

## Thermal reactivity of *cis*- and *trans*-bis(triphenylgermyl)bis(tertiary phosphine)platinum(II)

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### Abstract

The complex *cis*-Pt(Ph<sub>3</sub>Ge)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> underwent smooth isomerization to give the *trans*-isomer at room temperature via an associative five-coordinated intermediate. Thermodynamic parameters and activation energy for the *cis* to *trans* isomerization were obtained,  $\Delta H^\ddagger = 105 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = 12.5 \text{ J mol}^{-1} \text{ K}^{-1}$ , and  $E_a = 107 \text{ kJ mol}^{-1}$ , respectively. Heating of *trans*-Pt(Ph<sub>3</sub>Ge)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> at 50 °C for 36 days produced *trans*-PtPh(Ph<sub>3</sub>Ge)(PMe<sub>2</sub>Ph)<sub>2</sub> followed by the formation of *trans*-PtPh<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>, Pt(PMe<sub>2</sub>Ph)<sub>4</sub>, and Ph<sub>4</sub>Ge finally via elimination of the phenyl group from Ph<sub>3</sub>Ge ligand with liberation of the Ph<sub>2</sub>Ge unit and subsequent reductive elimination of the remaining Ph<sub>3</sub>Ge ligand at 80 °C for 1 month.

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### 1. Introduction

Bis(silyl)- and bis(germyl)platinum(II) complexes are important intermediates in Pt-catalyzed synthetic reactions such as the bis-silylation and bis-germylation of C–C triple and double bonds and the dehydrocoupling of group 14 element compounds [1–4]. These complexes also act as useful starting materials for group 14 element-containing compounds. In order to develop new metal catalysts for the synthesis of such compounds a good understanding of the reactivity of metal–silyl and metal–germyl bonds is needed. While the preparation,

structures, and reactivity of bis(silyl)- and bis(germyl)platinum(II) complexes have been amply investigated, there has been few reports regarding both *cis* and *trans* isomers having the same chemical formula. Moreover, many papers of these complexes are limited to the insertion and reductive elimination processes that provide a carbon–group 14 element bond. To elucidate the role of bis(germyl)platinum(II) complexes as key intermediates in platinum-catalyzed processes [4], we examined the thermolysis of both *cis*- and *trans*-Pt(Ph<sub>3</sub>Ge)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> that hitherto has not been observed. We describe herein (1) *cis*–*trans* isomerization at platinum for *cis*-Pt(Ph<sub>3</sub>Ge)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>, and (2) unexpected Ge–Ph bond cleavage and formation via germylene intermediate for *trans*-Pt(Ph<sub>3</sub>Ge)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>.

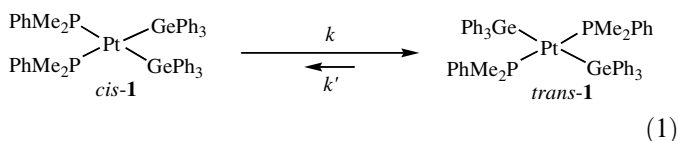
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## 2. Results and discussion

### 2.1. Thermal reactivity of *cis*-Pt(Ph<sub>3</sub>Ge)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>

The complex *cis*-Pt(Ph<sub>3</sub>Ge)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> (*cis*-1), prepared by photo-isomerization of *trans*-1 with a Xenon lamp ( $\lambda > 450$  nm) at room temperature for 30 min [5], was stable in solid state, but the dissolution of *cis*-1 in CH<sub>2</sub>Cl<sub>2</sub> or benzene caused a smooth isomerization to give a *cis*-1/*trans*-1 equilibrium mixture.



The isomerization of *cis*-1 to *trans*-1 in CD<sub>2</sub>Cl<sub>2</sub> at 30–50 °C was followed by monitoring the change in the two methyl signals of the PMe<sub>2</sub>Ph ligands by means of <sup>1</sup>H NMR spectroscopy. Fig. 1 shows the decay of *cis*-1 and the build up of *trans*-1 at 30–50 °C. From the concentrations of *cis* and *trans* isomers after equilibria were reached, the following thermodynamic parameters were obtained:  $\Delta H^\ddagger$ , 105 kJ mol<sup>-1</sup> and  $\Delta S^\ddagger$ , 12.5 J mol<sup>-1</sup> K<sup>-1</sup>.

The assumption of the equilibration reaction (Eq. (1)) following the first-order rate law leads to a kinetic expression, Eq. (2), where *K* represents to *k/k'* [6]

$$kt = \frac{K}{K+1} \cdot \ln \frac{[cis-1] - [cis-1]_0}{[cis-1] - [cis-1]_0} \quad K = k/k' \quad (2)$$

The isomerization of *cis*-1 exhibited first-order kinetics, as shown in Fig. 2. From the plots shown in Fig. 2, the following isomerization rate constants were estimated by using Eq. (2) at the early stage of the reaction. The following first-order isomerization rate constants (*k*) at 30–50 °C in benzene-*d*<sub>6</sub> were obtained from Fig. 2: 10<sup>5</sup> *k/s* = 1.94 (30 °C), 9.67 (40 °C), 20.3 (45 °C), 35.2 (50 °C). From the Arrhenius plots, the energy of apparent activation (*E*<sub>a</sub>) in the isomerization of *cis*-1 to *trans*-1 was estimated to be 107 kJ mol<sup>-1</sup>.

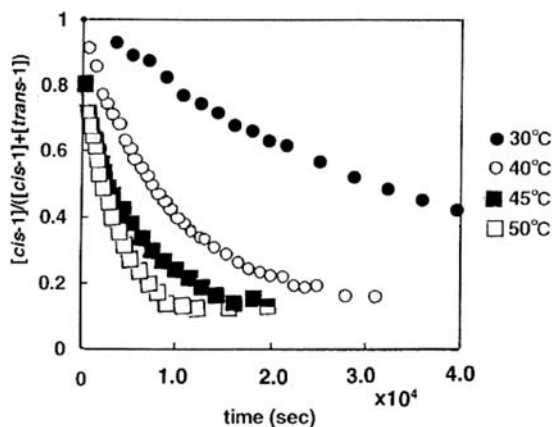


Fig. 1. The progress with time of isomerization of *cis*-1 to *trans*-1 at 30–50 °C.

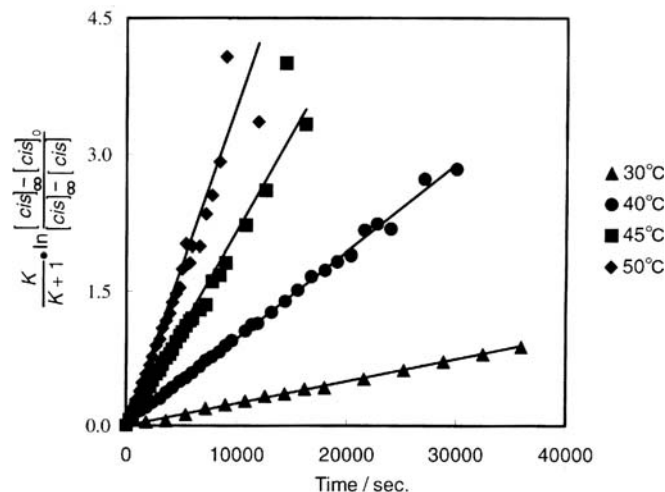


Fig. 2. The kinetics of isomerization of *cis*-1.

The addition of free PMe<sub>2</sub>Ph (0.6 equiv. of PMe<sub>2</sub>Ph per mol of *cis*-1) to the system caused acceleration of the isomerization of the *cis* isomer: 10<sup>3</sup> *k/s* = 1.12 (30 °C). Thus, 80 times acceleration effect by addition of PhMe<sub>2</sub>Ph was observed. These results suggest that the isomerization of *cis*-1 proceeds through an associative pathway involving a five-coordinate intermediate formed upon association of *cis*-1 with PMe<sub>2</sub>Ph. The *cis* to *trans* isomerization observed for the *cis*-1 dissolved in benzene along with an entropy increase may be due to the effect of releasing the steric repulsion between the bulky ligands in the *cis* form by isomerization into the *trans* form.

*Ab initio* molecular orbital calculation using the HF/LANL2DZ method supported the associative five-coordinated mechanism with a Berry pseudo-rotation and located the transition state for model compound Pt(GeH<sub>3</sub>)<sub>2</sub>(PH<sub>3</sub>)<sub>2</sub> [7].

Although many reductive elimination processes of *cis*-bis(silyl)- and *cis*-bis(germyl)platinum complexes have been reported [3,4], there has been little study of *cis*–*trans* isomerization of these Pt-complexes [4a,4d]. Relative thermodynamic stability between *cis* and *trans* isomers of Pt(ER<sub>3</sub>)<sub>2</sub>L<sub>2</sub> (E = Si, Ge, and Sn) has been briefly described [8]. The intramolecular twist-rotational motion between two ER<sub>3</sub> groups was observed with *cis*-Pt(ER<sub>3</sub>)<sub>2</sub>L<sub>2</sub> (E = Si, Sn) [9].

### 2.2. Thermal reactivity of *trans*-Pt(Ph<sub>3</sub>Ge)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>

The complex *trans*-Pt(Ph<sub>3</sub>Ge)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> (*trans*-1), prepared by treatment of *cis*-PtCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> with two molar amounts of Ph<sub>3</sub>GeLi [4d], was stable both in solid state and in solution, and did not isomerize to the corresponding *cis* isomer, even at 70 °C for 1 h. However, heating of the benzene-*d*<sub>6</sub> solution of *trans*-1 at 50 °C for 36 days slowly but unexpectedly gave *trans*-PtPh(Ph<sub>3</sub>Ge)(PMe<sub>2</sub>Ph)<sub>2</sub> in ca. 40% yield together with unidentified oligomers containing probably the Ph<sub>2</sub>Ge unit. Half of the *trans*-1 at this stage unreacted. The phenylplatinum complex *trans*-

PtPh(Ph<sub>3</sub>Ge)(PMe<sub>2</sub>Ph)<sub>2</sub> was identified by comparing the spectroscopic data of the authentic Pt-complex. The presence of oligomers was confirmed by their characteristic broad signals in the range 7–8 ppm due to the phenyl groups based on NMR spectroscopy as well as by GPC spectrum.

Furthermore, heating of this sample at 80 °C for 1 month gave formation of *trans*-PtPh<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> and Ph<sub>4</sub>Ge in 40% yields together with germylene oligomers (Scheme 1). These products (*trans*-PtPh<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> and Ph<sub>4</sub>Ge) were identified by comparison with their spectroscopic data reported previously [10]. The formation of Pt(PhMe<sub>2</sub>P)<sub>4</sub> was also confirmed by its <sup>1</sup>H and <sup>31</sup>P NMR spectra [11]. The yield of Pt(PhMe<sub>2</sub>P)<sub>4</sub> was roughly estimated (ca. 30%). The structure of PtPh<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> was established by X-ray diffraction analysis and the molecular structure of *trans*-PtPh<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> is shown in Fig. 3. Selected bond lengths and angles of the *trans*-PtPh<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> are tabulated in Table 1. The crystallographic data are summarized in Section 3.

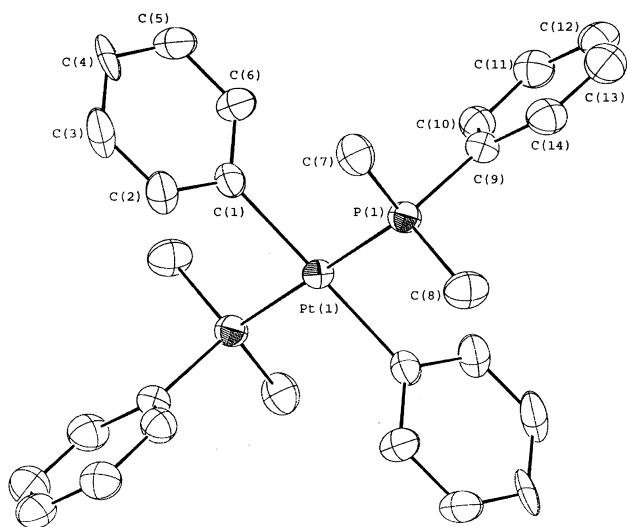
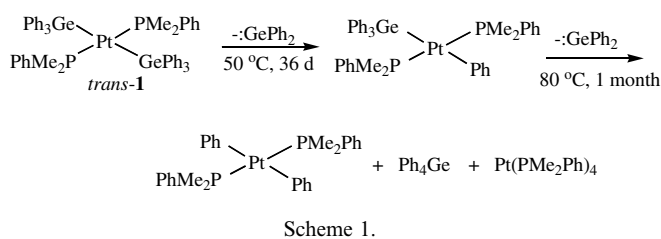


Fig. 3. Molecular structure of *trans*-PtPh<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>. Thermal ellipsoids are drawn at the 30% probability level.

The *trans*-PtPh<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> has a square-planar geometry, and the sum of four angles about platinum was 360°. The C–Pt–C and C–Pt–P bond angles are 179.999(1)° and 88.54(8)°, respectively. The Pt–C(phenyl) (2.088(3)Å) and Pt–P bond lengths (2.2861(18) Å) for *trans*-PtPh<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> are slightly longer than that for *trans*-PtPhMe(PMe<sub>2</sub>Ph)<sub>2</sub> (2.058(4) and 2.2773(av) Å, respectively) [10]. These results correspond to greater *trans* influence of the phenyl group than the methyl group.

A mechanism for the present unexpected formation of *trans*-PtPh<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>, Ph<sub>4</sub>Ge, and Pt(PhMe<sub>2</sub>P)<sub>4</sub> together with oligomers containing Ph<sub>2</sub>Ge units is proposed as shown in Scheme 2 from these results and related experiments [4d].

The stepwise formation of *trans*-PtPh(Ph<sub>3</sub>Ge)(PMe<sub>2</sub>Ph)<sub>2</sub> and *trans*-PtPh<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> by degrees suggests the generation of complexes having a germylene-platinum bond in the thermal reaction of *trans*-1. Thus, the thermolysis of *trans*-1 may proceed with liberation of one of the two PMe<sub>2</sub>Ph ligands in solution to give a coordinatively unsaturated, three-coordinate bis(germyl)platinum intermediate. Following α-elimination of the phenyl group attached to the germanium by platinum may yield a phenylplatinum complex having a germylene–platinum bond. Reductive elimination of the phenyl

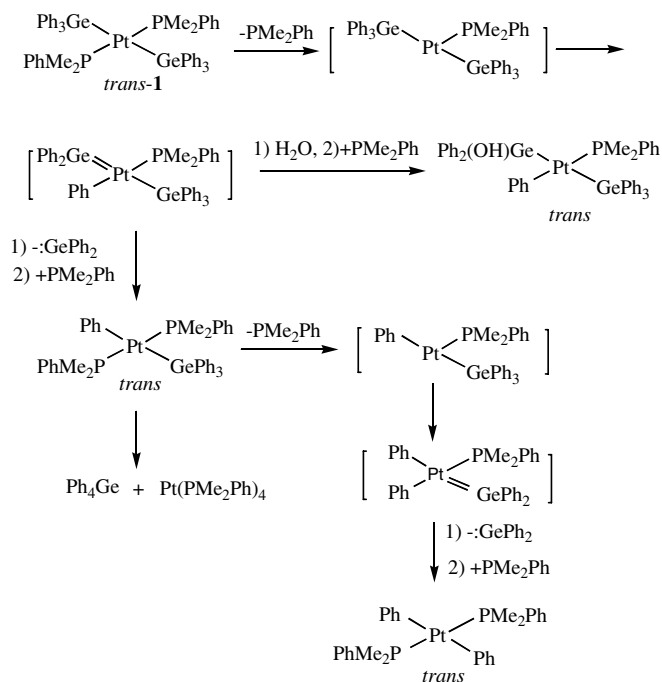


Table 1  
Selected bond length (Å) and bond angles (°) of *trans*-PtPh<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>

Pt1–P1	2.2861(18)	Pt1–C1	2.088(3)	P1–C7	1.820(4)	P1–C8	1.835(9)
P1–C9	1.822(4)	C1–Pt1–C1'	179.999(1)	C1–Pt1–P1	88.54(8)		

group with the remaining  $\text{Ph}_3\text{Ge}$  ligand produces  $\text{Ph}_4\text{Ge}$ , and the rest of the germylene unit may be converted into oligomers.

In order to detect the germylene–platinum intermediate complex,  $\text{PtPh}_3\text{Ge}(\text{Ph})(\text{Ph}_2\text{Ge}=\text{O})(\text{PMe}_2\text{Ph})$ , we heated very carefully *trans*-**1** in  $\text{C}_6\text{D}_6$  at  $50^\circ\text{C}$  by observing the change of signals in the  $\text{PMe}_2\text{Ph}$  ligand by means of  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectroscopy. After 2 days, the signals for a new species appeared at 1.45 ppm ( $t$ ,  $^2J_{\text{H-P}} = 6.8$  Hz,  $^3J_{\text{H-Pt}} = 31$  Hz) in  $^1\text{H}$  NMR and  $-9.5$  ppm ( $s$ ,  $^1J_{\text{Pt-P}} = 2585$  Hz) in  $^{31}\text{P}\{^1\text{H}\}$  NMR, suggesting the formation of new species with the *trans* geometry. Half of the complex *trans*-**1** remained unreacted. Fortunately, the new species was isolated by quick elution using preparative silica-gel TLC with a mixture of hexane and benzene. Two times recrystallization from a mixture of hexane and toluene gave colorless crystals with a composition of  $\text{Pt}(\text{Ph}_2\text{GeOH})(\text{Ph}_3\text{Ge})(\text{PMe}_2\text{Ph})_2$ . The structure of *trans*- $\text{Pt}(\text{Ph}_2\text{GeOH})(\text{Ph}_3\text{Ge})(\text{PMe}_2\text{Ph})_2$  was unequivocally established by spectroscopic methods coupled with X-ray diffraction analysis. The molecular structure of the *trans* Pt-complex is shown in Fig. 4. Selected bond lengths and angles in the Pt-complex are tabulated in Table 2. The crystallographic data are summarized in Section 3.

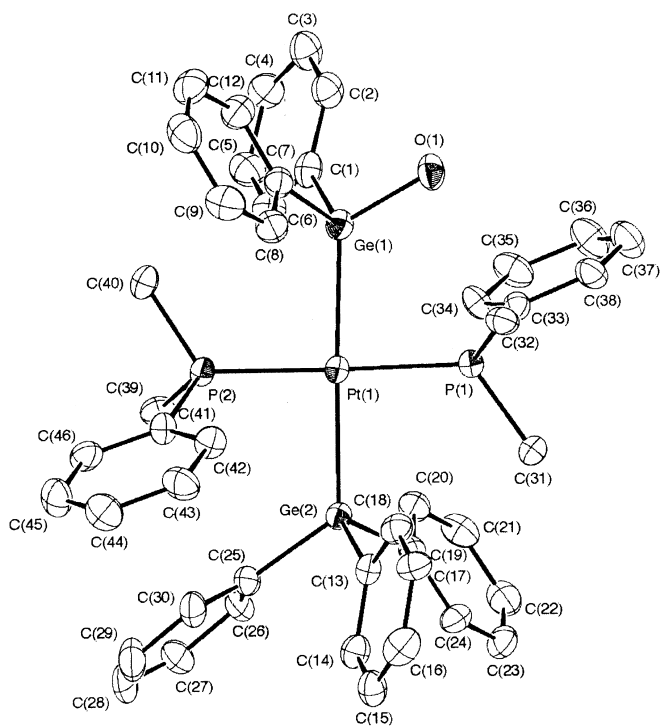


Fig. 4. Molecular structure of *trans*- $\text{Pt}(\text{Ph}_2\text{GeOH})(\text{Ph}_3\text{Ge})(\text{PMe}_2\text{Ph})_2$ . Thermal ellipsoids are drawn at the 30% probability level.

The *trans*- $\text{Pt}(\text{Ph}_2\text{GeOH})(\text{Ph}_3\text{Ge})(\text{PMe}_2\text{Ph})_2$  has a distorted square-planar geometry, with the dihedral angles between the planes composed of  $\text{Pt1-Ge1-P1}$  and  $\text{Pt1-Ge2-P2}$  being  $4.92^\circ$ . The sum of four angles about platinum was  $353.2^\circ$ . The  $\text{P1-Pt1-Ge1}$  and  $\text{P2-Pt1-Ge2}$  bond angles are  $86.37(3)^\circ$  and  $90.06(3)^\circ$ , respectively. The  $\text{Pt-Ge}$  bond lengths ( $2.4739(5)$  and  $2.5049(5)$  Å) for *trans*- $\text{Pt}(\text{Ph}_2\text{GeOH})(\text{Ph}_3\text{Ge})(\text{PMe}_2\text{Ph})_2$  are shorter than those for *trans*-**1** ( $2.5207(3)$  and  $2.5239(4)$  Å). The  $\text{Pt-P}$  bond lengths for *trans*- $\text{Pt}(\text{Ph}_2\text{GeOH})(\text{Ph}_3\text{Ge})(\text{PMe}_2\text{Ph})_2$  are similar to those for *trans*-**1** [4d].

The formation of *trans*- $\text{Pt}(\text{Ph}_2\text{GeOH})(\text{Ph}_3\text{Ge})(\text{PMe}_2\text{Ph})_2$  may be initiated by nucleophilic attack of  $\text{H}_2\text{O}$  as an impurity to the electrophilic germylene ligand [12]. It is consistent with the results of MO calculations for germylene complexes, which predict that the  $\text{Ge}=\text{M}$  double bond of germylene complexes is polarized in the sense of  $\text{Ge}^{\delta+}-\text{M}^{\delta-}$  similarly to the silylene complexes [13,14].

### 3. Experimental

#### 3.1. General methods

All manipulations of air-sensitive compounds were performed under  $\text{N}_2$  or argon using standard Schlenk techniques.  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  NMR spectra were recorded on a Varian Unity Inova-400 MHz. GC–MS spectra were measured with a JEOL JMS-DX 303 mass spectrometer. The UV and UV–vis spectra were recorded on a Shimadzu UV 2200 spectrometer. IR spectra were recorded on a Shimadzu FT IR 4200 spectrometer. Gas chromatographic analyses were performed with Shimadzu GC-8A equipped with 1 m 20% SE30. X-ray crystallographic data and diffraction intensities were collected on a MacScience DIP2030 diffractometer utilizing graphite-monochromated  $\text{Mo K}\alpha$  ( $\lambda = 0.71073$  Å) radiation. The structures were solved by direct methods using the program system SIR-92 and refined with all data on  $F^2$  by means of SHELXL-97. A refinement was performed by a SILICON Graphics O<sub>2</sub> with MAXUS (see Table 3).

#### 3.2. Materials

Solvents were dried by refluxing over sodium benzophenone ketyl under a nitrogen atmosphere and were distilled just before use. *cis*- $\text{PtCl}_2(\text{PMe}_2\text{Ph})_2$  and  $\text{Pt}(\text{PMe}_2\text{Ph})_4$  are commercially available.  $\text{Ph}_4\text{Ge}$  [15],  $\text{Ph}_3\text{GeLi}$  [16], *trans*- $\text{Pt}(\text{Ph}_3\text{Ge})_2(\text{PMe}_2\text{Ph})_2$  [4d] and *trans*- $\text{PtCl}(\text{Ph}_3\text{Ge})(\text{PMe}_2\text{Ph})_2$  [30] were prepared according to the reported procedures.

Table 2  
Selected bond length (Å) and bond angles ( $^\circ$ ) of *trans*- $\text{Pt}(\text{Ph}_2\text{GeOH})(\text{Ph}_3\text{Ge})(\text{PMe}_2\text{Ph})_2$

Pt1–P1	2.3017(12)	Pt1–P2	2.3080(12)	Pt1–Ge1	2.4739(5)	Pt1–Ge2	2.5049(5)
Ge1–O1	1.837(3)	Ge1–C1	1.968(5)	P1–Pt1–P2	175.19(4)	Ge1–Pt1–Ge2	177.235(17)
P1–Pt1–Ge1	86.37(3)	P2–Pt1–Ge1	91.67(3)	P1–Pt1–Ge2	92.07(3)	P2–Pt1–Ge2	90.06(3)

Table 3

Crystallographic data for of *trans*-PtPh<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> and *trans*-Pt(Ph<sub>2</sub>-GeOH)(Ph<sub>3</sub>Ge)(PMe<sub>2</sub>Ph)

	<i>trans</i> -PtPh <sub>2</sub> - (PMe <sub>2</sub> Ph) <sub>2</sub>	<i>trans</i> -Pt(Ph <sub>2</sub> GeOH)(Ph <sub>3</sub> Ge)- (PMe <sub>2</sub> Ph) <sub>2</sub>
Formula	C <sub>28</sub> H <sub>32</sub> P <sub>2</sub> Pt	C <sub>49</sub> H <sub>52</sub> OP <sub>2</sub> Ge <sub>2</sub> Pt
Molecular weight	625.57	1059.12
Crystal size (mm)	0.25 × 0.2 × 0.2	0.1 × 0.1 × 0.1
Crystal system	Monoclinic	Monoclinic
Space group	P2 <sub>1</sub> /n	P2 <sub>1</sub> /c
<i>Unit cell dimensions</i>		
<i>a</i> (Å)	10.3230(5)	9.8650(3)
<i>b</i> (Å)	7.7120(4)	36.5590(9)
<i>c</i> (Å)	16.9110(5)	12.7300(2)
$\alpha$ (°)	90.00	90.00
$\beta$ (°)	105.547(3)	106.74
$\gamma$ (°)	90.00	90.00
<i>V</i> (Å <sup>3</sup> )	1297.04(10)	4396.50(19)
<i>Z</i>	2	4
Radiation Mo K $\alpha$ (Å)	0.7170	0.7170
Temperature (K)	293(2)	293(2)
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.602	1.600
Number of unique reflections	2716	10476
Goodness-of-fit	1.026	0.960
<i>R</i> <sub>1</sub> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0361	0.0428
<i>wR</i> <sub>2</sub>	0.1180	0.1308

### 3.3. Preparation of *cis*-Pt(Ph<sub>3</sub>Ge)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> (*cis*-1)

The *trans*-Pt(Ph<sub>3</sub>Ge)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> (*trans*-1) (21.0 mg, 0.021 mmol) was dissolved in dry CD<sub>2</sub>Cl<sub>2</sub> (1.5 cm<sup>3</sup>) in an NMR tube. The tube was degassed in vacuum and filled with argon. The sample was irradiated with a 500-W Xenon lamp (Sen Tokushu Kogan Co., Ltd.) using Y-45 color filter (HOYA,  $\lambda$  > 450 nm) at room temperature for 30 min. NMR analysis of the reaction showed *ca.* 95% conversion of *trans*-1. Concentration of the reaction mixture followed by preparative column chromatography (silica-gel, hexane–CH<sub>2</sub>Cl<sub>2</sub>) and recrystallization from a mixture of hexane and CH<sub>2</sub>Cl<sub>2</sub>. The pure *cis*-1 could be isolated as yellow crystals (8.4 mg, 0.008 mmol, 40.0% yield). <sup>1</sup>H NMR ( $\delta$ , CD<sub>2</sub>Cl<sub>2</sub>) 0.72 (d, <sup>2</sup>*J*<sub>H-P</sub> = 8.4 Hz, <sup>3</sup>*J*<sub>H-Pt</sub> = 20.2 Hz, 12 H, PCH<sub>3</sub>), 2.20 (s, 18H, GeC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 6.87–7.53 (m, 34H, GeC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>, PC<sub>6</sub>H<sub>5</sub>); <sup>13</sup>C NMR ( $\delta$ , CD<sub>2</sub>Cl<sub>2</sub>) 15.7, 21.9, 126.2, 128.0, 128.1, 129.3, 130.2, 132.7, 135.4, 137.0, 148.2; <sup>31</sup>P NMR ( $\delta$ , CD<sub>2</sub>Cl<sub>2</sub>) –12.7 (s, <sup>1</sup>*J*<sub>P-Pt</sub> = 2032 Hz). Anal. Calc. for C<sub>52</sub>H<sub>52</sub>Ge<sub>2</sub>P<sub>2</sub>Pt: C, 52.88%; H, 4.86%. Found: C, 52.92%; H, 4.90%.

### 3.4. Preparation of *trans*-PtPh(Ph<sub>3</sub>Ge)(PMe<sub>2</sub>Ph)<sub>2</sub>

The *trans*-PtCl(Ph<sub>3</sub>Ge)(PMe<sub>2</sub>Ph)<sub>2</sub> (0.1 g, 0.12 mmol), Ph<sub>2</sub>Zn (0.026 g, 0.12 mmol), and THF (2 ml) were placed in a 5-ml Pyrex test tube. The solution was degassed in a vacuum and stirred under argon in a sealed tube at 0 °C for 1 h. After MeOH was slowly added, the organic layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> several times. After the solution was concentrated to *ca.* 5 ml, hexane (10 ml) was added.

Then, the organic layer was filtered through filter-paper. Upon allowing the organic layer to stand at room temperature for 1 day, pure *trans*-PtPh(Ph<sub>3</sub>Ge)(PMe<sub>2</sub>Ph)<sub>2</sub> was formed as yellow crystals. <sup>1</sup>H NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) 1.08 (t with two satellites, *J*<sub>H-P</sub> = 6.8 Hz, *J*<sub>H-Pt</sub> = 32 Hz, 12H), 6.86–7.83 (m, 25H); <sup>31</sup>P NMR ( $\delta$ , CD<sub>2</sub>Cl<sub>2</sub>) –9.6 (s, <sup>1</sup>*J*<sub>P-Pt</sub> = 2725 Hz). Anal. Calc. for C<sub>40</sub>H<sub>42</sub>GeP<sub>2</sub>Pt: C, 61.61%; H, 5.43%. Found: C, 61.85%; H, 5.73%.

### 3.5. Kinetic studies of isomerization of *cis*-Pt(Ph<sub>3</sub>Ge)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> (*cis*-1)

The *cis*-Pt(Ph<sub>3</sub>Ge)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> (*cis*-1) (11.0 mg, 0.011 mmol) was dissolved in dry CD<sub>2</sub>Cl<sub>2</sub> (0.75 cm<sup>3</sup>) in an NMR tube. The tube was degassed in vacuum and filled with argon. The sample was placed in an NMR sample probe controlled at 30, 40, 45, and 50 °C, and examined by <sup>1</sup>H NMR. The time course of the isomerization was followed by monitoring the relative peak integration of the methyl signals of *cis*-1 and *trans*-1.

### 3.6. Kinetic studies of isomerization of *cis*-Pt(Ph<sub>3</sub>Ge)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> (*cis*-1) with Dimethylphenylphosphine

A mixture of *cis*-1 (11.0 mg, 0.011 mmol), PMe<sub>2</sub>Ph (0.9 mg, 0.007 mmol) and CD<sub>2</sub>Cl<sub>2</sub> (0.75 cm<sup>3</sup>) was heated under argon in a sealed NMR tube at 30 °C, and examined by <sup>1</sup>H NMR. The time course of the isomerization was followed by measuring the relative peak integration of the methyl signal of *cis*-1 and *trans*-1.

### 3.7. Thermolysis of *trans*-Pt(Ph<sub>3</sub>Ge)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> (*trans*-1) at 50 °C for 36 Days

The *trans*-Pt(Ph<sub>3</sub>Ge)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> (*trans*-1) (3.0 mg, 0.003 mmol) was dissolved in dry C<sub>6</sub>D<sub>6</sub> (0.70 cm<sup>3</sup>) containing toluene (1  $\mu$ l, 0.01 mmol) in an NMR tube. The tube was degassed in vacuum and filled with argon. The progress of the reaction was monitored at 50 °C for 36 days by means of NMR spectroscopy. The NMR signals assigned to *trans*-1 decayed (*ca.* 50% conversion yield), and a buildup of new NMR signals of *trans*-PtPh(Ph<sub>3</sub>Ge)(PMe<sub>2</sub>Ph)<sub>2</sub> (*ca.* 40% yield). *trans*-PtPh(Ph<sub>3</sub>Ge)(PMe<sub>2</sub>Ph)<sub>2</sub> was observed. <sup>1</sup>H NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) 1.08 (t with two satellites, <sup>2</sup>*J*<sub>H-P</sub> = 16.1 Hz, <sup>3</sup>*J*<sub>H-Pt</sub> = 3.3 Hz, 6H), 6.96–7.78 (m, 30H); <sup>31</sup>P NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) –9.6 (<sup>1</sup>*J*<sub>Pt-P</sub> = 2725 Hz).

### 3.8. Thermolysis of a mixture of *trans*-Pt(Ph<sub>3</sub>Ge)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> (*trans*-1) and *trans*-PtPh(Ph<sub>3</sub>Ge)(PMe<sub>2</sub>Ph)<sub>2</sub> at 80 °C for 1 month

After heating a C<sub>6</sub>D<sub>6</sub> solution of *trans*-1 (5.0 mg, 0.005 mmol) at 50 °C for 36 days, this reaction mixture was continuously heated at 80 °C for 1 month. Complex

*trans*-PtPh<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> was formed together with oligomers containing Ph<sub>2</sub>Ge units. Pure *trans*-PtPh<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> could be isolated by recrystallization from a mixture of hexane and benzene at room temperature.

### 3.9. Formation of *trans*-Pt(Ph<sub>2</sub>GeOH)(Ph<sub>3</sub>Ge)(PMe<sub>2</sub>Ph)<sub>2</sub> by heating of *trans*-Pt(Ph<sub>3</sub>Ge)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> (*trans*-1)

The *trans*-Pt(Ph<sub>3</sub>Ge)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> (*trans*-1) (5.0 mg, 0.005 mmol) was dissolved in dry C<sub>6</sub>D<sub>6</sub> (0.70 cm<sup>3</sup>) containing toluene (1 μl, 0.01 mmol) in an NMR tube. The tube was degassed in vacuum and filled with argon. The progress of the reaction was monitored at 50 °C by means of <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy. The NMR signals at 1.24 ppm (*vt* with two satellites, <sup>2</sup>J<sub>H-P</sub> = 29.3 Hz, <sup>3</sup>J<sub>H-Pt</sub> = 6.6 Hz) and -11.0 ppm (<sup>1</sup>J<sub>Pt-P</sub> = 2616 Hz) assigned to *trans*-1 decayed (*ca.* 50% conversion yield), and a buildup of new NMR signals at 1.45 ppm (*t* with two satellites, <sup>2</sup>J<sub>H-P</sub> = 6.8 Hz, <sup>3</sup>J<sub>H-Pt</sub> = 31 Hz) and -9.5 ppm (<sup>1</sup>J<sub>Pt-P</sub> = 2585 Hz) (approximately 1:1) was observed. The reaction mixture was eluted by separative silica gel TLC, treated with Et<sub>3</sub>N (1%), with a 1:1 mixture of hexane and benzene. Recrystallization from a mixture of hexane and toluene two times gave colorless crystals with a composition of *trans*-Pt(Ph<sub>2</sub>GeOH)(Ph<sub>3</sub>Ge)(PMe<sub>2</sub>Ph)<sub>2</sub>.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2006.05.065](https://doi.org/10.1016/j.jorganchem.2006.05.065).

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