

Platinum-Catalyzed Bis-Germylation of Alkynes with Organodigermanes and Cyclic Oligogermanes

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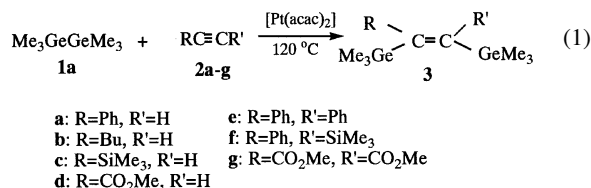
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Hexamethyldigermane, Me₃GeGeMe₃, reacted with various alkynes in the presence of platinum complexes at 120 °C to afford Z-1,2-bis(germyl)ethenes in moderate to good yields. Terminal alkynes exhibit higher reactivities than internal ones. [Pt(acac)₂] and [Pt(dba)₂] serve as efficient catalysts, while [Pt(PPh₃)₄], [PtCl₂(PPh₃)₂], and [Pt(dba)₂]-phosphite were found to be inactive. Four- and six-membered cyclic oligogermanes, such as dodecamethylcyclohexagermane, (Me₂Ge)₆, reacted with alkynes in the presence of platinum catalysts to yield 1,4-digermacyclohexa-2,5-dienes in ca. 30% yield. The reactions of phenylacetylene with 1,2-digermacyclohexa-3,5-dienes afforded the corresponding 1,4-digermacycloocta-2,5,7-trienes in 93% yield. Bis(germyl)platinum complexes having various tertiary phosphine ligands have been prepared as models of a key intermediate in the above mentioned catalytic bis-germylation of alkynes, and their structures have been established by spectroscopic methods and X-ray crystallography. Bis(germyl)platinum complexes reacted with phenylacetylene to give the corresponding insertion products, germyl(germylvinyl)platinum species, whose structures have been determined by spectroscopic and X-ray analysis. Germyl(germylvinyl)platinum complexes were found to liberate a bis-germylation product of the alkyne upon heating. The result supports a mechanism involving the oxidative addition of a digermane to a Pt(0) complex, the insertion of an alkyne into one of the two Pt–Ge bonds to give a germyl(germylvinyl)platinum species, and the reductive elimination of the bis-germylation product of the alkyne. Evidence suggesting the extrusion of a germylene unit from the bis-germylplatinum species has been obtained, accounting for the generation courses of other by-products.

A transition metal-catalyzed addition of group-14 element compounds to unsaturated organic substrates is a useful fundamental process in group-14 element chemistry. The addition of Si–Si bonds to C–C triple and double bonds, i.e., bis-silylation, has attracted considerable current interest in the synthesis of functional molecules and in applications to selective organic synthesis.^{1–8} For the bis-silylation of C–C triple bonds, palladium complexes have often been used as catalysts. In contrast to the extensive use of the bis-silylation method and of considerable studies on reaction mechanisms, there have been few reports on bis-germylation reactions, except for the reaction of strained digermiranes,⁹ chlorine-substituted digermanes,¹⁰ and ocatamethyltrigermanes.¹¹ We report herein on the digermylation of alkynes using various substituted digermanes, (Me₂RGe)₂ (R = Me, Cl, Ph), cyclic oligogermanes, (R₂Ge)_n (R = Me, n = 6; 'Pr, n = 4), and 1,2-digermacyclohexa-3,5-dienes in the presence of platinum complexes. We also report on the characterization and reactivities of bis(germyl)platinum complexes and germyl(germylvinyl)platinum complexes that are assumed as key intermediates in these platinum-catalyzed processes.

Results

Platinum-Catalyzed Reactions of Substituted Digermanes, Me₂RGeGeMe₂R (R = Me, Cl, Ph) with Alkynes. When a degassed toluene solution of 1 mol equiv of hexamethyldigermane, Me₃GeGeMe₃ (**1a**) containing 5 mol equiv of phenylacetylene (**2a**), and [Pt(acac)₂] (acac = acetylacetonate) (0.05 mol equiv based on **1a**) was heated at 120 °C for 16 h, Z-1-phenyl-1,2-bis(trimethylgermyl)ethene (**3a**) was obtained as a sole product in moderate yield (59% GC yield based on **1a**) (Eq. 1). The rest of the digermane remained unreacted. The concentration of the reaction mixture by the evaporation of toluene followed by preparative TLC with silica gel gave pure **3a**, which showed satisfactory NMR, IR, and MS data.



The geometry was confirmed to be *Z* on the basis of their spectroscopic data¹² and by a comparison with those of the authentic *E* isomer prepared separately by a reaction of chlorotrimethylgermane Me_3GeCl , and phenylacetylene, with Mg metal in HMPA.¹³ In contrast to the fairly good catalytic activity shown by $[\text{Pt}(\text{acac})_2]$, a similar reaction of **1a** with phenylacetylene in the presence of a palladium complex has been reported to give only 1.3% yield of **3a**.¹⁰

Besides $[\text{Pt}(\text{acac})_2]$, a zero-valent platinum complex, $[\text{Pt}(\text{dba})_2]$ (dba = dibenzylideneacetone), also catalyzed the bis-germylation of **2a** to give **3a** in moderate yields. Under similar conditions, the use of $[\text{PtCl}_2(\text{cod})]$ (cod = 1,5-cyclooctadiene) resulted in low yields of **3a**, and conventional Pt catalysts such as $[\text{Pt}(\text{PPh}_3)_4]$ and $[\text{PtCl}_2(\text{PPh}_3)_2]$, and $[\text{Pt}(\text{dba})_2]$ -phosphite systems (phosphite = $\text{P}(\text{OMe})_3$ and $\text{P}(\text{OCH}_2)_3\text{CET}$) proved to be inactive. The effects of various platinum catalysts on the addition of Ge–Ge bonds of **1a** to **2a** are summarized in Table 1. The effect of other experimental conditions on the yield of **3** in the present process was examined using the $[\text{Pt}(\text{acac})_2]$ catalyst. Lowering the reaction temperature from 120 to 80 °C resulted in lower yields of **3a** (56 to 10%), while raising the temperature to 140 °C had a deteriorating effect, yielding **3a** in only 10%. Formation of several unidentified by-products in minor amounts was noted in the process carried out at 140 °C. Extending the reaction time scarcely improved the yield of **3a**. Decreasing the ratio of **2a**/**1a** from 5:1 to 1:1 caused a lowering of the yield of **3a** (59 to 26%). An increase in the concentration of $[\text{Pt}(\text{acac})_2]$ relative to the digermene **1a** (from 1.0 to 10 mol%) did not influence the yields of **3a**.

The reactivities of other terminal and internal alkynes, **2a–2g**, with the digermene **1a** and with the dichloro- and diphenyl-substituted digermenes **1b** and **1c** (Eq. 2) were also examined with $[\text{Pt}(\text{acac})_2]$ as catalyst, as summarized in Table 2. (Trimethylsilyl)acetylene (**2c**) reacted with **1a** under the same reaction conditions as those for **2a** to give 1,2-bis(trimethylgermyl)-1-trimethylsilylethene (**3c**) in 55% yield. Other terminal alkynes, such as 1-hexyne (**2b**) and methyl propiolate (**2d**), gave the corresponding 1,2-bis(trimethylgermyl)ethenes (**3b, d**) in low yields. The reaction of **2d** resulted in the formation of a complex mixture. Each compound of

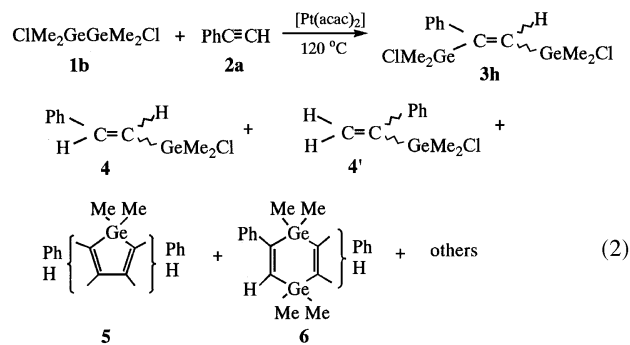
Table 2. Reactions of Digermenes (**1**) with Alkynes (**2**) in the Presence of $[\text{Pt}(\text{acac})_2]$ ^{a)}

Run	Digermene	Alkyne	Conversion of 1 /%	Product 3 , yield/% ^{b)}
1	1a	2a	60	59 (<i>Z/E</i> = 100/0)
2	1a	2b	17	8
3	1a	2c	58	55
4	1a	2d	10	8
5	1a	2e	0	0
6	1a	2f	0	0
7	1a	2g	0	0
8	1b	2a	100	19
9	1c	2a	0	0

a) **1** (0.10 mmol), **2** (0.50 mmol), $[\text{Pt}(\text{acac})_2]$ (0.005 mmol), toluene (1 ml), 120 °C, 16 h. b) GC yield based on **1**.

3b–3d was obtained as a single stereoisomer, probably the *Z*-isomer. Internal alkynes, such as diphenylacetylene (**2e**), 1-phenyl-2-(trimethylsilyl)acetylene (**2f**), and dimethyl acetylenedicarboxylate (**2g**), proved to be unreactive toward **1a** under similar conditions.

In contrast to the platinum-catalyzed reactions of alkyl-digermene **1a** with alkynes, the reaction of its chlorinated analog, 1,2-dichloro-1,1,2,2-tetramethyldigermene, $\text{ClMe}_2\text{GeGeMe}_2\text{Cl}$ (**1b**) with phenylacetylene (**2a**) in the presence of $[\text{Pt}(\text{acac})_2]$ under the same conditions as those for **1a** gave a complex mixture of germylation products. The starting digermene **1b** was completely consumed and converted into 1,2-bis(chlorodimethylgermyl)-1-phenylethene (**3h**, 19%), 1- or 2-(chlorodimethylgermyl)styrene (**4** or **4'**, 17%), germole (**5**, 5%), 1,4-digermacyclohexa-2,5-diene (**6**, 5%), and some unidentified products (Eq. 2).



The bis-germylstyrene **3h** produced by alkyne-insertion into the Ge–Ge bond in **1b** was found to be a mixture of two stereoisomers (*E/Z* = 50/50). The bis-germylstyrene **3h** was easily hydrolyzed with moisture. Therefore, the yield and stereoisomer ratio of **3h** were estimated by a comparison with the authentic *E* isomer by means of GC and NMR analysis of the corresponding methylated compound after treating the reaction mixture with MeMgI . Compounds **4–6** were obtained as regioisomeric mixtures, and their configurations have not been unambiguously established. Similar results were obtained when $[\text{Pt}(\text{dba})_2]$ was employed. The reaction carried out in the presence of the $[\text{Pt}(\text{dba})_2]$ - $\text{P}(\text{OCH}_2)_3\text{CET}$ system under similar reaction conditions gave **3h** (9%) as the major product with a lower conversion (36%).

Table 1. Effects of Platinum Catalysts on the Reaction of Hexamethyldigermene (**1a**) with Phenylacetylene (**2a**)^{a)}

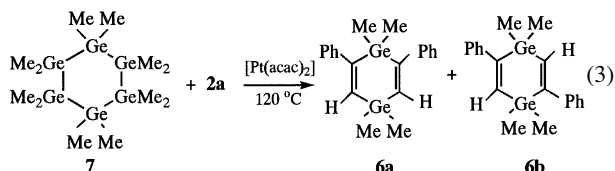
Run	Catalyst	Conversion of 1a	Product 3a , yield/% ^{b)}
1	$[\text{Pt}(\text{PPh}_3)_4]$	0	0
2	$[\text{PtCl}_2(\text{PPh}_3)_2]$	0	0
3	$[\text{Pt}(\text{dba})_2]$ ^{c)}	40	36
4	$[\text{Pt}(\text{dba})_2] + \text{ETBP}$ ^{d)}	trace	trace
5	$[\text{Pt}(\text{dba})_2] + 2\text{P}(\text{OMe})_3$	trace	trace
6	$[\text{Pt}(\text{acac})_2]$ ^{e)}	60	59
7 ^{f)}	$[\text{Pt}(\text{acac})_2]$	30	26
8	$[\text{PtCl}_2(\text{cod})]$ ^{g)}	10	10

a) **1** (0.10 mmol), **2** (0.50 mmol), $[\text{Pt}(\text{acac})_2]$ (0.005 mmol), toluene (1 ml), 120 °C, 16 h. b) GC yields were calculated on the basis of the amounts of **1a** used. c) dba = dibenzylideneacetone. d) ETBP = $\text{P}(\text{OCH}_2)_3\text{CET}$. e) acac = acetylacetonato. f) **1a** (0.5 mmol), **2a** (0.5 mmol), $[\text{Pt}(\text{acac})_2]$ (0.005 mmol). g) cod = 1,5-cyclooctadiene.

Bis-germylation of phenylacetylene with 1,2-dichloro-1,1,2,2-tetramethyldigermene (**1b**) has been reported to proceed in the presence of the $[\text{Pd}(\text{dba})_2]\text{-P}(\text{OCH}_2)_3\text{CEt}$ system in moderate to good yields.¹⁰

The reaction of 1,2-diphenyl-1,1,2,2-tetramethyldigermene, $\text{Me}_2\text{PhGeGePhMe}_2$ (**1c**), with **2a** did not proceed, even at higher temperature, with longer reaction times and with higher concentrations of platinum complexes.

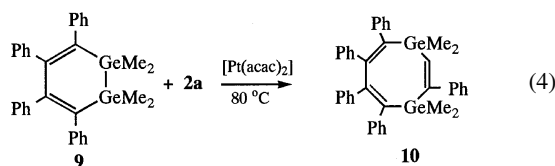
Reactions of Cyclic Oligogermanes with Phenylacetylene. As an extension of studies on the reactions of digermanes with alkynes, the reactions of cyclic oligogermanes with alkynes were examined. A degassed toluene solution containing dodecamethylcyclohexagermane, $(\text{Me}_2\text{Ge})_6$ (**7**) (1 mol equiv) and 30 mol equiv of phenylacetylene (**2a**) (alkyne/Ge ratio = 5:1) in the presence of $\text{Pt}(\text{acac})_2$ (0.05 mol equiv of **2a**) was heated at 120 °C for 32 h to give a 1:1 mixture of 1,1,4,4-tetramethyl-1,4-digerma-2,6-diphenylcyclohexa-2,5-diene (**6a**) and 1,1,4,4-tetramethyl-1,4-digerma-2,5-diphenylcyclohexa-2,5-diene (**6b**) in a total yield of 38% (relative to **7**) with the rest of **7** (67%) recovered unreacted from the toluene solution (Eq. 3).



No acyclic alkyne-inserted products were detected by means of GC and MS analyses. Other platinum complexes, such as $[\text{Pt}(\text{dba})_2]$ and $[\text{PtCl}_2(\text{cod})]$, also catalyzed the reaction to give **6** in 31–33% yields. In contrast to the platinum complexes, the $[\text{Pd}(\text{dba})_2]\text{-2P}(\text{OCH}_2)_3\text{CEt}$ catalyst system was much less reactive, and converted only 10% of **7** into **6** in 10% total yield.

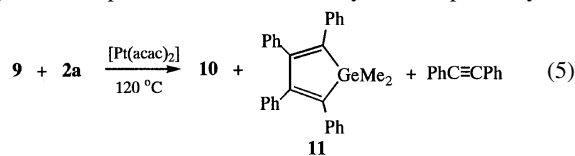
The reaction of strained octaisopropylcyclotetragermane ($(\text{Pr}_2\text{Ge})_4$ (**8**)) with **2a** did not occur under the same conditions as those for **7**. The result is in marked contrast to that in the reaction of **8** with **2a** performed in the presence of palladium complexes. With the $[\text{Pd}(\text{dba})_2]\text{-2P}(\text{OCH}_2)_3\text{CEt}$ as the catalyst system, the cyclotetragermane **8** reacted with **2a** to give the corresponding alkyne-inserted tetragermacyclohexene in good yields (70%).¹⁴

Reactions of 1,2-Digermacyclohexa-3,5-dienes with Phenylacetylenes. 1,1,2,2-Tetramethyl-3,4,5,6-tetraphenyl-1,2-digermacyclohexa-3,5-diene (**9**) reacted with 1.5 equiv of **2a** in the presence of a catalytic amount of $[\text{Pt}(\text{acac})_2]$ at 80 °C in 36 h with cleavage of the Ge–Ge bond to give the phenylacetylene-inserted compound **10** in 96% yield as colorless crystals (Eq. 4).



The yield of the alkyne-insertion product **10** decreased from 96 to 26% upon raising the reaction temperature from 80 to 120

°C. At the same time, 1,1-dimethyl-2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-diene (tetraphenylgermole) (**11**) and diphenylacetylene were produced in 20 and 19% yields, respectively.



It was confirmed that the tetraphenylgermole (**11**) and the diphenylacetylene were produced upon the thermolysis of **10** above 100 °C in the presence of a catalytic amount of $[\text{Pt}(\text{acac})_2]$ without any involvement of phenylacetylene. The results indicate that the phenylacetylene-inserted product **10** is decomposed at higher temperatures in the presence of the platinum catalyst without the participation of phenylacetylene to give the germole **11** and diphenylacetylene. The time course of the reaction of **9** with **2a** in the presence of $[\text{Pt}(\text{acac})_2]$ is shown in Fig. 1.

Fig. 1 shows that 1,2-digermacyclohexadiene **9** is decomposed, but that the alkyne-insertion product **10**, tetraphenylgermole **11**, and diphenylacetylene are not formed during the early stage of the reaction.

The formation of the tetraphenylgermole **11** from **9** indicates that a germylene unit was extruded in the platinum-catalyzed thermolysis of the cyclic digermene **9**. For trapping the germylene in the platinum-catalyzed reactions, the cyclic digermene **9** was treated with a catalytic amount of $[\text{Pt}(\text{acac})_2]$ at 120 °C for 16 h in toluene containing excess CCl_4 which is known to trap germylene.¹⁵ The reaction gave Me_2GeCl_2 (26%) and Cl_3CCCl_3 (10%) together with the germole **11** and diphenylacetylene in support of the liberation of the dimethylgermylene entity in the platinum-catalyzed thermolysis of the digermene **9**.

The reactivities of other dimetallacyclohexadienes **12** and related compounds with **2a** were examined with $[\text{Pt}(\text{acac})_2]$ as a catalyst in toluene (Eq. 6); the results are included in Table 3. 1,1,2,2-Tetramethyl-3,4,5,6-tetraphenyl-1,2-disilacyclohexa-3,5-diene (**12a**) reacted with **2a** under similar reaction conditions as those for **9** to give the alkyne-insertion product **13a** (19%), tetraphenylsilol (**14a**) (21%) together with a trace amount of diphenylacetylene (run 3 in Table 3). Other

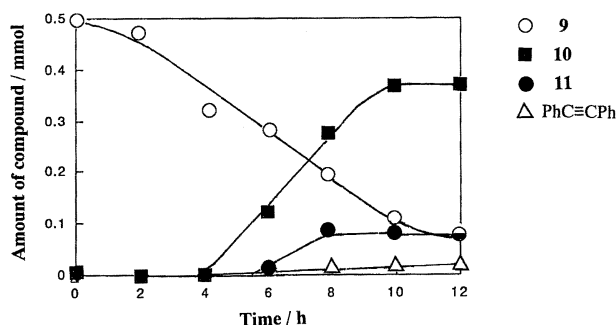


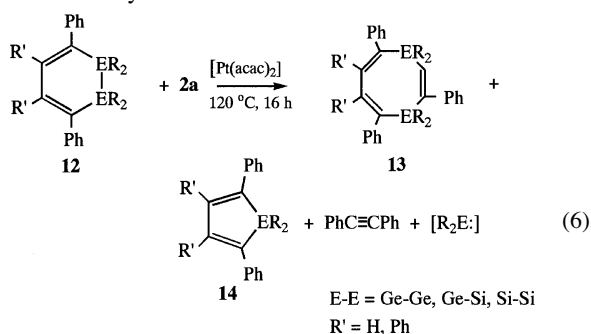
Fig. 1. The time-course of reaction of 1,1,2,2-tetramethyl-3,4,5,6-tetraphenyl-1,2-digermacyclohexa-3,5-diene (**9**) with phenylacetylene (**2a**) in the presence of $[\text{Pt}(\text{acac})_2]$ at 100 °C.

Table 3. Reactions of Dimetallatetraphenylcyclohexadienes (**9**, **12**) with Phenylacetylene (**2a**) in the Presence of [Pt(acac)₂]^a

Run	R ₂ E-ER ₂ Unit in cyclohexadiene	R'	Products, yield/% ^b		
			10 or 13	11 or 14	PhC≡CPh
1 ^c	Me ₂ Ge-GeMe ₂ (9)	Ph	96		
2	Me ₂ Ge-GeMe ₂ (9)	Ph	26	20	19
3	Me ₂ Si-SiMe ₂ (12a)	Ph	19	21	trace
4	Me ₂ Si-GeMe ₂ (12b)	Ph	trace	0	0
5	Me ₂ Ge-CH ₂ (12c)	H	0	0	0
6	Et ₂ Ge-GeEt ₂ (12d)	Ph	trace	0	0
7	Et ₂ Si-SiEt ₂ (12e)	Ph	0	0	0
8	Et ₂ Si-GeEt ₂ (12f)	Ph	trace	0	0

a) **9** or **12** (0.5 mmol), **2a** (0.5 mmol), [Pt(acac)₂] (0.025 mmol), toluene (1 ml), 120 °C, 16 h. b) GC yield based on **9** or **12**. c) At 80 °C for 36 h.

dimetallacyclohexadienes (**12b**, **12d**–**12f**) and monogermacyclohexadiene **12c** did not react with phenylacetylene. The alkyne-insertion product by the reaction of **12a** with acetylenedicarboxylate (**2g**) in the presence of [PdCl₂(PPh₃)₂] was observed by Sakurai and co-workers.¹⁶



The structure of the new type of germanium-containing eight-membered ring compound **10** was fully established by spectroscopic and X-ray diffraction methods. The molecular structure of **10** is shown in Fig. 2 and the crystallographic data are summarized in Table 4. Selected bond lengths and angles in complex **10** are tabulated in Table 5. Compound **10** has a twisted geometry between the two planes Ge(1)–C(6)–C(5)–Ge(2) and C(1)–C(2)–C(3)–C(4). The Ge(1)–C(6) and Ge(2)–C(5) bond lengths (1.955–1.962 Å) are shorter than those of Ge(1)–C(1) and Ge(2)–C(4) (1.977–1.985 Å).

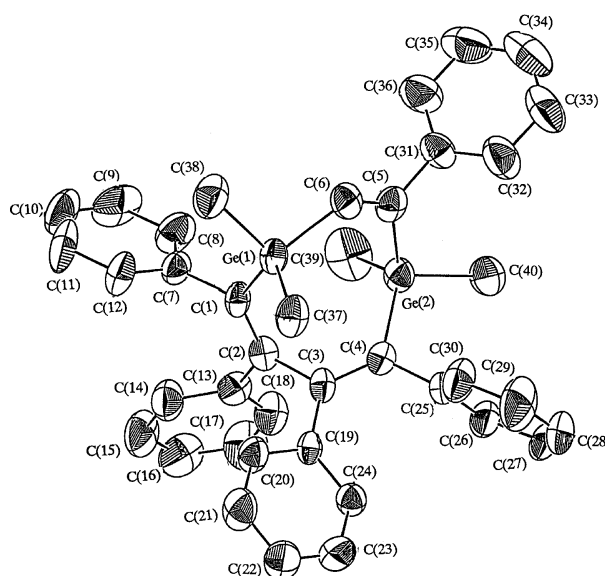


Fig. 2. Molecular structure of the 1,1,4,4-tetramethyl-2,5,6,7,8-pentaphenyl-1,4-digermacyclohexa-2,5,7-triene (**10**) (30% probability thermal ellipsoids drawn by ORTEPII*). Hydrogen atoms are omitted for clarity.

Table 4. Crystallographic Data for **10**, *cis*-**15**, *cis*-**16**, *trans*-**17**, **18**, **19**, and *cis*-**21**

	10	<i>cis</i> - 15	<i>cis</i> - 16	<i>trans</i> - 17	18	19	<i>cis</i> - 21
Chem formula	C ₄₀ H ₃₈ Ge ₂	C ₃₂ H ₄₄ Ge ₂ Pt ₂	C ₄₂ H ₄₈ Ge ₂ Pt ₂	C ₅₂ H ₅₂ Ge ₂ Pt ₂	C ₅₂ H ₃₀ Ge ₂ Pt ₂ ·C ₆ H ₆	C ₃₂ H ₄₂ Ge ₂ Pt ₂	C ₅₀ H ₅₄ Ge ₂ Pt ₂
fw	664.00	830.88	955.02	1079.15	1135.08	828.89	1057.14
Cryst syst	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
Space group	<i>P</i> 1	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 1
<i>a</i> /Å	9.160 (2)	17.417 (1)	15.672 (5)	16.4320 (5)	15.754 (2)	10.686 (1)	11.349 (2)
<i>b</i> /Å	19.221 (4)	11.430 (1)	14.708 (5)	11.2320 (2)	19.864 (2)	18.669 (1)	11.515 (2)
<i>c</i> /Å	21.234 (4)	17.424 (1)	18.012 (5)	25.4170 (6)	17.025 (2)	17.660 (1)	20.271 (3)
α /deg	108.25 (1)	90	90	90	90	90	98.370 (7)
β /deg	98.75 (2)	108.895 (5)	105.891 (5)	105.918 (1)	105.401 (9)	105.581 (2)	98.342 (7)
γ /deg	102.5 (2)	90	90	90	90	90	115.056 (8)
<i>V</i> /Å ³	3368 (1)	3281.8 (5)	3963 (2)	4511.19 (19)	5136 (1)	3393.6 (2)	2310.2 (6)
<i>Z</i>	4	4	4	4	4	4	2
<i>D</i> _{calc} /g cm ^{−3}	1.31	1.682	1.589	1.589	1.468	1.622	1.520
<i>T</i> (K)	296	296	296	296	296	296	120
Cryst dims/mm	0.50 × 0.10 × 0.05	0.20 × 0.15 × 0.10	0.30 × 0.25 × 0.20	0.30 × 0.30 × 0.20	0.30 × 0.20 × 0.20	0.15 × 0.10 × 0.08	0.25 × 0.2 × 0.2
Reflns (hkl) limits	−10 ≤ <i>h</i> ≤ 0 −22 ≤ <i>k</i> ≤ 22 −24 ≤ <i>l</i> ≤ 25	0 ≤ <i>h</i> ≤ 22 0 ≤ <i>k</i> ≤ 14 −21 ≤ <i>l</i> ≤ 18	−17 ≤ <i>h</i> ≤ 17 −16 ≤ <i>k</i> ≤ 8 −19 ≤ <i>l</i> ≤ 20	0 ≤ <i>h</i> ≤ 21 0 ≤ <i>k</i> ≤ 14 −32 ≤ <i>l</i> ≤ 31	−19 ≤ <i>h</i> ≤ 20 0 ≤ <i>k</i> ≤ 25 −22 ≤ <i>l</i> ≤ 0	0 ≤ <i>h</i> ≤ 14 0 ≤ <i>k</i> ≤ 24 −23 ≤ <i>l</i> ≤ 22	0 ≤ <i>h</i> ≤ 14 −14 ≤ <i>k</i> ≤ 13 −26 ≤ <i>l</i> ≤ 25
Unique rflns	11827	3503	2852	9907	11766	7774	9008
No. of rflns used	5961(> 2σ(<i>I</i>))	3503(> 2σ(<i>I</i>))	2680(> 2σ(<i>I</i>))	9227(> 2σ(<i>I</i>))	7173(> 2σ(<i>I</i>))	6004(> 2σ(<i>I</i>))	9008(> 2σ(<i>I</i>))
<i>R</i>	0.0460	0.0601	0.0181	0.0367	0.0532	0.032	0.065
<i>R</i> _w	0.0668	0.1674	0.0454	0.1115	0.1233	0.034	0.1753
Goodness of fit	0.39857	1.467	1.097	1.041	1.333	1.022	1.296

Table 5. Selected Bond Distances (Å) and Angles (deg) for **10**

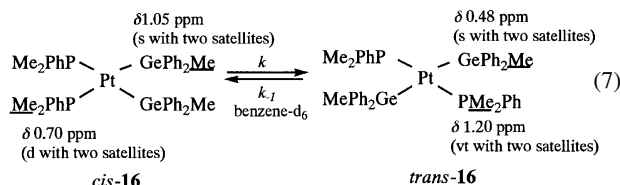
Ge(1)–C(1)	1.977 (7)	Ge(1)–C(6)	1.955 (8)
Ge(1)–C(37)	1.929 (8)	Ge(1)–C(38)	1.949 (9)
Ge(2)–C(4)	1.985 (7)	Ge(2)–C(5)	1.963 (8)
Ge(2)–C(39)	1.931 (8)	Ge(2)–C(40)	1.963 (8)
C(1)–C(2)	1.332 (10)	C(2)–C(3)	1.527 (9)
C(3)–C(4)	1.343 (10)	C(5)–C(6)	1.321 (11)
C(1)–Ge(1)–C(6)	112.3 (3)	C(1)–Ge(1)–C(37)	114.3 (4)
C(1)–Ge(1)–C(38)	108.8 (4)	C(6)–Ge(1)–C(37)	109.4 (4)
C(6)–Ge(1)–C(38)	104.7 (4)	C(37)–Ge(1)–C(38)	106.7 (4)
C(4)–Ge(2)–C(5)	109.7 (3)	C(4)–Ge(2)–C(39)	114.7 (4)
C(5)–Ge(2)–C(39)	109.2 (4)	C(5)–Ge(2)–C(39)	109.9 (4)

Synthesis and Reaction of Bis(germyl)platinum Complex.

In the platinum-catalyzed reaction of digermane **1** with alkynes **2**, a bis(germyl)platinum complex is a possible intermediate to undergo further insertion of alkynes to give the bis-germylated product of alkynes. Thus, information concerning the behavior of bis(germyl)platinum type complexes is critical in understanding the reaction mechanism of the bis-germylation of alkynes. We set out to prepare model compounds of the intermediate bis(germyl)platinum complex stabilized by tertiary phosphine ligands. Using dimethylphenylphosphine as supporting ligands, we have been able to prepare bis(germyl)platinum complexes, [(Me₂PhGe)₂Pt(PMe₂Ph)₂] (**15**), [(MePh₂Ge)₂Pt(PMe₂Ph)₂] (**16**), and [(Ph₃Ge)₂Pt(PMe₂Ph)₂] (**17**). The treatment of *cis*-[PtCl₂(PMe₂Ph)₂] with two equiv of Me₂PhGeLi in THF at room temperature for 12 h afforded yellow crystals with a composition of [(Me₂PhGe)₂Pt(PMe₂Ph)₂] (**15**). NMR examination of a C₆D₆ solution of the yellow crystals showed a single *cis*-isomer: ¹H NMR (C₆D₆) δ 0.73 (d, ²J_{H-P} = 8.1 Hz, ³J_{H-Pt} = 29.9 Hz, PCH₃), 1.05 (s, ³J_{H-Pt} = 17.6 Hz), ³¹P NMR (C₆D₆) δ –10.1 (s, ¹J_{Pt-P} = 2007 Hz). Complex *cis*-**15** in C₆D₆ was stable and did not isomerize to the *trans* isomer, even at 70 °C. The complex *cis*-[PtCl₂(PMe₂Ph)₂] reacted with two equiv of MePh₂GeLi in THF at room temperature for 12 h. The concentration of the reaction mixture by evaporation of THF followed by crystallization from a 4:1 mixture of hexane and benzene gave yellow crystals with a composition of [(MePh₂Ge)₂Pt(PMe₂Ph)₂] (**16**). A NMR examination of the C₆D₆ solution of the yellow crystals **16** showed the presence of *cis* and *trans* isomers of bis-germylbis(tertiary phosphine)platinum in an approximately 60:40 ratio. The ¹H NMR of complex *cis*-**16** displayed the two methyl signals of the PMe₂Ph ligands at 0.70 ppm (deformed q, ²J_{H-P} = 8.2 Hz, ³J_{H-Pt} = 20.8 Hz) and the platinum bound methyl diphenylgermyl groups at 1.05 ppm (s, ³J_{H-Pt} = 18.6 Hz). The ³¹P NMR showed a singlet signal with satellites at –10.99 ppm (¹J_{Pt-P} = 2049 Hz). The *trans*-**16** isomer exhibited ¹H NMR spectrum of the germanium-bound methyl groups at 1.20 (vt, ²J_{H-P} = 6.0 Hz, ³J_{H-Pt} = 30.8 Hz) and the ³¹P NMR showed a singlet at –10.63 ppm with satellites (¹J_{Pt-P} = 2731 Hz). The smaller ¹J_{Pt-P} value in *cis*-**16** is consistent with the larger *trans* influence of the germanium ligand situated at the position *trans* to the phosphine ligand. From the *cis* and *trans* mixture, *cis*-**16** could be isolated as yellow crystals by recrystallization from a

5:1 mixture of hexane and benzene at room temperature for 3–5 days.

Complex *cis*-[PtCl₂(PMe₂Ph)₂] reacted with two equiv of Ph₃GeLi in THF under similar conditions to give yellow crystals of only one species [(Ph₃Ge)₂Pt(PMe₂Ph)₂] (**17**) having a *trans* geometry: ¹H NMR (C₆D₆) δ 1.24 (vt, ²J_{H-P} = 29.3 Hz, ³J_{H-Pt} = 6.6 Hz, PCH₃), ³¹P NMR (C₆D₆) δ –11.0 (s, ¹J_{Pt-P} = 2616 Hz). The complex *trans*-**17** in C₆D₆ was stable and did not isomerize to the *cis* isomer, even at 70 °C. Thus, the stable geometry for [(R₃Ge)₂Pt(PMe₂Ph)₂] complexes varies dependent on the number of phenyl groups on the germanium atom. The structures of *cis*-**15**, *cis*-**16**, and *trans*-**17** were established by NMR, IR, and MS spectra and by X-ray analysis. Although crystallized **16** has a *cis* geometry, the dissolution of *cis*-**16** in benzene caused a gradual isomerization to give a *cis/trans* equilibrium mixture.



The isomerization of *cis*-**16** to *trans*-**16** in C₆D₆ at various temperatures was followed by observing the change in the two methyl signals of the PMe₂Ph ligands by means of ¹H NMR spectroscopy. Figure 3 shows the decay of *cis*-**16** and the building up of *trans*-**16** at 45–60 °C. From the concentrations of the *cis* and *trans* isomers after equilibria were reached, the following thermodynamic parameters were obtained: ΔH⁰, 6.0 kJ mol^{–1} and ΔS⁰, 13.0 J mol^{–1} K^{–1}.

The assumption of the equilibration reaction (Eq. 7) following the first-order rate law leads to a kinetic expression, Eq. 8, where *K* is equal to *k*/*k*_{–1}.¹⁷

$$\ln \frac{(K+1)[cis-16]_t - [cis-16]_0}{K[cis-16]_0} = -\frac{K+1}{K} kt \quad (8)$$

The isomerization of *cis*-**16** exhibited first-order kinetics, as shown in Fig. 4. From the plots shown in Fig. 4, the following isomerization rate constants were estimated by using Eq. 8 at

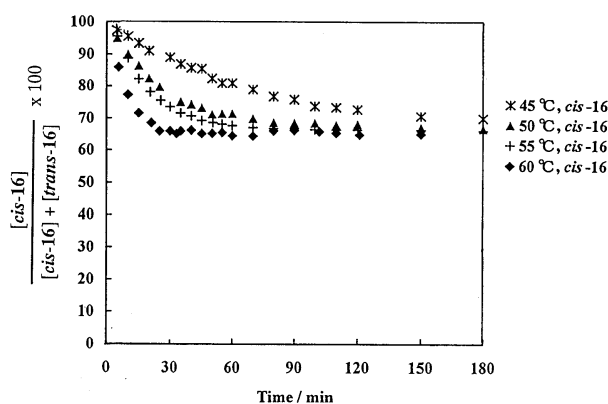


Fig. 3. The progress with time of isomerization of *cis*-bis(methyldiphenylgermyl)bis(dimethylphenylphosphine) platinum (**16**) to *trans*-**16** at 45–60 °C.

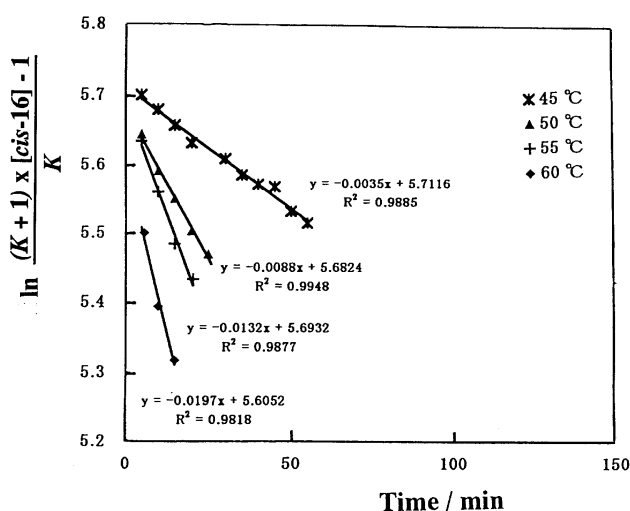


Fig. 4. The kinetics of isomerization of *cis*-bis-(methyldiphenylgermyl)bis(dimethylphenylphosphine) platinum (**16**).

the early stage of the reaction. The following first-order isomerization rate constants (k) at 45–60 °C were obtained from Fig. 4: $10^5 k/s = 1.89$ (45 °C), 4.89 (50 °C), 7.46 (55 °C), 11.4 (60 °C). From Arrhenius plots, the energy of activation in the isomerization of *cis*-**16** to *trans*-**16** was estimated to be 103 kJ mol⁻¹.

The addition of 0.3 equiv of PPhMe₂ per mol of *cis*-**16** caused a very rapid isomerization to give a *cis/trans* equilibrium mixture within a few minutes. These results suggest that the isomerization of *cis*-**16** to *trans*-**16** proceeds through an associative pathway involving a five-coordinate intermediate formed upon the association of the phosphine to *cis*-**16**.

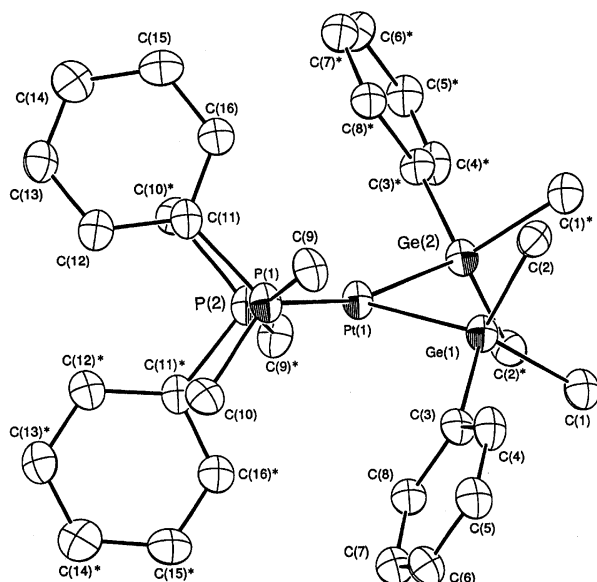


Fig. 5. Molecular structure of the *cis*-bis(dimethyldiphenylgermyl)bis(dimethylphenylphosphine)platinum (**15**) (30% probability thermal ellipsoids). Hydrogen atoms are omitted for clarity.

A similar behavior in the isomerization of *cis*-[Pt(GeClMe₂)₂(PEt₃)₂] to a *cis/trans* mixture in hydrocarbon solvents was observed by Tanaka and co-workers.¹⁸

The structures of bis(germyl)platinum(II) complexes, *cis*-**15**, *cis*-**16**, and *trans*-**17** were confirmed by X-ray diffraction analysis, as shown in Fig. 5–7. The crystallographic data are included in Table 4, and Tables 6 to 8 summarize selected bond lengths and angles in these complexes.

Both *cis*-**15** and *cis*-**16** have distorted square-planar *cis* geometries, with the dihedral angles between the planes composed of P(1)–Pt(1)–P(2) and Ge(1)–Pt(1)–Ge(2) being 21.6 and 37.8°, respectively. The deformation from planarity is con-

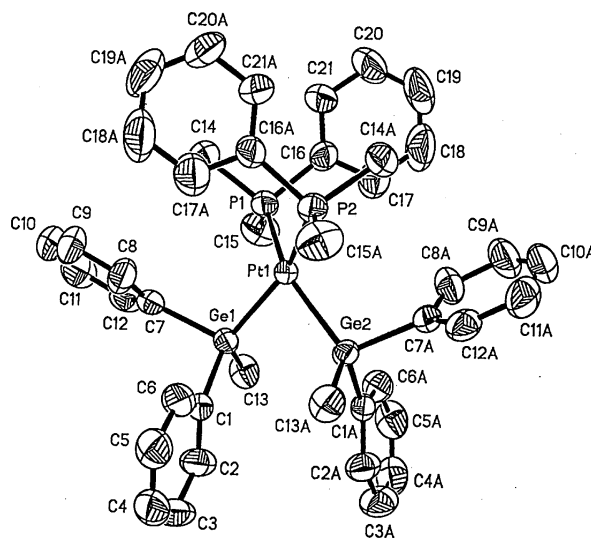


Fig. 6. Molecular structure of the *cis*-bis(methyldiphenylgermyl)bis(dimethylphenylphosphine)platinum (**16**) (30% probability thermal ellipsoids). Hydrogen atoms are omitted for clarity.

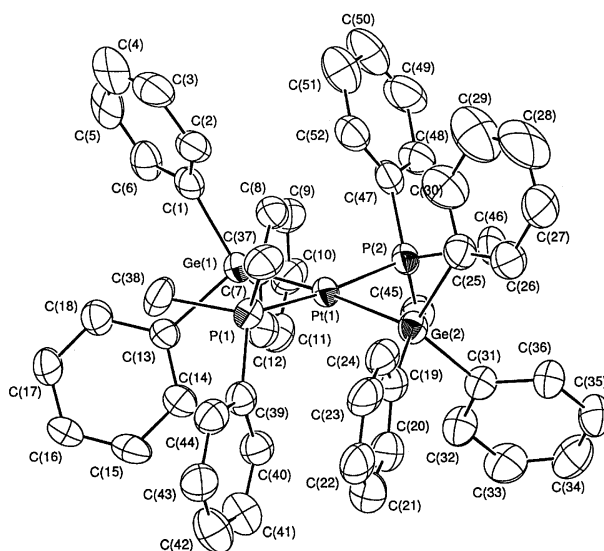


Fig. 7. Molecular structure of the *trans*-bis(triphenylgermyl)bis(dimethylphenylphosphine)platinum (**17**) (30% probability thermal ellipsoids). Hydrogen atoms are omitted for clarity.

Table 6. Selected Bond Distances (Å) and Angles (deg) for *cis*-**15**

Pt(1)–P(1)	2.334 (2)	Pt(1)–P(2)	2.334 (2)
Pt(1)–Ge(1)	2.4455 (9)	Pt(1)–Ge(2)	2.43455 (9)
Ge(1)–C(3)	1.973 (9)	Ge(1)–C(1)	1.987 (9)
Ge(1)–C(2)	1.993 (8)	P(1)–C(11)	1.811 (8)
P(1)–C(10)	1.812 (9)	P(1)–C(9)	1.835 (8)
P(1)–Pt(1)–P(2)	94.29 (10)	P(2)–Pt(1)–Ge(1)	164.14 (6)
P(1)–Pt(1)–Ge(1)	92.27 (6)	P(2)–Pt(1)–Ge(2)	92.28 (6)
P(1)–Pt(1)–Ge(2)	164.15 (6)	Ge(1)–Pt(1)–Ge(2)	85.15 (4)
C(3)–Ge(1)–C(1)	96.4 (3)	C(3)–Ge(1)–C(2)	106.1 (3)
C(1)–Ge(1)–C(2)	104.4 (4)	C(3)–Ge(1)–Pt(1)	111.8 (2)
C(1)–Ge(1)–Pt(1)	117.6 (3)	C(1)–Ge(1)–Pt(1)	118.0 (2)
C(11)–P(1)–C(10)	104.7 (4)	C(11)–P(1)–C(9)	98.8 (4)
C(10)–P(1)–C(9)	101.6 (4)	C(11)–P(1)–Pt(1)	108.7 (3)
C(10)–P(1)–Pt(1)	122.7 (3)	C(9)–P(1)–Pt(1)	117.3 (3)

Table 7. Selected Bond Distances (Å) and Angles (deg) for *cis*-**16**

Pt(1)–P(1)	2.318 (2)	Pt(1)–P(2)	2.318 (2)
Pt(1)–Ge(1)	2.4387 (9)	Pt(1)–Ge(2)	2.4387 (9)
Ge(1)–C(13)	1.956 (8)	Ge(1)–C(1)	1.977 (7)
Ge(1)–C(7)	2.004 (8)	P(1)–C(15)	1.795 (10)
P(1)–C(16)	1.822 (9)	P(1)–C(14)	1.821 (9)
P(1)–Pt(1)–P(2)	97.02 (11)	P(2)–Pt(1)–Ge(1)	153.99 (6)
P(1)–Pt(1)–Ge(1)	92.86 (6)	P(2)–Pt(1)–Ge(2)	92.86 (6)
P(1)–Pt(1)–Ge(2)	153.98 (6)	Ge(1)–Pt(1)–Ge(2)	88.56 (4)
C(13)–Ge(1)–C(1)	105.0 (4)	C(13)–Ge(1)–C(7)	105.5 (4)
C(1)–Ge(1)–C(7)	100.9 (3)	C(13)–Ge(1)–Pt(1)	124.7 (3)
C(1)–Ge(1)–Pt(1)	113.0 (2)	C(7)–Ge(1)–Pt(1)	104.8 (2)
C(15)–P(1)–C(16)	100.4 (5)	C(15)–P(1)–C(14)	100.3 (5)
C(16)–P(1)–C(14)	103.9 (4)	C(15)–P(1)–Pt(1)	115.9 (4)
C(16)–P(1)–Pt(1)	109.0 (3)	C(14)–P(1)–Pt(1)	124.3 (3)
C(2)–C(1)–Ge(1)	123.6 (6)	C(6)–C(1)–Ge(1)	120.0 (6)

Table 8. Selected Bond Distances (Å) and Angles (deg) for *trans*-**17**

Pt(1)–P(1)	2.3011 (9)	Pt(1)–P(2)	2.3120 (9)
Pt(1)–Ge(1)	2.5207 (3)	Pt(1)–Ge(2)	2.5239 (4)
Ge(1)–C(13)	1.985 (4)	Ge(1)–C(1)	1.985 (3)
Ge(1)–C(7)	1.999 (3)	Ge(2)–C(31)	1.990 (4)
Ge(2)–C(25)	1.991 (4)	P(1)–C(37)	1.817 (4)
P(1)–C(39)	1.813 (4)	P(2)–C(45)	1.823 (4)
P(2)–C(47)	1.831 (4)		
P(1)–Pt(1)–P(2)	173.17 (3)	P(1)–Pt(1)–Ge(1)	92.24 (2)
P(2)–Pt(1)–Ge(1)	89.39 (2)	P(1)–Pt(1)–Ge(2)	87.51 (2)
P(2)–Pt(1)–Ge(2)	91.44 (2)	Ge(1)–Pt(1)–Ge(2)	175.075 (12)
C(13)–Ge(1)–C(1)	103.39 (15)	C(13)–Ge(1)–C(7)	98.91 (14)
C(1)–Ge(1)–C(7)	103.51 (15)	C(13)–Ge(1)–Pt(1)	112.13 (10)
C(1)–Ge(1)–Pt(1)	108.3 (2)	C(7)–Ge(1)–Pt(1)	120.49 (9)
C(39)–P(1)–C(37)	100.4 (5)	C(39)–P(1)–C(38)	97.83 (19)
C(37)–P(1)–C(38)	98.7 (2)	C(39)–P(1)–Pt(1)	116.71 (12)
C(37)–P(1)–Pt(1)	109.96 (15)	C(38)–P(1)–Pt(1)	123.14 (13)

sidered to be caused by a steric repulsion between the bulky ligands. The two germyl groups are bound to the platinum center in positions *cis* to each other, with the bite angle, Ge(1)–Pt(1)–Ge(2), being 88.6° for *cis*-**15** and 85.2° for *cis*-**16**. On the other hand, the complex *trans*-**17** has a somewhat distorted square-planar geometry with a dihedral angle of 8.1° between

the planes composed of P(1)–Pt–Ge(1) and P(2)–Pt–Ge(2). The four bond angles of Ge–Pt–P are close to 90°, as shown in Table 9. The bond lengths of Pt–Ge (2.5207(3) and 2.5239(4) Å) of *trans*-**17** are longer than those of *cis*-**15** and *cis*-**16** (2.4455(9) and 2.4410(7) Å, respectively). On the contrary, the Pt–P lengths of *trans*-**17** (2.3011(9) and 2.3120(9) Å) are shorter than those of *cis*-**15** and *cis*-**16** (2.334(2) and 2.324(1) Å, respectively). These results indicate the greater *trans* influence of the germyl ligand than the phosphine ligand in support of the NMR observation.

A distorted square-planar structure with a dihedral angle of 28.5° has been reported for the *cis*-bis(chlorodimethylgermyl)platinum complex prepared by the oxidative addition of ClMe₂GeGeMe₂Cl (**1b**) to [Pt(PEt₃)₃].¹⁸ The structures of *cis*-bis(stannyl)bis(phosphine)platinum with the dihedral angle between the PtP₂ and PtSn₂ planes being 16.8° and *cis*-bis(silyl)bis(phosphine)platinum (dihedral angle 38.1°) are also distinctly distorted from planarity.¹⁹ The distortion from planarity has been ascribed to steric congestion.

For a comparison of the reactivities and structures of the bis(germyl)platinum complexes, bis(methyldiphenylgermyl)platinum complexes **18** and **19** having chelate diphosphines, dppe (dppe = 1,2-bis(diphenylphosphino)ethane), and dmpe (dmpe = 1,2-bis(dimethylphosphino)ethane), were prepared in a way similar to the synthesis of **15**–**17** by a treatment of [PtCl₂(dppe)] and [PtCl₂(dmpe)], respectively, with methyldiphenylgermyllithium. The molecular structures of these bis(germyl)platinum complexes with the chelate ligands are shown in Figs. 8 and 9. The crystallographic data are included in Table 4, and Tables 9 and 10 summarize selected bond lengths and angles of the chelated complexes, **18** and **19**.

Complex **18** has a slightly distorted square-planar geometry with the dihedral angle between the P(1)–Pt–P(2) and Ge(1)–Pt–Ge(2) being 7.58°, whereas **19** showed an undistorted square planar geometry.

The thermolysis behavior of these bis(germyl)platinum complexes having two monodentate ligands (**16**) and chelating ligands (**18** and **19**) have been examined in sealed NMR tubes. The thermolysis of **16** in the absence of added triphenylphos-

Table 9. Selected Bond Distances (Å) and Angles (deg) for **18**

Pt(1)–P(1)	2.294 (3)	Pt(1)–P(2)	2.320 (3)
Pt(1)–Ge(1)	2.4616 (12)	Pt(1)–Ge(2)	2.4729 (12)
Ge(1)–C(13)	1.994 (10)	Ge(1)–C(7)	2.000 (6)
Ge(1)–C(1)	2.009 (6)	Ge(2)–C(26)	1.954 (12)
Ge(2)–C(20)	1.989 (7)	Ge(2)–C(14)	1.994 (6)
P(1)–C(33)	1.826 (6)	P(1)–C(39)	1.839 (11)
P(1)–C(27)	1.843 (6)	P(2)–C(47)	1.809 (6)
P(2)–C(41)	1.813 (6)	P(2)–C(40)	1.818 (14)
P(1)–Pt(1)–P(2)	85.20 (10)	P(1)–Pt(1)–Ge(1)	176.46 (8)
P(2)–Pt(1)–Ge(1)	94.78 (8)	P(1)–Pt(1)–Ge(2)	95.24 (7)
P(2)–Pt(1)–Ge(2)	173.60 (8)	Ge(1)–Pt(1)–Ge(2)	85.18 (4)
C(13)–Ge(1)–C(7)	106.7 (4)	C(13)–Ge(1)–C(1)	99.1 (4)
C(7)–Ge(1)–C(1)	102.1 (4)	C(13)–Ge(1)–Pt(1)	117.0 (4)
C(7)–Ge(1)–Pt(1)	111.1 (2)	C(1)–Ge(1)–Pt(1)	119.1 (2)
C(26)–Ge(2)–C(20)	97.2 (5)	C(26)–Ge(2)–C(14)	108.2 (5)
C(26)–Ge(2)–C(14)	105.4 (4)	C(26)–Ge(2)–Pt(1)	117.9 (4)
C(20)–Ge(2)–Pt(1)	120.1 (3)	C(14)–Ge(2)–Pt(1)	106.9 (2)

fraction analysis. The ^{31}P NMR of complex **21** exhibited two sets of doublets ($^2J_{\text{P-P}} = 18 \text{ Hz}$) at $\delta -15.0$ and -18.7 with $^1J_{\text{Pt-P}}$ values of 1811 and 1819 Hz, respectively.

The addition of 0.5–5.0 equiv of PMe_2Ph hindered the alkyne insertion and caused a lowering in the yield of *cis*-**21** from 100% down to 30% in the reaction of **16** with phenylacetylene performed at 65°C and for 1.5 h. A similar inhibition effect of PMe_2Ph in the reaction of bis(silyl)bis(phosphine)platinum complex with phenylacetylene **2a** was observed by Ozawa and co-workers.^{20–23}

Figure 10 shows the molecular structure of *cis*-**21**. The crystallographic data are included in Table 4 and Table 11. The platinum atom in *cis*-**21** has a square-planar geometry, the sum of the four angles about platinum being 360.2° . The C(1)–C(2) distance (1.351 (13) Å) is in the typical range of a carbon-carbon double bond. The *Z* arrangement of the platinum and germanium atoms bound to the C=C double bond clearly shows the occurrence of the *cis* insertion of phenylacetylene **2a** into one of the two Pt–Ge bonds.

The thermolysis of *cis*-**21** was carried out to confirm the intermediacy of the *cis*-germyl(germylvinyl)platinum complex **21** in the reactions of bis(germyl)platinum complex **16** with phenylacetylene **2a**. Heating of *cis*-**21** in C_6D_6 at 80°C for 8 h led to the decomposition of *cis*-**21** (45%) with the formation of *Z*-1,2-bis(diphenylmethylgermyl)-1-phenylethene **20** in 40% yield. Interestingly, the addition of 5 equiv of PMe_2Ph per **21** completely suppressed the thermolysis of **21** under the same conditions (80°C and 8 h) with **21** recovered.

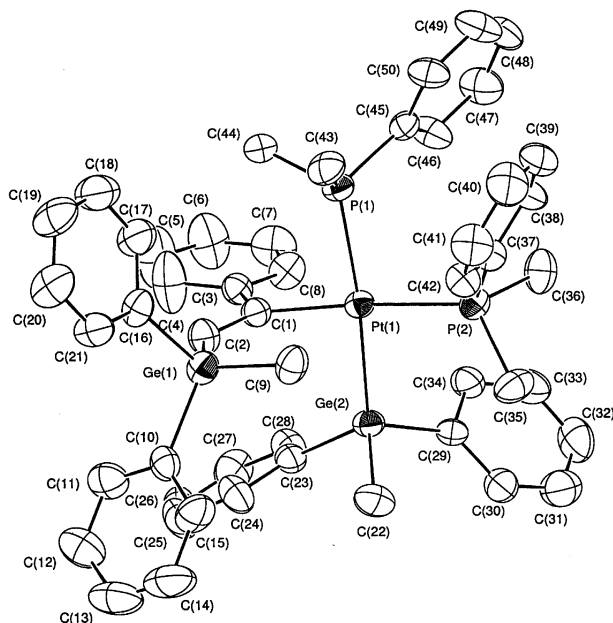
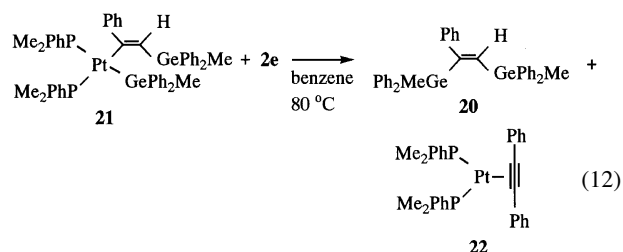


Fig. 10. Molecular structure of the methyl-diphenylgermyl(1-phenyl-2-methyldiphenylgermylethenyl)-bis(dimethylphenylphosphine)platinum (**21**) (30% probability thermal ellipsoids). Hydrogen atoms are omitted for clarity.

Table 11. Selected Bond Distances (Å) and Angles (deg) for **21**

Pt(1)–C(1)	2.108 (9)	Pt(1)–P(2)	2.315 (3)
Pt(1)–P(1)	2.353 (3)	Pt(1)–Ge(2)	2.4682 (11)
Ge(1)–C(2)	1.927 (10)	Ge(1)–C(10)	1.968 (12)
Ge(1)–C(9)	1.976 (12)	C(1)–C(2)	1.351 (13)
P(1)–C(44)	1.815 (12)	P(1)–C(45)	1.829 (10)
C(1)–Pt(1)–P(2)	175.8 (3)	C(1)–Pt(1)–P(1)	88.3 (3)
P(2)–Pt(1)–P(1)	94.99 (10)	C(1)–Pt(1)–Ge(2)	84.2 (3)
P(2)–Pt(1)–Ge(2)	92.69 (7)	P(1)–Pt(1)–Ge(2)	171.04 (7)
C(2)–Ge(1)–C(10)	110.3 (5)	C(2)–Ge(1)–C(16)	107.3 (4)
C(2)–Ge(1)–C(9)	116.4 (5)	C(10)–Ge(1)–C(16)	108.2 (5)
C(10)–Ge(1)–C(9)	108.3 (6)	C(16)–Ge(1)–C(9)	106.0 (5)
C(22)–Ge(2)–C(29)	106.3 (5)	C(22)–Ge(2)–C(23)	101.3 (6)
C(29)–Ge(2)–C(23)	103.6 (4)	C(22)–Ge(2)–Pt(1)	116.7 (4)
C(29)–Ge(2)–Pt(1)	109.9 (3)	C(23)–Ge(2)–Pt(1)	117.7 (3)
C(44)–P(1)–C(45)	100.9 (5)	C(44)–P(1)–C(43)	102.2 (6)
C(45)–P(1)–C(43)	103.9 (6)	C(44)–P(1)–Pt(1)	115.7 (4)
C(45)–P(1)–Pt(1)	114.9 (4)	C(43)–P(1)–Pt(1)	117.0 (4)
C(2)–C(1)–C(3)	119.9 (9)	C(2)–C(1)–Pt(1)	123.5 (8)
C(3)–C(1)–Pt(1)	116.6 (7)	C(1)–C(2)–Ge(1)	132.4 (8)

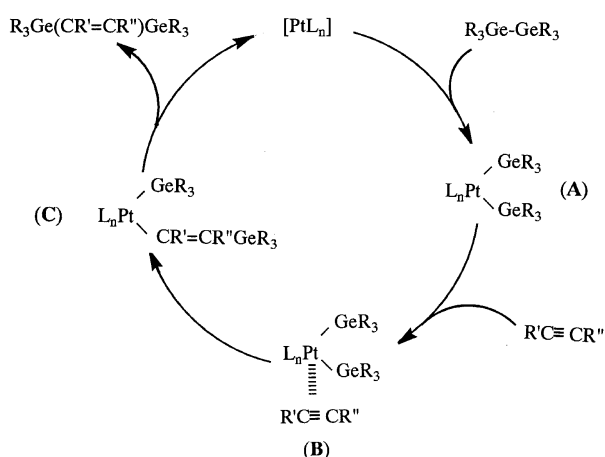


On the other hand, the addition of 5 equiv of diphenylacetylene **2e** per **21** under similar conditions, accelerated the reaction to have **21** cleanly liberate bis(dimethylphenylphosphine)(diphenylacetylene)platinum, $[\text{Pt}(\text{PhC}\equiv\text{CPh})(\text{PMe}_2\text{Ph})_2]$ (**22**) and **20** in quantitative yields (Eq. 12).

Discussion

Mechanism of the Platinum-catalyzed Bis-germylation of Alkynes. As a mechanism for the bis-germylation of alkynes with a digermane, we propose a catalytic cycle (Scheme 1) driven by a $\text{Pt}(0)$ species generated from a catalyst precursor. The catalytic cycle is composed of (a) the oxidative addition of digermane to the platinum species to form a bis(germyl)platinum intermediate (**A**), (b) the coordination of an alkyne to **A** to form an alkyne-coordinated bis-germylation complex (**B**), (c) the insertion of the coordinated alkyne into one of the Pt–Ge bonds to form the insertion product (**C**) having the germlyl and vinyl ligands, (d) the reductive elimination of the bis-germylation product of the alkyne with the regeneration of the active platinum species that further carries the catalytic cycle.

Since the zero-valent complex $[\text{Pt}(\text{dba})_2]$ was found to be effective in the bis-germylation of the hexamethyldigermane **1a**, a zero-valent platinum complex may be playing the main role in the catalysis. The fact that the PPh_3 -coordinated zero-valent complex $[\text{Pt}(\text{PPh}_3)_4]$ proved to be ineffective may be due to an unfavorable effect of the coordinated tertiary phosphine ligands. Why $[\text{Pt}(\text{acac})_2]$ serves as the best catalyst among the platinum complexes examined remains to be clarified. How-



ever, it is known that the O-bonded acetylacetonato ligand in $[\text{Pt}(\text{acac})_2]$ can be converted into a C-bonded acetylacetonato complex.^{24–28} This conversion may further lead to Pt–C bond fission to yield a catalytically active Pt(0) species.

For obtaining further information we attempted the detection of an intermediate species involved in the process by a NMR examination of the reaction system, but without success. However, since dichlorotetramethyldigermene is known to readily oxidatively add to Pt(0) complexes to give a bis-germylation product,^{18,29} it is probable that the hexamethyldigermene also oxidatively adds, although less readily, to a Pt(0) species to give a bis(germyl)platinum complex.

The formation of the bis-germylation product **20** of phenylacetylene upon a treatment of *cis*-**16** with phenylacetylene at 65 °C (Eq. 10) lends support to the involvement of the bis(germyl)platinum complex in the catalytic bis-germylation of alkynes, as proposed in Scheme 1. For examining whether the isolated bis(germyl)platinum complex **16** in fact acts as a catalyst for the bis-germylation of phenylacetylene, hexamethyldigermene **1a** was treated with phenylacetylene **2a** in the presence of **16** at 65 °C for 24 h. The bis-germylation product of phenylacetylene **2a** was obtained in 2% yield. The low yield may be partly due to an interference effect of the phosphine ligand, which was used to stabilize the bis(germyl)platinum complex in the oxidative addition of the digermene to a Pt(0) species.

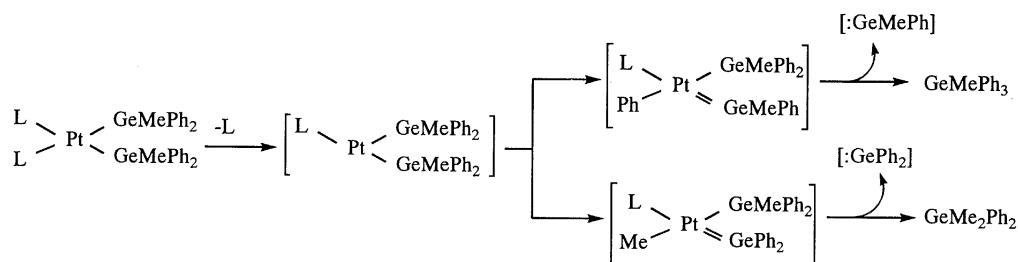
The structures of the bis(germyl)platinum complexes (*cis*-**15** and *cis*-**16**) having two dimethylphenylphosphine ligands and chelating diphosphine ligands (**18** and **19**) deserve comments. Complexes **15** and **16**, having dimethylphenylgermyl

and methylphenylgermyl groups, respectively, and the common dimethylphenylphosphine ligands, have considerably distorted *cis* square planar configurations with the dihedral angles between the P(1)–Pt–P(2) and Ge(1)–Pt–Ge(2) planes of 21.6° and 37.8°, respectively. They also have P–Pt–P bite angles 94.2° for *cis*-**15** and 97.2° for *cis*-**16**, both larger than 90°. On the other hand, complex **17**, having sterically more demanding triphenylgermyl groups, has a *trans* square-planar geometry with some distortion, as reflected by the dihedral angle of 8.1° between the P(1)–Pt–Ge(1) and P(2)–Pt–Ge(2) planes. The expulsion between the two bulky triphenylgermyl groups in the *cis* configuration is considered to be released by taking the *trans* configuration in **17**.

The *cis* to *trans* isomerization observed for the *cis*-**16** dissolved in benzene along with an entropy increase may be due to the effect of releasing the repulsion in the *cis* form by isomerization into the *trans* form. In the dppe-coordinated methylphenylgermylplatinum complex **18**, a dihedral angle of 7.58° between the P(1)–Pt–P(2) and Ge(1)–Pt–Ge(2) planes, reflecting the distortion from planarity, is smaller than in the monophosphine-coordinated complexes, whereas in the dmpe-coordinated complex **19** no distortion is observed. Complexes having diphosphine ligands, **18** and **19**, show smaller bite angles of P(1)–Pt–P(2) of 85.12° and 85.1°, respectively, causing a release in the steric repulsion in the chelated complexes. The less bulky dmpe ligand may exert less strain on the complex, giving the undistorted square-planar geometry for **19**.

It is noted that the thermolysis of *cis*-**16** liberated 1,2-dimethyl-1,1,2,2-tetraphenyldigermene as the main thermolysis product together with minor amounts of monogermenes and germanium oligomers (Eq. 9), and the addition of triphenylphosphine to the system cleanly gave the digermene. This result suggests the involvement of a coordinatively unsaturated species in the thermolysis of **16** in extrusion of the germylene unit. Possible processes to liberate the germylene unit are given in Scheme 2.

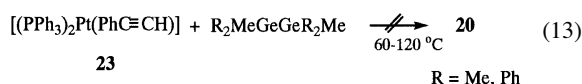
The thermolysis of *cis*-**16** in the absence of the added triphenylphosphine may proceed with the liberation of one of the two dimethylphenylphosphine ligands in solution to give a coordinatively unsaturated, three coordinate bis-germyl intermediate. The α -elimination of the phenyl or methyl group attached to the germanium by platinum may yield a phenyl- or methylplatinum complex having a germylene-platinum bonding. The reductive elimination of the methyl or phenyl group with the remaining GeMePh₂ ligand produces monogermene,



MePh_3Ge or $\text{Me}_2\text{Ph}_2\text{Ge}$, and the rest of the germylene unit may be converted into oligomers. A similar mechanism involving the α -elimination of the chlorine atom in the chlorodimethylgermanium complex has been proposed by Tanaka and co-workers.¹⁸

The regioselective formation of the germyl(germylvinyl)platinum complex **21** upon the treatment of *cis*-**16** with phenylacetylene supports on involvement of possible intermediates corresponding to **B** and **C** in Scheme 1. The addition of dimethylphenylphosphine to the system retarded the insertion of phenylacetylene into one of the two Ge–Pt bonds in *cis*-**16**.

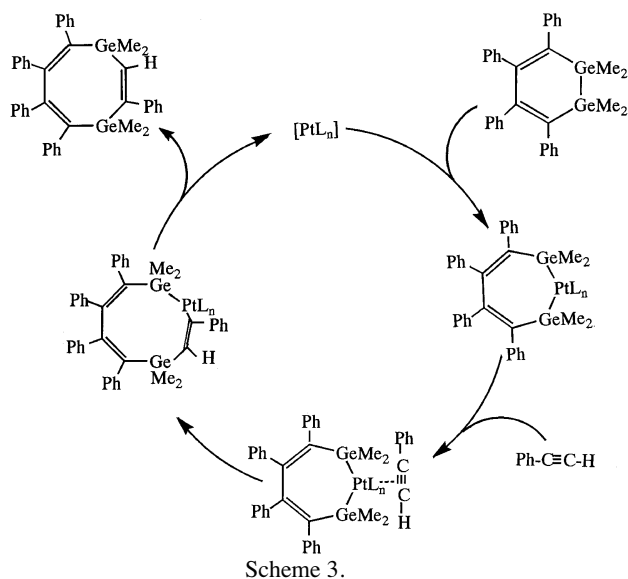
As an alternative route to give **C**, a process involving a prior coordination of the alkyne to a Pt(0) species followed by the oxidative addition of digermene is conceivable. However, a phenylacetylene-coordinated triphenylphosphine complex **23** did not react with $\text{MePh}_2\text{GeGePh}_2\text{Me}$ or $\text{Me}_3\text{GeGeMe}_3$ upon heating at 60–120 °C for 16 h, and no bis-germylation product of phenylacetylene was produced.



Presumably, the coordination of phenylacetylene to the Pt(0) complex through a π bond makes the platinum complex less electron-rich by back-donation, and renders it less susceptible to an oxidative addition reaction with the digermene.

The platinum-catalyzed formation of the eight-membered cyclodigermaoctatriene **13** in the reaction of **12** and phenylacetylene **2a** (Eq. 6) can be also accounted for by assuming the oxidative addition of **12** to a Pt(0) species with the Ge–Ge bond cleavage, followed by the alkyne insertion and reductive elimination, as shown in Scheme 3.

The platinum-catalyzed formation of **3h**, the bis-germylation product of phenylacetylene **2a** in the reaction of 1,2-dichloro-1,2-tetramethyldigermene **1b** with **2a**, as shown in Eq. 2, can also be accounted for by a mechanism similar to Scheme 1 involving the formation of a bis(germyl)platinum intermediate. For explaining the formation of the monogerm-



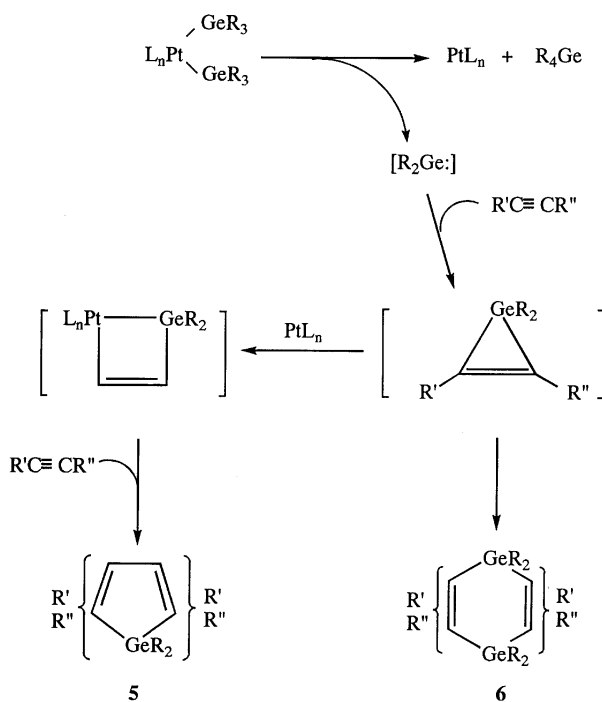
lated products, **4** and **4'**, as well as the germole **5** and 1,4-diger-macyclohexa-2,5-diene **6**, the elimination of a germylene unit from the bis(germyl)platinum species is required. Scheme 4 provides possible courses to account for the formation of the by-products in Eq. 2.

In this Scheme the expulsion of a germylene unit from a bis(germyl)platinum intermediate is assumed along with the liberation of a monogermene by the reductive elimination of trialkylgermyl and alkyl groups, as proposed in Scheme 2. The liberated germylene unit may be trapped by free alkyne to form a germacyclopentene, which may interact with a Pt(0) species and further with alkyne to give the germole **5**, while the 1,4-diger-macyclohexadiene **6** may be produced by dimerization of the germacyclopentene.¹⁵

A similar oxidative-addition process involving the Ge–Ge bond cleavage followed by germylene unit expulsion may be also invoked to account for the formation of **6a** and **6b** in the platinum-catalyzed reaction of cyclohexagermane **7** with phenylacetylene **2a** (Eq. 3).

Conclusion

Platinum complexes were found to act as catalysts for the digermylation of alkynes with digermanes as well as with cyclo-germane oligomers. Bis(germyl)platinum (II) complexes with tertiary phosphine ligands assumed as the intermediate in the catalytic cycle were prepared as models of the reaction intermediates and unequivocally characterized by spectroscopic means and X-ray crystallography. Thermolysis studies of the bis(germyl)platinum complexes revealed the simple reductive elimination course of the digermanes as well as the α -elimination course with the extrusion of a germylene unit. The bis(germyl)platinum complexes reacted with phenylacetylene under mild conditions to give the corresponding insertion complexes,



Scheme 4.

germyl(germylvinyl)platinum species. The thermolysis the germyl(germylvinyl)platinum complex gave the bis-germylation product of the alkyne. The mechanism for the catalytic digermylation of alkynes comprises alkyne insertion into the germylplatinum bond, followed by the reductive elimination of the germyl and germylvinyl ligands to liberate the digermylated alkyne.

Exeperimental

General Methods. The NMR spectra were obtained on a Varian Unity Inova 400 MHz NMR spectrometer. The GC-MS spectra were measured on a JEOL JMS-DX 303 mass spectrometer. The UV and UV-vis spectra were recorded with a Shimadzu UV 2200 spectrometer. The infrared spectra were recorded with a Shimadzu FT IR 4200 spectrometer. Gas chromatography was performed on a Shimadzu GC 8A with 1 m 20% SE30 column. Liquid chromatography was performed on a Twinkle with an Asahipak GS 310 column. X-ray crystallographic data and diffraction intensities were collected on a Rigaku AFC6/S diffractometer for **10**, a Siemens SMART diffractometer for *cis*-**16**, Rigaku AFC-7R diffractometer for **18** and **19**, and a MacScience DIP2030 diffractometer for *cis*-**15**, *trans*-**17**, and *cis*-**21** utilizing graphite-monochromated Mo K α ($\lambda = 0.71073$ Å) radiation. The structures were solved by direct methods using the program system MULTAN 78 for **10**, and SHELXL-97 for *cis*-**15**, *cis*-**16**, **18**, and **19**, and SIR-92 for *trans*-**17** and *cis*-**21**. Calculations were carried out by a FACOM M-780 with UNICS III for **10**. A refinement was performed by full-matrix least-square using program SHELXL97 for *cis*-**16**, **18**, and **19**, and a SILICON Graphics O₂ with maXus for *cis*-**15**, *trans*-**17**, and *cis*-**21**. Toluene, benzene, hexane, and other solvents were purified and dried as reported in the literature.

Materials. Hexamethyldigermane,³⁰ 1,2-dichloro-1,1,2,2-tetramethyldigermane,³¹ 1,1,2,2-tetramethyl-1,2-diphenyldigermane,³¹ dodecamethylcyclohexagermane,³² octaisopropylcyclo-tetragermane,³³ 1,1,2,2-tetramethyl-3,4,5,6-tetraphenyl-1,2-digermacyclohexa-3,5-diene,³⁴ 1,1,2,2-tetramethyl-3,4,5,6-tetraphenyl-1,2-disilacyclohexa-3,5-diene,³⁵ 1,1,2,2-tetraethyl-3,4,5,6-tetraphenyl-1,2-digermacyclohexa-3,5-diene,³⁵ 1,1,2,2-tetraethyl-3,4,5,6-tetraphenyl-1,2-disilacyclohexa-3,5-diene,³⁵ 1,1,2,2-tetraethyl-3,4,5,6-tetraphenyl-1-germa-2-silacyclohexa-3,5-diene,³⁵ 1,1-dimethyl-2,5-diphenyl-1-germacyclohexa-2,4-diene,³⁶ 1,1-dimethyl-2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-diene,³⁷ 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopenta-2,4-diene,³⁸ [Pt(acac)]₂,³⁹ [Pt(dba)]₂,⁴⁰ bis(triphenylphosphine)(styrene)platinum,⁴¹ and bis(dimethylphenylphosphine)(diphenylacetylene)platinum²² were prepared as reported in the literature. Alkynes and other platinum complexes were commercially available.

Preparation of *E*-1-phenyl-1,2-bis(trimethylgermyl)ethene. A mixture of chlorotrimethylgermane (7.9 g, 52 mmol), Mg metal (0.46 g, 19 mmol), and HMPA (15 ml) was heated at 120 °C. To this solution was added phenylacetylene (2.6 g, 26 mmol). After refluxing at 130 °C for 48 h, the reaction mixture was extracted with hexane. After the solvent was evaporated, the residue was purified by preparative column chromatography (silica gel, hexane). Pure *E*-1-phenyl-1,2-bis(trimethylgermyl)ethene was obtained in 15% yield. ¹H NMR (CDCl₃) δ -0.02 (s, 3H), 0.26 (s, 3H), 6.33 (s, 1H), 6.95–7.31 (m, 5H). ¹³C NMR (CDCl₃) δ -2.03, -0.21, 125.58, 126.93, 127.64, 141.90, 145.36, 164.69. IR (neat) 706, 824, 1235, 2972 cm⁻¹. GC-MS *m/z* (relative intensity) 338 (4, M⁺), 323 (20), 221 (9), 181 (8), 119 (100), 89 (9).

Preparation of *cis*-Bis(dimethylphenylgermyl)bis(dimethyl-

phenylphosphine)platinum(II) (15). To a solution of dichlorobis(dimethylphenylphosphine)platinum (1.30 g, 2.76 mmol) in THF (10 ml) was added a THF solution (4 ml) of dimethylphenylgermyllithium (5.70 mmol) at room temperature. The mixture was stirred at room temperature for 12 h and the solution was concentrated to ca. 5 ml. After benzene (10 ml) was slowly added, the organic layer was filtered through a filter-paper. When the organic layer was allowed to stand at room temperature for 1 day, *cis*-[(Me₂PhGe)₂Pt(PMe₂Ph)₂] (**15**) (0.15 g, 0.19 mmol, 6.7%) was formed as yellow crystals. Recrystallization from benzene/hexane (1/5) at room temperature afforded pure *cis*-**15**: ¹H NMR (C₆D₆) δ 0.73 (d with two satellites, ²J_{H-P} = 8.1 Hz, ³J_{H-Pt} = 29.9 Hz, 6H), 1.05 (s, with two satellites, ³J_{H-Pt} = 17.6 Hz, 6H), 6.86–7.90 (m, 30H). ³¹P NMR (C₆D₆) δ -10.1 (¹J_{Pt-P} = 2007 Hz). Found: C, 46.46; H, 5.50%. Calcd for C₃₂H₄₄Ge₂P₂Pt: C, 46.26; H, 5.34%.

Preparation of *cis*-Bis(methyldiphenylgermyl)bis(dimethylphenylphosphine)platinum(II) (16). To a solution of dichlorobis(dimethylphenylphosphine)platinum (0.33 g, 0.61 mmol) in THF (5 ml) was added a THF solution (4 ml) of methyldiphenylgermyllithium (1.83 mmol) at room temperature. The mixture was stirred at room temperature for 12 h, and the solution was concentrated to ca. 5 ml. After benzene (10 ml) was slowly added, the organic layer was filtered through filter-paper. When the organic layer was allowed to stand at room temperature for 1 day, *cis*- and *trans*-[(MePh₂Ge)₂Pt(PMe₂Ph)₂] (**16**) (0.36 g, 0.38 mmol, 62.0%) were formed as yellow crystals. Recrystallization from benzene/hexane (1/5) at room temperature afforded pure *cis*-**16**: ¹H NMR (C₆D₆) δ 0.70 (d with two satellites, ²J_{H-P} = 8.2 Hz, ³J_{H-Pt} = 20.8 Hz, 12H), 1.05 (s, with two satellites, ³J_{H-Pt} = 18.6 Hz, 6H), 6.91–6.95 (m, 30H). ³¹P NMR (C₆D₆) δ -10.99 (¹J_{Pt-P} = 2049 Hz), ¹⁹⁵Pt NMR (C₆D₆) δ 5274.48 (t, *J* = 1998.4 Hz). Found: C, 52.62; H, 5.27%. Calcd for C₄₂H₄₈Ge₂P₂Pt: C, 52.82; H, 5.07%. *trans*-**16**: ¹H NMR (C₆D₆) δ 0.48 (d with two satellites, ³J_{H-Pt} = 9.3 Hz, 6 H), 1.21 (vt, with two satellites, ²J_{H-P} = 6.0 Hz, ³J_{H-Pt} = 30.8 Hz, 12 H), 7.01–7.72 (m, 30H). ³¹P NMR (C₆D₆) δ -10.63 (¹J_{Pt-P} = 2731 Hz).

Preparation of *trans*-Bis(triphenylgermyl)bis(dimethylphenylphosphine)platinum(II) (17). To a solution of dichlorobis(dimethylphenylphosphine)platinum (0.23 g, 0.42 mmol) in THF (5 ml) was added a THF solution (4 ml) of triphenylgermyllithium (2.06 mmol) at room temperature. The mixture was stirred at room temperature for 12 h, and the solution was concentrated to ca. 5 ml. After benzene (10 ml) was slowly added, the organic layer was filtered through filter-paper. When the organic layer was allowed to stand at room temperature for 2 days, *trans*-[(Ph₃Ge)₂Pt(PMe₂Ph)₂] (**17**) (0.01 g, 0.01 mmol, 2.0%) was formed as yellow crystals. Recrystallization from benzene/hexane (1/5) at room temperature afforded pure *trans*-**17**: ¹H NMR (C₆D₆) δ 1.24 (vt with two satellites, ²J_{H-P} = 29.3 Hz, ³J_{H-Pt} = 6.6 Hz, 12 H), 7.04–7.63 (m, 48 H). ³¹P NMR (C₆D₆) δ -11.0 (¹J_{Pt-P} = 2616 Hz). Found: C, 52.92; H, 4.90%. Calcd for C₅₂H₅₂Ge₂P₂Pt: C, 57.88; H, 4.86%.

Preparation of *cis*-Bis(methyldiphenylgermyl)[1,2-bis(dimethylphosphino)ethane]platinum (18). To a solution of dichloro[1,2-bis(dimethylphosphino)ethane]platinum (0.80 g, 1.20 mmol) in THF (10 ml) was added a THF solution (8 ml) of methyldiphenylgermyllithium (4.0 mmol) at room temperature. The mixture was stirred at room temperature for 12 h, and the solution was concentrated to ca. 5 ml. After benzene (30 ml) was slowly added, the organic was filtered through a filter-paper. Upon allowing the organic layer to stand at room temperature for 1 day, [(MePh₂Ge)₂Pt(dppe)] (**18**) (0.60 g, 0.58 mmol, 48.3%) was

formed as yellow crystals. Recrystallization from benzene/hexane (1/5) at room temperature afforded pure **18**: mp 180–181 °C. ^1H NMR (C_6D_6) δ 0.89 (d with two satellites, $^2J_{\text{H-P}} = 1.83$ Hz, $^3J_{\text{H-Pt}} = 16.8$ Hz, 6H), 1.44–1.60 (m, 4H), 6.93–7.48 (m, 40H). ^{13}C NMR (C_6D_6) δ 6.53, 32.34–32.61, 126.25, 127.01, 128.43, 130.41, 131.17, 133.57, 136.16, 151.03. ^{31}P NMR (C_6D_6) δ 55.3 ($J_{\text{Pt-P}} = 944$ Hz). Found: C, 59.32; H, 3.02%. Calcd for $\text{C}_{52}\text{H}_{30}\text{Ge}_2\text{P}_2\text{Pt}$: C, 59.09; H, 2.86%.

Preparation of *cis*-Bis(methyldiphenylgermyl)[1,2-bis(dimethylphosphino)ethane]platinum (19). To a solution of dichloro[1,2-bis(dimethylphosphino)ethane]platinum (0.21 g, 0.50 mmol) in THF (5 ml) was added a THF solution (4 ml) of methyldiphenylgermyllithium (1.5 mmol) at room temperature. The mixture was stirred at room temperature for 12 h, and the solution was concentrated to ca. 5 ml. After benzene (30 ml) was slowly added, the organic layer was filtered through filter-paper. Upon allowing the organic layer to stand at room temperature for 1 day, $[(\text{MePh}_2\text{Ge})_2\text{Pt}(\text{dmpe})]$ (**19**) (0.22 g, 0.26 mmol, 52.0%) was formed as yellow crystals. Recrystallization from benzene/hexane (1/5) at room temperature afforded pure **19**: mp 206–207 °C. ^1H NMR (C_6D_6) δ 0.56–0.63 (d with two satellites, $^2J_{\text{H-P}} = 9.5$ Hz, $^3J_{\text{H-Pt}} = 23.1$ Hz, 12H), 1.01 (d with two satellites, $^2J_{\text{H-P}} = 1.8$ Hz, $^3J_{\text{H-P}} = 17.5$ Hz, 6H), 6.95–7.50 (m, 40H). ^{13}C NMR (C_6D_6) δ 2.58, 6.72, 24.0–24.61, 128.71, 133.08, 135.40, 139.08. ^{31}P NMR (C_6D_6) δ 12.8 ($J_{\text{Pt-P}} = 900$ Hz). Found: C, 46.45; H, 5.22%. Calcd for $\text{C}_{32}\text{H}_{42}\text{Ge}_2\text{P}_2\text{Pt}$: C, 46.37; H, 5.11%.

Platinum-Catalyzed Reactions of Organodigermanes (1) with Alkynes (2). As a representative example, the reaction of hexamethyldigermene (**1a**) with phenylacetylene (**2a**) is described. A mixture of **1a** (0.1 mmol), **2a** (0.5 mmol), $[\text{Pt}(\text{acac})_2]$ (0.005 mmol), and toluene (1.0 ml) was prepared in a Pyrex tube ($\phi = 8$ mm). The solution was degassed in a vacuum and heated under argon in a sealed tube for 16 h at 120 °C. GC and GC-MS analyses of the reaction mixture showed 59% conversion of **1a**, along with the formation of *Z*-1-phenyl-1,2-bis(trimethylgermyl)ethene (**3a**). Concentration of the reaction mixture followed by preparative TLC (silica gel, hexane) gave **3a** (59% yield). ^1H NMR (CDCl_3) δ 0.30 (s, 3H), 0.36 (s, 3H), 6.56 (s, 1H), 7.03–7.04 (m, 5H). ^{13}C NMR (CDCl_3) δ 0.83, 1.14, 125.73, 126.27, 127.90, 143.30, 149.76, 163.37. IR (neat) 706, 825, 1236, 2951 cm^{-1} . GC-MS m/z (relative intensity) 338 (3, M^+), 321 (18), 181 (11), 119 (100), 104 (10), 87 (15). Found: C, 50.04; H, 7.37%. Calcd for $\text{C}_{14}\text{H}_{24}\text{Ge}_2$: C, 49.82; H, 7.17%. 1,2-Bis(trimethylgermyl)-1-hexene (**3b**): ^1H NMR (CDCl_3) δ 0.10 (s, 9H), 0.91 (t, $J = 6.0$ Hz, 3H), 1.24–1.27 (m, 4H), 2.22 (t, $J = 6.4$ Hz, 2H), 6.29 (s, 1H). ^{13}C NMR (CDCl_3) δ 0.49, 0.62, 13.92, 22.31, 31.97, 43.85, 128.92, 141.19. GC-MS m/z (relative intensity) 318 (5.6, M^+), 186 (38), 171 (31), 119 (100), 89 (18). 1,2-Bis(trimethylgermyl)-1-trimethylsilylethylene (**3c**): ^1H NMR (CDCl_3) δ 0.10 (s, 9H), 0.16 (s, 9H), 0.19 (s, 9H), 7.34 (s, 1H). ^{13}C NMR (CDCl_3) δ -0.15, 0.68, 1.77, 161.10, 167.55. GC-MS m/z (relative intensity) 336 (M^+). Found: C, 39.35; H, 8.64%. Calcd for $\text{C}_{11}\text{H}_{28}\text{Ge}_2\text{Si}$: C, 39.60; H, 8.46%. 1-Methylcarbonyl-1,2-bis(trimethylgermyl)ethylene (**3d**): ^1H NMR (CDCl_3) δ 0.24 (s, 9H), 0.25 (s, 9H), 3.62 (s, 3H), 7.16 (s, 1H). ^{13}C NMR (CDCl_3) δ 0.31, 0.42, 60.29, 128.21, 153.31, 157.65. GC-MS m/z (relative intensity) 306 (32, M^+), 247 (5), 203 (15), 135 (15), 119 (100), 89 (18).

Platinum-Catalyzed Reactions of 1,2-Dichloro-1,1,2,2-tetramethyldigermene (1b) with Alkynes (2). The reaction of **1b** with **2a** was carried out in a similar manner as described above for **1a**. After the reaction mixture was treated with methyl-

magnesium iodide, the products were characterized by comparing the NMR and GC-MS data of previously reported similar compounds.

Platinum-Catalyzed Reaction of Dodecamethylcyclohexgermane (7) with Phenylacetylene (2a). The reaction of **7** with **2a** was carried out in a similar manner as above for **1a**. A mixture of **7** (0.1 mmol), **2a** (0.5 mmol), $\text{Pt}(\text{acac})_2$ (0.005 mmol), and toluene (1.0 ml) was heated under argon in a sealed tube at 120 °C for 32 h. GC and GC-MS analyses of the reaction mixture showed 33% conversion of **7**. The concentration of the reaction mixture followed by preparative TLC (silica gel, hexane) gave **6**. ^1H NMR (C_6D_6) δ 0.40 (s, 6H), 0.43 (s, 6H), 6.82 (s, 1H), 6.90 (s, 1H), 7.20–7.37 (m, 10H). ^{13}C NMR (C_6D_6) δ -1.20, -0.26, 0.09, 126.02, 126.24, 126.43, 126.45, 128.18, 128.31, 143.34, 144.05, 145.52, 146.43, 159.95, 161.70. GC-MS m/z (relative intensity) 410 (22, M^+), 395 (21), 308 (17), 293 (30), 206 (19), 191 (27), 173 (41), 119 (100), 89 (100).

Platinum-Catalyzed Reactions of Dimetallacyclohexadienes (9, 12) with Phenylacetylene (2a). As a representative example, the reaction of 1,1,2,2-tetramethyl-3,4,5,6-tetraphenyl-1,2-digermacyclohexa-3,5-diene (**9**) with **2a** is described. The reaction of **9** with **2a** was carried out in a similar manner as above for **1a**. A mixture of **9** (0.1 mmol), **2a** (0.5 mmol), $[\text{Pt}(\text{acac})_2]$ (0.005 mmol), and toluene (1.0 ml) was heated under argon in a sealed tube at 80 °C for 36 h. GC and GC-MS analyses of the reaction mixture showed 96% conversion of **10**. Concentration of the reaction mixture followed by preparative TLC (silica gel, hexane) gave pure **10**. ^1H NMR (C_6D_6) δ -0.12 (s, 3H), 0.09 (s, 3H), 0.83 (s, 3H), 0.97 (s, 3H), 6.78 (s, 1H), 7.01–7.33 (m, 25H). ^{13}C NMR (C_6D_6) δ 0.41, 0.83, 2.06, 3.89, 125.37, 125.44, 125.86, 126.24, 126.55, 126.95, 127.03, 127.51, 127.75, 127.87, 128.55, 128.68, 130.14, 130.32, 139.37, 139.44, 141.75, 141.95, 143.15, 143.40, 146.80, 147.87, 151.87, 152.13, 162.05. GC-MS m/z (relative intensity) 664 (12, M^+), 634 (20), 619 (18), 589 (42), 443 (80), 207 (76), 105 (100). 1,1,4,4-Tetramethyl-2,5,6,7,8-pentaphenyl-1,4-disilaoceta-2,5,7-triene (**13a**): ^1H NMR (C_6D_6) δ -0.25 (s, 3H), 0.06 (s, 3H), 0.82 (s, 3H), 1.25 (s, 3H), 6.66 (s, 1H), 7.00–7.30 (m, 25H). ^{13}C NMR (C_6D_6) δ 1.21, 1.54, 2.09, 2.83, 103.08, 125.36, 125.77, 126.27, 126.43, 126.55, 126.86, 126.91, 127.35, 127.60, 127.78, 129.21, 130.22, 130.45, 139.43, 139.60, 140.34, 140.74, 143.11, 143.76, 148.80, 149.59, 154.34, 154.84, 163.58. GC-MS m/z (relative intensity) 576 (12, M^+), 546 (10), 529 (18), 500 (21), 443 (100), 207 (76), 105 (100). Found: C, 72.40; H, 5.80%. Calcd for $\text{C}_{40}\text{H}_{38}\text{Ge}_2$: C, 72.35; H, 5.77%.

Thermolysis of 1,1,2,2-Tetramethyl-3,4,5,6-tetraphenyl-1,2-digermacyclohexa-3,5-diene (9) in the presence of $[\text{Pt}(\text{acac})_2]$. A mixture of **9** (0.1 mmol), $[\text{Pt}(\text{acac})_2]$ (0.005 mmol), and toluene (1.0 ml) was heated under argon in a sealed tube under various conditions. The yields of reaction products were estimated with GC.

Reaction of *cis*-Bis(methyldiphenylgermyl)bis(dimethylphenylphosphine)platinum (16) with Phenylacetylene (2a) at 65 °C for 1.5 h. A mixture of *cis*-**16** (0.04 mmol), **2a** (0.08 mmol), and C_6D_6 (0.5 ml) was prepared in a Pyrex NMR tube. The tube was degassed in a vacuum and heated with stirring under argon at 65 °C for 1.5 h. NMR analyses of the reaction mixture showed the formation of (1-phenylethylenyl-2-phenylmethylgermyl)bis(dimethylphenylphosphine)platinum (**21**) in a quantitative yield. Concentration of the reaction mixture followed by crystallization in hexane/benzene gave pure **21** as pale yellow crystals in 88% yields. ^1H NMR (C_6D_6) δ 0.76 (d, $J_{\text{P-H}} = 8.2$ Hz, $J_{\text{Pt-H}} = 18.4$ Hz, 3H), 0.97–1.07 (m, 9 H), 1.20 (d, $J_{\text{P-H}} = 8.2$ Hz, $J_{\text{Pt-H}} =$

18.8 Hz, 3H), 1.65 (s, 3 H), 6.80–8.20 (m, 36 H); ^{31}P NMR (C_6D_6) δ –18.7 (d, $J_{\text{P-P}} = 18$ Hz, $J_{\text{P-H}} = 1819$ Hz), –15.0 (d, $J_{\text{P-P}} = 18$ Hz, $J_{\text{P-H}} = 1811$ Hz). Found: C, 56.92; H, 5.24%. Calcd for $\text{C}_{50}\text{H}_{54}\text{Ge}_2\text{P}_2\text{Pt}$: C, 56.81; H, 5.15%.

Reaction of *cis*-Bis(methyldiphenylgermyl)bis(dimethylphenylphosphine)platinum (16) with Phenylacetylene (2a) with Dimethylphenylphosphine at 65 °C for 1.5 h. A mixture of **16** (0.04 mmol), **2a** (0.08 mmol), PMe_2Ph (0.2 mmol), and C_6D_6 (0.6 ml) was heated under argon in a sealed NMR tube at 65 °C for 1.5 h. NMR analyses showed the formation of **21** in 30% yield.

Reaction of *cis*-Bis(methyldiphenylgermyl)bis(dimethylphenylphosphine)platinum (16) with Phenylacetylene (2a) at 65 °C for 24 h. A mixture of *cis*-**16** (0.1 mmol), **2a** (0.3 mmol), and benzene (1.0 ml) was prepared in a 25 ml-Schlenk tube. The tube was degassed in a vacuum and heated with stirring under argon at 65 °C for 24 h. GC and GC-MS analyses of the reaction mixture showed the formation of 1,2-bis(methyldiphenylgermyl)-1-phenylethylene (**20**) in 31% yield. Concentration of the reaction mixture followed by preparative TLC (silica gel, hexane) gave pure **20**. NMR (C_6D_6) δ 0.30 (s, 3H), 0.48 (s, 3H), 7.1–7.3 (m, 31H), GC-MS m/z (relative intensity) 586 (1.2, M^+), 345 (16), 243 (100), 151 (16).

Thermolysis of Bis-germylplatinum Complexes. As a representative example, the thermolysis of *cis*-bis(methyldiphenylgermyl)bis(dimethylphenylphosphine)platinum (**16**) is described. A mixture of **16** (0.01 mmol), toluene (2 μl , 0.02 mmol) as an internal standard, and C_6D_6 (0.6 ml) was heated under argon in a sealed NMR tube at 120 °C for 5 h. NMR, GC-MS, and GPC analyses showed the formation of $\text{MePh}_2\text{GeGePh}_2\text{Me}$ (60%), $\text{Ph}_2\text{Me}_2\text{Ge}$ (12%), Ph_3MeGe (6%), and oligomers containing germanium.

Thermolysis of *cis*-Bis(methyldiphenylgermyl)bis(dimethylphenylphosphine)platinum (16) with Triphenylphosphine. A mixture of **16** (0.01 mmol), toluene (2 μl , 0.02 mmol) as an internal standard, PPh_3 (0.05 mmol), and C_6D_6 (0.6 ml) was heated under argon in a sealed NMR tube at 120 °C for 5 h. NMR and GC-MS analyses showed the formation of $\text{MePh}_2\text{GeGePh}_2\text{Me}$ in 97%.

Kinetic Studies of Isomerization of *cis*-Bis(methyldiphenylgermyl)bis(dimethylphenylphosphine)platinum (16). A typical procedure for the isomerization of **16** is as follows. *cis*-**16** (0.005 mmol) and C_6D_6 (0.6 ml) were placed in an NMR sample tube equipped with a rubber septum cap, and the system was replaced with argon at room temperature. The sample was placed in an NMR sample probe controlled at 45, 50, 55, and 60 °C, and examined by ^1H NMR. The time course of the isomerization was followed by measuring the relative peak integration of the methyl signal of **16**.

Kinetic Studies of Isomerization of *cis*-Bis(methyldiphenylgermyl)bis(dimethylphenylphosphine)platinum (16) with Dimethylphenylphosphine. A mixture of *cis*-**16** (0.005 mmol), PMe_2Ph (0.0015 mmol), and C_6D_6 (0.6 ml) was heated under argon in a sealed NMR tube at 45 °C and examined by ^1H NMR. The time course of the isomerization was followed by measuring the relative peak integration of the methyl signal of **16**.

Thermolysis of Germyl(germylvinyl)platinum Complex (21). A mixture of **21** (0.08 mmol) and C_6D_6 (0.6 ml) was heated under argon in a sealed NMR tube at 80 °C for 8 h. NMR and GC-MS analyses showed the formation of **20** (40%). The germyl(germylvinyl)platinum **21** was recovered in 55% yield.

Thermolysis of Germyl(germylvinyl)platinum Complex

(21) with Dimethylphenylphosphine. A mixture of **21** (0.08 mmol), PMe_2Ph (0.40 mmol), and C_6D_6 (0.6 ml) was heated under argon in a sealed NMR tube at 80 °C for 8 h. The NMR spectra showed that the germyl(germylvinyl)platinum **21** remained completely unreacted.

Reaction of Germyl(germylvinyl)platinum Complex (21) with Diphenylacetylene (2e). A mixture of **21** (0.08 mmol), diphenylacetylene (0.40 mmol), and C_6D_6 (0.6 ml) was heated under argon in a sealed NMR tube at 80 °C for 8 h. NMR and GC-MS analyses showed the formation of **20** and bis(dimethylphenylphosphine)(diphenylacetylene)platinum (**22**) in quantitative yields, respectively.

Reaction of Bis(triphenylphosphine)(phenylacetylene)platinum (23) with Hexamethyldigermene (1a). A mixture of **23** (0.08 mmol), $\text{Me}_3\text{GeGeMe}_3$ (**1a**) (0.40 mmol), and C_6D_6 (0.6 ml) was heated under argon in a sealed NMR tube at 60–120 °C for 12 h. The NMR spectra showed no-germylation products of phenylacetylene.

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