 14 elements. For Ge−Ge bond formation at a platinum center, a few dinuclear platinum complexes [$(R_3P)_2Pt(H)(GeR'_2GeR'_2)Pt(H)(PR_3)_2$] containing the Pt−Ge−Ge−Pt unit are formed by the reaction of a mononuclear platinum complex with a secondary germane.[6b,d] Banaszak Holl et al. have reported that *trans*-[$Pt(PEt_3)_2(GeHAr_2)_2$] (Ar = 3,5-$(CF_3)_2C_6H_3$) incu-

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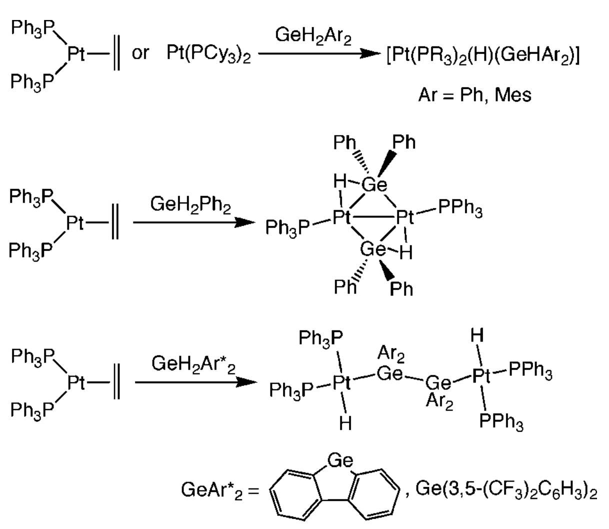
Scheme 1



bated at 75 °C is converted into *cis*-[Pt(PEt$_3$)$_2$(H)(GeAr$_2$GeAr$_2$H)], but the crystal structures of both mononuclear platinum complexes were not reported.

We are interested in the properties of germylplatinum complexes, including the thermal dynamics and photoresponse, and have synthesized these complexes using trialkylgermanes.[8] We report herein that mononuclear and dinuclear germylplatinum complexes in the reaction of [Pt(PPh$_3$)$_2$(η^2-C$_2$H$_4$)] (**1**) with the germanium trihydride GeH$_3$Mes (Mes = 2,4,6-trimethylphenyl), which has a sterically encumbering mesityl group, can be identified using X-ray diffraction (XRD) and NMR spectroscopy.

Results and Discussion

A toluene/pentane solution of **1** and GeH$_3$Mes in a molar ratio of 1:1 was allowed to stand for a few days at −30 °C to obtain a mixture of orange crystals (complex **2**) as a minor product and pale yellow crystals (complex **3**) as a major product (eq 1). In the crystal structure of **2** ([Pt$_2$(PPh$_3$)$_3$(μ-GeH$_2$Mes)$_2$], Figures 1, S1), one of the platinum centers has four-coordinate tetrahedral geometry with a P$_2$Ge$_2$ ligand set and the other has three-coordinate planar geometry with a PGe$_2$ ligand set. The Pt(1)−Ge(1) and Pt(2)−Ge(2) bond lengths in **2**, which are longer than those of previously reported germylplatinum complexes,[6,8] indicate a nonclassical 3c-2e interaction. The two mesityl groups have a *cis*-configuration since this prevents steric interactions with the phenyl groups of the PPh$_3$ ligands. The two Pt−H bond lengths were within the bond length range of diplatinum complexes with a bridging Pt−H−E (E = Si, Ge) hydride.[4,7] The silyl analogue of the unsymmetrical diplatinum complexes [(PPh$_3$)$_2$Pt(H)(μ-SiR$_2$)(μ-SiHR$_2$)Pt(PPh$_3$)] has a terminal hydride at the Pt(PPh$_3$)$_2$ site and a bridging hydride at the Pt(PPh$_3$) site, as shown by NMR spectroscopy.[4c] However, the binding mode of the two hydrides of **2** could not be determined from the ^{1}H NMR data at −80 °C due to the broad Pt−H and Ge−H signal, which is attributed to the dynamic behavior of **2** related to the rapid elimination/rebinding of PPh$_3$ at the Pt(PPh$_3$)$_2$ site (Figure S2). In a standing toluene solution of **2** at −20 °C, liberation of a PPh$_3$ group at the Pt(PPh$_3$)$_2$ site in **2** afforded *cis*-**3** due to a steric repulsion between the phenyl groups on the P atom and the mesityl group on the Ge atom (Figure 2). Subsequently, most of *cis*-**3** isomerized to *trans*-**3** upon heating to 20 °C to obtain a mixture of *cis*/*trans*-**3**, which is associated with a rotation of the bridging germyl group observed in the silyl analogue.[9] On the other hand, complex **3** was identified as the symmetrical diplatinum complex [Pt(PPh$_3$)(μ-GeH$_2$Mes)]$_2$,[10] and the structure of *trans*-**3** was

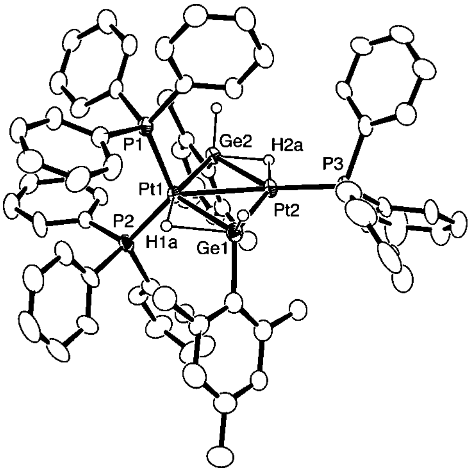


Figure 1. Crystal structure of **2**, showing 50% probability thermal ellipsoids. The hydrogen atoms except for H1a, H1b, H2a, and H2b are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt(1)−Pt(2) 2.8333(4), Pt(1)−P(1) 2.327(2), Pt(1)−P(2) 2.3048(19), Pt(1)−Ge(1) 2.5326(8), Pt(1)−Ge(2) 2.4259(8), Pt(1)-H(1a) 1.77(8), Pt(2)−P(3) 2.2451(18), Pt(2)−Ge(1) 2.4079(9), Pt(2)−Ge(2) 2.4733(8), Pt(2)−H(2a) 1.65(8), Ge(1)−H(1a) 1.95(8), Ge(2)−H(2a) 1.68(9); P(1)−Pt(1)−P(2) 120.31(7), P(1)−Pt(1)−Ge(1) 110.38(5), P(1)−Pt(1)−Ge(2) 94.05(5), P(1)−Pt(1)−Pt(2) 109.23(5), P(2)−Pt(1)−Ge(1) 115.64(5), P(2)−Pt(1)−Ge(2) 104.96(5), P(2)−Pt(1)−Pt(2) 128.31(5), Ge(1)−Pt(1)−Ge(2) 108.37(3), P(3)−Pt(2)−Ge(1) 101.85(6), P(3)−Pt(2)−Ge(2) 145.75(6), Ge(1)−Pt(2)−Ge(2) 110.94(3), P(3)−Pt(2)−Pt(1) 156.00(6).

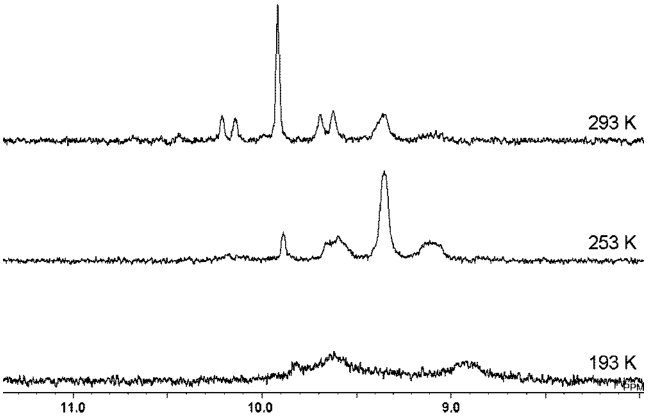


Figure 2. VT ^{1}H NMR spectra in the terminal Ge−H region of **2**.

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(10) Complex **3** could be separated from complex **2** when the recrystallization of their mixture was carried out at room temperature in toluene/pentane.

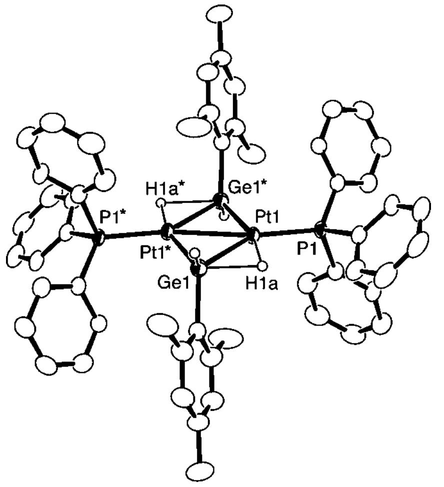
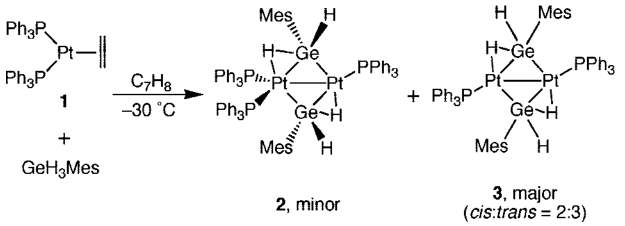


Figure 3. Crystal structure of *trans*-**3**, showing 50% probability thermal ellipsoids. The hydrogen atoms except for H1a are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt(1)–Pt(1)* 2.7614(5), Pt(1)–P(1) 2.2371(15), Pt(1)–Ge(1) 2.4757(7), Pt(1)–Ge(1)* 2.4057(8), Pt(1)–H(1a) 1.95(8), Ge(1)–H(1a) 1.97(9); P(1)–Pt(1)–Ge(1) 146.60(5), P(1)–Pt(1)–Ge(1)* 101.95(5), Ge(1)–Pt(1)–Ge(1)* 111.12(2), P(1)–Pt(1)–Pt(1)* 158.25(5).

determined by XRD analysis (Figure 3). The Pt–Pt bond length of **3** is 0.07 Å shorter than that of **2**, and the Pt–P and Pt–Ge bond lengths are similar to those of $[Pt(PPh_3)(\mu\text{-}GeHPh_2)]_2$[7] and the $Pt(PPh_3)$ site in **2**. The ^1H NMR data of **3** exhibited a mixture of *cis/trans*-isomers in the ratio of 2:3 (Figure S3), which was estimated from the integral value of the aromatic proton of the mesityl groups; further, the ratio of *cis/trans*-isomers exhibited no change in the range of −20 to 20 °C, which was similar to the silyl analogue $[Pt(PPh_3)(\mu\text{-}SiH_2Mes)]_2$.[9] The $^{31}P\{^1H\}$ NMR spectrum of **3** exhibited part of an AA′XX′ spin system pattern characteristic of a symmetrical diplatinum complex, but the signals of the two isomers could not be distinguished since they overlapped with each other.



(1)

After **1** and GeH_3Mes were mixed in a molar ratio of 1:2 in toluene/pentane at −30 °C, the resulting solution was allowed to stand for a few days at −30 °C to obtain only colorless microcrystals (complex **4**; eq 2), which is different from the product obtained using a 1:1 molar ratio. In the ^1H NMR spectrum of **4**, a Ge–H peak was observed as a pseudoseptet with ^{195}Pt satellites at 3.71 ppm ($^2J_{PtH}$ = 50 Hz, $^3J_{PH}$ = 14 Hz) due to an overlap of the satellites, which is similar to that of *cis*-bis(silyl)platinum complexes reported previously (Figure S4).[9,11] The ^{31}P NMR spectrum of **4** showed a singlet at 27.5 ppm with a $^1J_{PtP}$ of 2277 Hz, indicating that the two ^{31}P nuclei were equivalent. The bis(germyl)platinum complex $[Pt(PEt_3)_2(GeHAr_2)_2]$ (Ar = 3,5-$(CF_3)_2C_6H_3$) was reported as a *trans*-isomer by Holl,[6b] but we considered complex **4** as a *cis*-isomer because $^1J_{PtP}$ for the $^{31}P\{^1H\}$ NMR spectrum was close to the $^1J_{PtP}$ of the *cis*-isomer bis(germyl)platinum complexes (*cis*-$[Pt(PMe_2Ph)_2(GeMe_2Ph)_2]$, 2007 Hz; *cis*-$[Pt(PMe_2Ph)_2(GeMePh_2)_2]$, 2049 Hz) rather than that of the *trans*-isomer (*trans*-$[Pt(PMe_2Ph)_2(GePh_3)_2]$, 2616 Hz).[8a]

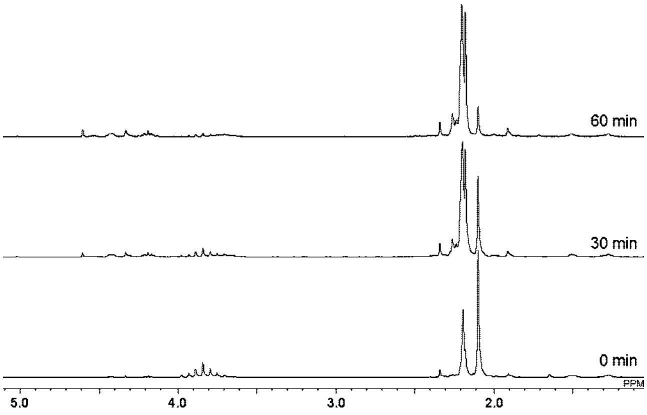
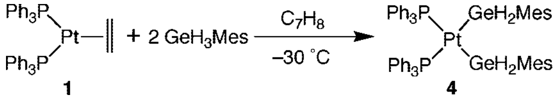
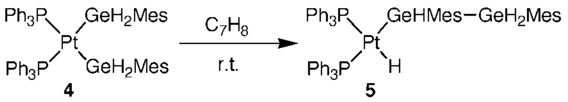


Figure 4. ^1H NMR spectral change of **4** in toluene-d_8 standing at 298 K after 0, 30, and 60 min.



(2)

When a toluene suspension of **4** was allowed to stand for a few hours at ambient temperature, **4** was converted to the digermanylplatinum hydride $[Pt(PPh_3)_2(H)(GeHMesGeH_2Mes)]$ (**5**; eq 3); this process involved the 1,2-migration of a germyl group.



(3)

The conversion of **4** to **5** obeyed a first-order rate law, and the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were estimated to be 20(2) kcal mol^{-1} and −7(8) cal K^{-1} mol^{-1}, respectively, using Eyring plots (Figures 4, S5), indicating that the small entropy of activation is a result of the intramolecular Ge–Ge bond formation. In the crystal structure of **5** (Figure 5), the platinum center has planar geometry with two PPh_3 ligands at *cis*-positions to each other, and the Pt–P and Pt–Ge bond lengths are similar to those of the germylplatinum complex $[Pt(PPh_3)_2(H)(GeHMes_2)]$.[6d] The Ge–Ge bond length is 2.457(1) Å, which is in the range of a typical Ge–Ge bond length, and the second germanium atom (Ge(2)) did not interact with the platinum center, as indicated by the large Pt(1)–Ge(2) bond length of 4.00 Å. To the best of our knowledge, a crystal structure of mononuclear platinum hydride coordinating a group 14 element compound containing an E–E bond $[Pt(PR_3)_2(H)(ER'_2EHR'_2)]$ has not been reported, although there have been reports of dinuclear platinum complexes with a bridging disilyl[12] and digermyl[6b,d] group between two platinum atoms.

The ^1H NMR spectrum of **5** showed three Ge–H signals including an apparent triplet at 5.02 ppm ($^3J_{PtH}$ = 63 Hz), a triplet with satellites at 4.84 ppm ($^3J_{PtH}$ = 31 Hz, $^4J_{PH}$ = 6.3 Hz), and a broad peak centered at 4.20 ppm (Figures S6, S7). According to the $^1H^1H$ COSY spectrum, the signals at 5.02 and

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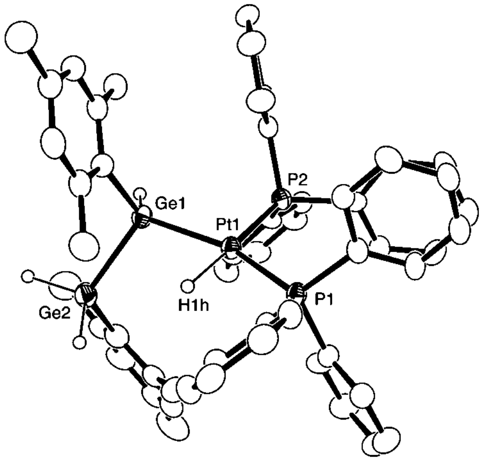

Figure 5. Crystal structure of **5**, showing 50% probability thermal ellipsoids. The hydrogen atoms except for those on Ge and Pt are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt(1)−P(1) 2.2971(18), Pt(1)−P(2) 2.3090(19), Pt(1)−Ge(1) 2.4348(8), Pt(1)−H(1h) 1.68(8), Ge(1)−Ge(2) 2.4571(12); P(1)−Pt(1)−P(2) 105.05(7), P(1)−Pt(1)−Ge(1) 157.90(5), P(1)−Pt(1)−H(1h) 79(3), P(2)−Pt(1)−Ge(1) 96.91(5), P(2)−Pt(1)−H(1h) 175(3), Ge(1)−Pt(1)−H(1h) 79(3).

4.84 ppm were assigned to the H nuclei on the second germanium atom, indicating that the two hydrogens are diastereotopic, and the broad peak at 4.20 ppm originates from the germanium atom bound to the platinum atom. The Pt−H signal was observed at −3.00 ppm as a doublet of doublets and was similar to that of germylplatinum hydride complexes. The $^{31}P\{^1H\}$ NMR spectrum exhibited two doublets with ^{195}Pt satellites at 31.7 ($^1J_{PtP}$ = 2280 Hz) and 30.8 ppm ($^1J_{PtP}$ = 2270 Hz).

The E−E bond formation is the most important step in the syntheses of polysilanes and polygermanes. Early transition metal complexes such as zirconocene and hafnocene were used for the polymerization of hydrosilanes in which σ-bond metathesis reactions between the d^0 M−Si bond and the Si−H bond resulted in Si−Si bond formation.[13] In a (germyl)(germylene)ruthenium complex, germyl migration gave rise to Ge−Ge bond formation during the polymerization of $GeHMe_3$.[14] In our system, Ge−Ge bond formation at the platinum center was also accomplished by the formation of a (germyl)(germylene)platinum hydride, although it could not be detected by NMR spectroscopy during the conversion of **4** to **5**, followed by the 1,2-migration of the germyl group to the germylene.

Conclusion

The reaction of $[Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)]$ (**1**) with the germanium trihydride GeH_3Mes in a molar ratio of 1:1 at −30 °C afforded the unsymmetrical diplatinum complex **2** and the symmetrical diplatinum complex **3**. The change in the molar ratio from 1:1 to 1:2 afforded the bis(germyl)platinum complex **4**; this complex was converted to digermanylplatinum hydride **5** via intramolecular Ge−Ge bond formation at room temperature.

Table 1. Crystallographic Data

	$2\cdot C_7H_8$	*trans*-**3**	**5**
formula	$C_{79}H_{79}Ge_2P_3Pt_2$	$C_{27}H_{28}GePPt$	$C_{54}H_{45}Ge_2P_2Pt$
fw	1656.69	651.14	1096.11
cryst syst	triclinic	triclinic	triclinic
space group	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)
a, Å	13.5140(9)	8.6380(6)	12.229(1)
b, Å	13.6660(9)	13.930(1)	13.241(1)
c, Å	22.421(1)	14.177(1)	16.754(1)
α, deg	90.904(3)	109.661(4)	81.668(6)
β, deg	76.472(3)	99.571(4)	73.344(6)
γ, deg	61.528(3)	107.007(4)	65.413(5)
V, Å^3	3499.5(4)	1468.3(2)	2362.4(4)
Z	2	2	2
ρ_{calcd}, g cm^{-3}	1.572	1.473	1.541
μ(Mo Kα), cm^{-1}	4.946	5.846	4.320
total no. of data	33 660	14 041	22 467
no. of unique data	15 526	6455	10 286
no. of params	787	277	544
R_1[a]	0.0550	0.0509	0.0591
wR_2 (all data)[b]	0.1531	0.1452	0.1505

[a] $I > 2.00\sigma(I)$. $R_1 = \Sigma|F_o| - |F_c|/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma(w(|F_o| - |F_c|)^2)/\Sigma wF_o^2\}^{1/2}$.

Experimental Section

General Procedure. All the experiments were carried out using a standard vacuum line and Schlenk techniques or in an M. Braun inert atmosphere drybox. All the reagents were of the highest grade available and were used without further purification. All the solvents used for the syntheses were distilled according to the general procedure. Benzene-d_6 and toluene-d_8 were distilled from potassium metal under an Ar atmosphere. CD_2Cl_2 was dried over activated 4 Å molecular sieves. GeH_3Mes[15] and $[Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)]$ (**1**)[16] were synthesized according to the previously reported method. The ^1H NMR spectral measurements were performed on a JEOL AL-300 NMR spectrometer at 300 MHz for ^1H and 122 MHz for ^{31}P. The chemical shifts of the protons are reported relative to the residual protonated solvents benzene-d_6 (7.15 ppm), toluene-d_8 (2.09 ppm), and CD_2Cl_2 (5.32 ppm). The chemical shifts of phosphine are corrected relative to external H_3PO_4 (0 ppm). Elemental analysis was performed on a CE Instruments EA1110 corrected by acetoanilide.

Syntheses of Platinum Complexes. $[Pt_2(PPh_3)_2(\mu\text{-}GeH_2Mes)_2]$ (2). To a toluene solution (2 mL) of **1** (150 mg, 0.201 mmol) was added a toluene solution (1 mL) of GeH_3Mes (39 mg, 0.201 mmol) at −30 °C, and the mixture was allowed to stand for 30 min. Pentane (2 mL) was added to the toluene solution, and the resulting solution was then allowed to stand for a day at −30 °C to precipitate the symmetrical diplatinum complex **3**. After the supernatant was transferred to another vessel, pentane (5 mL) was added. The resulting solution was allowed to stand at −30 °C to obtain orange crystals. Yield: 15.7 mg (10%). Anal. Calcd for $2\cdot C_7H_8$ ($C_{79}H_{79}Ge_2P_3Pt_2$): C, 57.27; H, 4.81. Found: C, 57.66; H, 4.86.

$[Pt(PPh_3)(\mu\text{-}GeH_2Mes)]_2$ (3). To a toluene solution (1 mL) of **1** (100 mg, 0.134 mmol) was added a toluene solution (1 mL) of GeH_3Mes (26 mg, 0.134 mmol) at room temperature, and the mixture was stirred for 10 min. To the resulting solution was added pentane (2 mL), and standing for a few days at room temperature gave yellow crystals. Yield: 58.8 mg (67%). ^1H NMR (C_6D_6, 300 MHz): δ 10.57 (br s, 2H, $^2J_{PtH}$ = 175, 136 Hz, GeH for *trans*-**3**), 10.00 (br s, 2H, GeH for *cis*-**3**), 7.62 (br s, 12H, PPh), 6.87 (br s, 18H, PPh), 6.70 (s, 2H, Mes for *cis*-**3**), 6.62 (s, 2H, Mes for *trans*-**3**), 2.26 (s, 12H, *o*-Me for *trans*-**3**), 2.23 (s, 12H, *o*-Me for *cis*-**3**), 2.15 (s, 6H, *p*-Me for *cis*-**3**), 2.11 (s, 6H, *p*-Me for *trans*-**3**). $^{31}P\{^1H\}$

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NMR (C_6D_6, 122 MHz): δ 34.6 (s, $^1J_{PtP} = 4395$ Hz, $^2J_{PtP} = 144$ Hz, $^3J_{PP} = 52$ Hz). Anal. Calcd for **3**·C_7H_8 ($C_{61}H_{64}Ge_2P_2Pt_2$): C, 52.54; H, 4.63. Found: C, 52.29; H, 4.71.

[Pt(PPh$_3$)$_2$(GeH$_2$Mes)$_2$] (4). To a toluene solution (2 mL) of **1** (200 mg, 0.267 mmol) was added a toluene solution (2 mL) of GeH_3Mes (102 mg, 0.523 mmol) at −30 °C, and the resulting solution was stored in a chilled box at −30 °C overnight. Pentane (2 mL) was added to the resulting solution. The solution was allowed to stand overnight in the chilled box to afford colorless microcrystals. Yield: 226 mg (76%). ^1H NMR (CD_2Cl_2, 300 MHz, −30 °C): δ 7.26 (m, 18H, PPh), 7.35 (t, 12H, $^3J_{HH} = 6.0$ Hz, PPh), 6.61 (s, 4H, Mes), 3.71 (t, 4H, $^2J_{PtH} = 50$ Hz, $^3J_{PH} = 14$ Hz, GeH), 2.17 (s, 6H, *p*-Me), 2.00 (s, 12H, *o*-Me). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 122 MHz, −30 °C): δ 27.5 (s, $^1J_{PtP} = 2277$ Hz). Anal. Calcd for **4** ($C_{54}H_{56}Ge_2P_2Pt$): C, 58.57; H, 5.10. Found: C, 58.45; H, 5.40.

[Pt(PPh$_3$)$_2$(H)(Ge$_2$H$_3$Mes$_2$)] (5). Complex **4** (30 mg, 26 μmol) was suspended in toluene, and standing overnight at room temperature gave colorless crystals. Yield: 4.0 mg (13%). ^1H NMR (toluene-d_8, 300 MHz, 20 °C): δ 7.39 (m, 6H, PPh), 7.30 (m, 6H, PPh), 6.95−6.75 (m, 18H, PPh), 6.74 (s, 2H, Mes), 6.70 (s, 2H, Mes), 5.02 (br s, 1H, $^3J_{PtH} = 63$ Hz, GeH), 4.84 (t, 1H, $^3J_{PtH} = 31$ Hz, $^4J_{PH} = 6.3$ Hz, GeH), 4.20 (br, 1H, GeH), 2.53 (s, 6H, *o*-Me), 2.42 (s, 6H, *o*-Me), 2.21 (s, 3H, *p*-Me), 2.17 (s, 3H, *p*-Me), −3.00 (dd, 1H, $^1J_{PtH} = 891$ Hz, $^2J_{PH} = 170$ Hz (*trans*), 19 Hz (*cis*), PtH). $^{31}P\{^1H\}$ NMR (toluene-d_8, 122 MHz, 20 °C): δ 31.7 (d, $^1J_{PtP} = 2280$ Hz, $^2J_{PP} = 11$ Hz, PPh_3 *cis* to H), 30.8 (d, $^1J_{PtP} = 2270$ Hz, $^2J_{PP} = 12$ Hz, PPh_3 *trans* to H). Anal. Calcd for **5** ($C_{54}H_{56}Ge_2P_2Pt$): C, 58.57; H, 5.10. Found: C, 58.26; H, 5.48.

Kinetics. The formation of complex **4** was confirmed by increasing the intensity of *p*-Me on the mesityl groups at 2.00 ppm in ^1H NMR spectra. A residual protonated solvent at 5.32 ppm in CD_2Cl_2 was used as an internal standard, and the conversion rate of **4** was estimated from the area ratio of the peak at 2.00 ppm to that at 5.32 ppm. The data collection was performed at 5 or 10 min intervals at 25, 30, and 35 °C over 3 times the half-life. The data were analyzed with Igor (WaveMatrics, Inc.) on a Macintosh computer and fitted to an exponential function by a nonlinear least-squares method.

X-ray Crystallography. Single crystals of **2**, *trans*-**3**, and **5** suitable for XRD analyses were obtained by allowing their corresponding toluene/pentane solutions or toluene suspension to stand for a few days. Each crystal was mounted on a loop, and the diffraction data of all the complexes were collected on a Bruker-AXS M06X^{CE} imaging plate using graphite-monochromated Mo Kα radiation at 120 K. The crystal data and experimental details are listed in Table 1.

All the structures were solved by the combination of the direct method 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 the International Tables for X-ray Crystallography IV.[17] Since the numbers of reflection data for the above-mentioned crystals were insufficient for refining all the parameters of the hydrogen atoms, they were not included for further refinement; their positions were obtained from difference Fourier maps. All the calculations were carried out on a Silicon Graphics workstation by the maXus program.

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Supporting Information Available: Experimental methods and selected ^1H and $^{31}P\{^1H\}$ NMR data. This material is available free of charge via the Internet at http://pubs.acs.org.

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