

Preparation and Structural Characterization of 1,4-Digerma-2-buten-1,4-diylplatinum(II) Complexes and Their Reactions with Alkynes, Carbon Monoxide, and Isocyanides

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1,4-Digerma-2-buten-1,4-diylplatinum(II) complexes were prepared by treatment of a (η -ethylene)(triphenylphosphine)platinum(0) complex with (*Z*)- α,β -bis(dialkylgermyl)styrenes, and their structures were determined by spectroscopic analysis coupled with X-ray diffraction methods. Thermolysis of 1,4-digerma-2-buten-1,4-diylplatinum(II) complexes afforded linear and cyclic trigermenes and a dinuclear platinum complex. The 1,4-digerma-2-buten-1,4-diylplatinum(II) complexes reacted with alkynes to give the corresponding insertion products, cyclic germyl(germylvinyl)platinum(II) species, whose structures have been determined by spectroscopic analysis. The cyclic germyl(germylvinyl)platinum(II) complexes were found to easily liberate 1,4-digermacyclohexa-2,5-dienes and a platinum(0) complex. The reactions of 1,4-digerma-2-buten-1,4-diylplatinum(II) complexes with carbon monoxide and isocyanides afforded the corresponding platinum complexes containing one carbon monoxide and one isocyanide ligand, respectively.

The transition metal-catalyzed addition of group 14 element catenate compounds to unsaturated organic substrates is a useful and fundamental process in group 14 element and organometallic chemistry.¹ The addition of group 14 element catenates to C–C triple and double bonds, i.e., bis-silylation,² has attracted considerable current interest as applied to the synthesis of functional molecules and in applications to selective organic synthesis and advanced materials. In such reactions, bis(silyl)palladium(II) and bis(silyl)platinum(II) complexes have been proposed as key intermediates, and their structures and reactivities have been amply investigated.³ In contrast to the extensive study of complexes containing Pd– and Pt–Si bonds, there have been few reports regarding bis(germyl)palladium(II) and bis-

(germyl)platinum(II) complexes.⁴ We have previously reported on the preparation, structural characterization, and interesting reactivity of bis(phenyl-substituted germyl)platinum(II) complexes.^{4e} We describe in this paper the preparation, structural characterization, and reactions of new cyclic bis(germyl)platinum(II) complexes.

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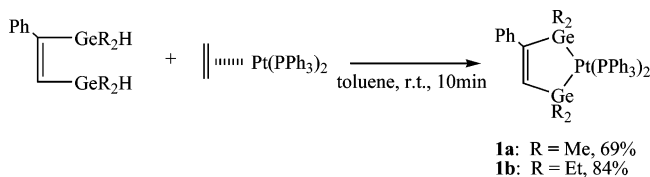
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Results and Discussion

Preparation and Structural Characterization of 1,4-Digerma-2-buten-1,4-diylplatinum(II) Complexes. We have previously reported that a strained germacycle having a Ge–Ge bond, 1,2-digermacyclobut-3-ene, reacts smoothly with alkynes in the presence of an appropriate catalyst to give the corresponding insertion products, 1,4-digermacyclohexa-2,5-dienes, in moderate to good yield.⁵ 1,4-Digerma-2-buten-1,4-diylplatinum(II) complexes have been proposed as key intermediates in platinum-catalyzed insertion reactions of alkynes into the Ge–Ge bond of 1,2-digermacyclobut-3-enes. Our interest in the structure and properties of the Ge–Pt bond prompted us to prepare a readily accessible strained 1,4-digerma-2-buten-1,4-diylplatinum(II) complex as a model compound for such intermediates.

The 1,4-digerma-2-buten-1,4-diylplatinum(II) (**1**) was prepared by the treatment of (η -ethylene)bis(triphenylphosphine)platinum(0) with 1.5 equiv of (*Z*)- α,β -bis-(dialkylgermyl)styrenes in toluene at room temperature for 10 min, which afforded 1,1,4,4-tetraalkyl-2-phenyl-1,4-digerma-2-buten-1,4-diylplatinum(II) (**1a**: alkyl = methyl, 69% yield; **1b**: alkyl = ethyl, 84% yield) as white crystals.⁶



Platinum(II) complex **1** is sensitive to air and moisture at room temperature. The structure of **1** was determined by spectroscopic methods coupled with X-ray crystallography. Fortunately, complex **1b** could be isolated as white crystals by recrystallization from a 1:1 mixture of hexane and toluene at room temperature for 3–5 days.

The structure of platinum complex **1b** was finally confirmed by X-ray diffraction analysis, as shown in Figure 1. The crystal data and refinement data are summarized in the Experimental Section. Selected bond lengths and angles are tabulated in Table 1.

Complex **1b** has a distorted square-planar geometry, with the dihedral angle between the planes composed of Ge(1)–Pt(1)–Ge(2) and P(1)–Pt(1)–P(2) being 9.7°. The deformation from planarity is considered to be caused by a steric repulsion between the bulky ligands. The two germyl groups are bound to the platinum center, with the bite angle, Ge(1)–Pt(1)–Ge(2), being 81.40°. In contrast, the P(1)–Pt(1)–P(2) bite angle is 95.87°. The bond lengths of Pt–Ge (2.4569(8) and 2.4850(7) Å) are shorter than those of *trans*-bis(germyl)platinum(II) complexes and similar to those of the *cis*-isomer. In contrast, the Pt–P bond length (2.3375(17) and 2.3458(18) Å) is longer than those of *trans*-bis-

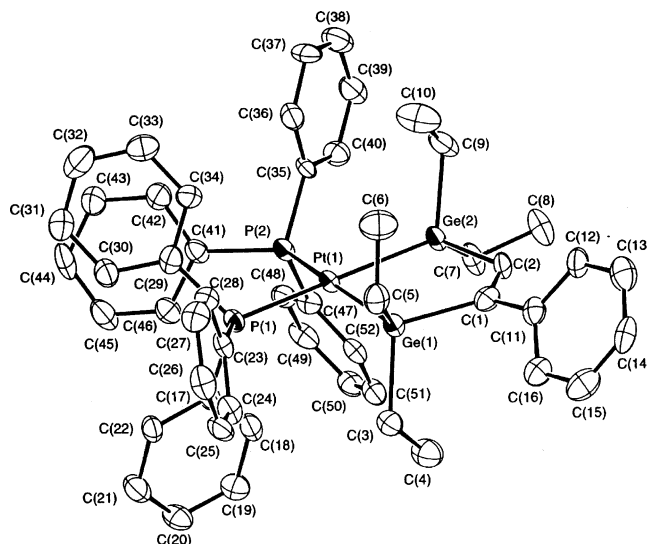


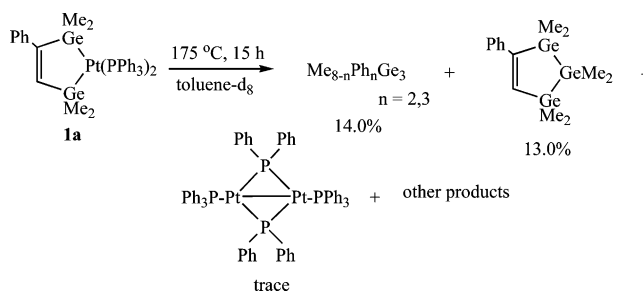
Figure 1. ORTEP view of **1b**. Thermal ellipsoids are drawn at 30% probability levels, and hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) of 1,4-Digerma-2-buten-1,4-diylplatinum(II) (**1b**)

Pt(1)–Ge(1) 2.4569(8)	Pt(1)–Ge(2) 2.4850(7)
Pt(1)–P(1) 2.3375(17)	Pt(1)–P(2) 2.3458(18)
Ge(1)–C(1) 2.003(7)	Ge(1)–C(1) 2.003(7)
C(1)–C(2) 1.324(10)	Ge(1)–Pt(2)–P(1) 92.23(5)
P(1)–Pt(1)–P(2) 95.87(6)	Ge(2)–Pt(1)–P(2) 90.95(5)
Ge(1)–Pt(1)–Ge(2) 81.40(3)	

(germyl)platinum(II) complexes and similar to those of the *cis*-isomer.^{4c}

Thermolysis. The thermolysis of platinum(II) complex **1a** was examined in a sealed NMR tube. In toluene it was thermally stable at 120 °C for 5 days. However, heating **1a** in toluene at 175 °C for 15 h led to complete decomposition with formation of trigermans (14%) and 1,2,3-trigermycyclopent-4-ene (13%) as the major products. Trace amounts of dinuclear platinum(II) complex



and unidentified products containing germanium also were detected. Fragments of linear and cyclic trigermane structures were carefully identified by NMR and GC-MS data by comparison with related germanium compounds.^{7–9} The structure of the dinuclear platinum(II) complex was established by spectroscopic and X-ray diffraction methods.¹⁰

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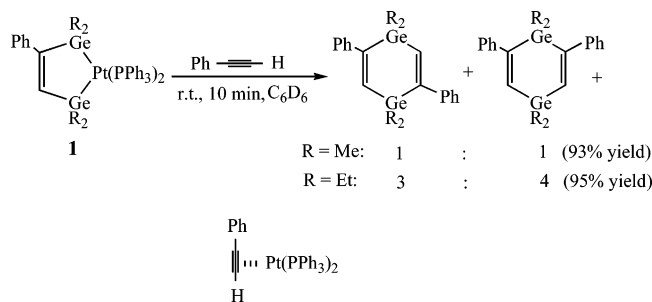
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The presence of trigermanes and 1,2,3-trigermacyclopent-4-ene may have been due to the generation of a dimethylgermylene unit from **1a**.¹² The germylene then inserted into the activated Ge–Ge bond of 1,2-digermacyclobut-3-ene, produced by reductive elimination from **1a** with the regeneration of platinum species to afford 1,2,3-trigermacyclopent-4-ene. It is well known that the dimerization of germynes gives the corresponding digermenes, followed by the addition of the germylene to the Ge–Ge double bond to afford trigermanes.^{4c,9,11,12} The position of the methyl and phenyl groups on the germanium atoms of the trigermanes is unclear. Methyl groups on the germanium atom may be exchanged with phenyl groups of phosphine ligands above 120 °C.

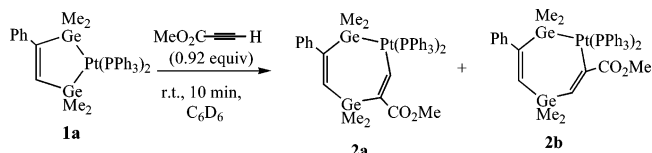
Reactions of Platinum(II) Complex 1 with Alkynes. As reported, platinum-catalyzed insertion reactions of acetylenes into the Ge–Ge bond of the strained 1,2-digermacyclobut-3-ene in toluene smoothly produced the corresponding 1,4-digermacyclohexa-2,5-dienes in moderate to good yield.^{4c,5} 1,4-Digermacyclobut-2-ene-1,4-diylplatinum(II) compounds **1** have been proposed as model compounds of intermediates in such reactions. To examine the reactivity of **1**, which is assumed to be involved in the platinum-catalyzed insertion of alkynes into the Ge–Ge bond of germacycles, we treated **1** with 5.0 molar equiv of phenylacetylene at room temperature for 10 min. The reaction gave a mixture of 3,5-diphenyl-1,4-digermacyclohexa-2,5-diene and 2,5-diphenyl-1,4-digermacyclohexa-2,5-diene (1:1) (**1a**) and (3:4) (**1b**), respectively, in moderate to good yield. (η -Phenylacetylene)bis(triphenylphosphine)platinum(0) also was formed. All compounds were identified by NMR spectroscopy and by GC-MS data.^{3n,m,p,4e,13}



The reactions of **1b** with other terminal and internal alkynes such as 1-hexyne, methyl propiolate, and 1-phenyl-1-propyne also gave the corresponding 1,4-digermacyclohexa-2,5-dienes in moderate to good yield. Internal alkynes such as diphenylacetylene, bis(trimethylsilyl)acetylene, and dimethyl acetylenedicarboxylate proved to be unreactive toward **1b** under various conditions. The results of **1b** with alkynes are summarized in the Experimental Section.

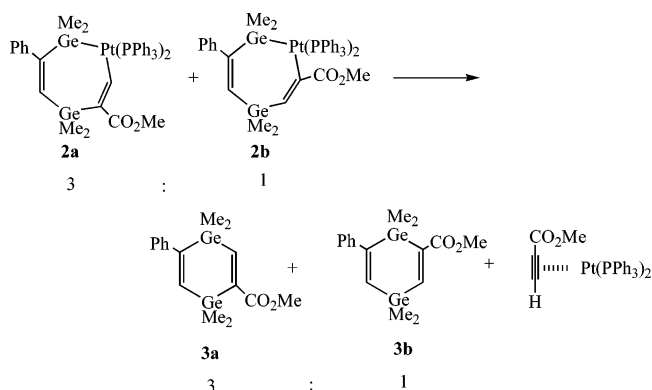
The cyclic germyl(vinylgermyl) type platinum(II) complex (**2**) is a possible intermediate in the reactions of **1** with alkynes in the process of liberating alkyne-insertion products.^{3n,4e} To detect the cyclic germyl(vinylgermyl) type platinum(II) complex, we treated **1** with alkynes under various conditions. Among the alkynes examined, methyl propiolate is the most suitable for

alkyne insertion reactions of **1a** based on NMR spectroscopy. Thus, the reaction of complex **1a** with 0.92 equiv of methyl propiolate at room temperature for 10 min in C_6D_6 was followed by NMR spectroscopy.



The ^{31}P NMR spectrum showed two signals at 29.0 ppm ($J_{\text{Pt}-\text{P}} = 2198$ Hz, $J_{\text{P}-\text{P}} = 17$ Hz) and 29.9 ppm ($J_{\text{t}-\text{P}} = 2219$ Hz, $J_{\text{P}-\text{P}} = 17$ Hz) in diminished intensity assigned to **1a** and two new sets (**2a** and **2b** in approximately 3:1 ratio), two signals: 24.1 ppm (d with two satellites, $J_{\text{Pt}-\text{P}} = 2200$ Hz, $J_{\text{P}-\text{P}} = 15$ Hz) and 25.3 ppm (d with two satellites, $J_{\text{Pt}-\text{P}} = 1822$ Hz, $J_{\text{P}-\text{P}} = 15$ Hz), and 22.5 ppm (d, $J_{\text{P}-\text{P}} = 15$ Hz) and 25.5 ppm (d, $J_{\text{P}-\text{P}} = 15$ Hz). The Pt satellites in **2b** could not be observed in the ^{31}P NMR spectrum due to its low intensity. The ^1H NMR spectrum of **2a** showed three singlets at -0.71 ppm ($J_{\text{Pt}-\text{H}} = 14$ Hz) due to the methyl group of the platinum-bound dimethylgermyl group ($\text{Pt}-\text{GeMe}_2$), at 1.03 ppm due to another dimethylgermyl group (GeMe_2), at 3.41 ppm due to the methyl ester group (CO_2Me), and multiplet signals in the range 6.80–7.80 ppm due to the phenyl groups and the olefinic proton. The ^1H NMR spectrum of **2b** showed three methyl signals at -0.44 ppm ($J_{\text{Pt}-\text{H}} = 11$ Hz) due to $\text{Pt}-\text{GeMe}_2$, at 1.15 ppm due to GeMe_2 , at 3.43 ppm due to CO_2Me , and multiplets in the range 6.75–7.70 ppm due to the phenyl groups and olefinic protons. The ^{13}C NMR spectrum of **2a/2b** could not be observed due to their short lifetimes.

Stirring the C_6D_6 solution of **2a/b** at room temperature for 10 h resulted in the decomposition of **2a/b** (100%) with formation of a 3:1 mixture of the corresponding insertion products (**3a,b**) together with (η -methylpropiolate)bis(triphenylphosphine)platinum(0). 1,4-Digermacyclohexa-2,5-dienes (**3a,b**) were characterized by NMR and GC-MS spectra.



These results indicate that cyclic germyl(vinylgermyl)platinum(II) complex **2** is an intermediate in the reactions of **1** with alkynes in the process of liberating alkyne-inserted products.¹⁴

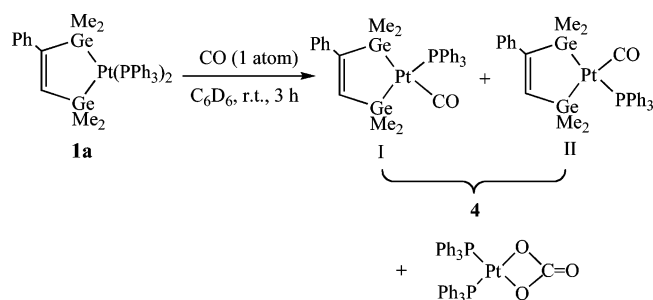
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Reactions of Platinum(II) Complex **1a with Carbon Monoxide.** Although many interesting reactions of bis(germyl)platinum(II) complexes toward unsaturated organic compounds via the Pt–Ge bond cleavage have been reported, there has been no study of the insertion of small molecules such as carbon monoxide into the Pt–Ge bond in these complexes. A large excess of carbon monoxide was bubbled into a C₆D₆ solution of **1a** at room temperature for 3 h. The product was identified to be the 1,4-digermma-2-butene-1,4-diyl platinum complex containing both phosphine and CO ligands (**4**). Evaporation of benzene followed by rapid chromatography on silica gel, elution with benzene, gave **4** as colorless crystals in 71% isolated yield. Platinum(II) complex **4** was formed by replacement of only one phosphine ligand of **1a** with CO despite the fact that CO was bubbled into the solution for a long time. Complex **4** was stable at room temperature in air. Bis-(triphenylphosphine)platinum carbonate ([Pt(PPh₃)₂CO₃]) was formed as a minor byproduct. The identity of all products was determined by IR and NMR spectroscopy. The structure of [Pt(PPh₃)₂CO₃] was established by X-ray diffraction. The IR spectrum of **4** displayed a strong absorption band at 2038 cm⁻¹ due to the ν(C=O) ligand. An NMR examination of **4** in C₆D₆ at 23 °C showed the presence of I and II, isomers of the platinum(II) complex in an approximately 1:1 ratio. The ¹H NMR spectrum of **4** displays two sets of methyl signals on germanium at 0.23, 1.00 ppm and 0.29, 1.09 ppm. The singlets at 0.23 and 0.29 ppm are flanked with Pt satellites (*J*_{Pt–H} = 15.7 and 18.7 Hz, respectively), whereas the doublets coupled with a phosphine ligand at 1.00 and 1.09 ppm are flanked with Pt satellites (*J*_{P–H} = 2.3 Hz and *J*_{Pt–H} = 20.1 Hz, *J*_{P–H} = 2.2 Hz and *J*_{Pt–H} = 20.5 Hz, respectively). The ³¹P NMR of **4** in C₆D₆ shows two singlet signals at 25.6 and 26.4 ppm with Pt satellites (*J*_{Pt–P} = 2022 and 2044 Hz, respectively). The *J*_{Pt–P} values in **4** are smaller than those of *trans*-bis-(silyl or germyl)(*tert*-phosphine)platinum(II) complexes (*J*_{Pt–P} = ca. 2600 Hz) and are consistent with those of *cis*-bis(silyl or germyl)(*tert*-phosphine)platinum(II) complexes and bis(germyl)platinum complexes with chelating diphosphines.^{4e}



The preparation of [Pt(PPh₃)₂CO₃] by the reaction of [Pt(PPh₃)₄] with oxygen under a carbon dioxide atmosphere and its structural characterization by X-ray analysis have been reported by Dell'Amico and co-workers¹⁵ and other groups.^{16,17}

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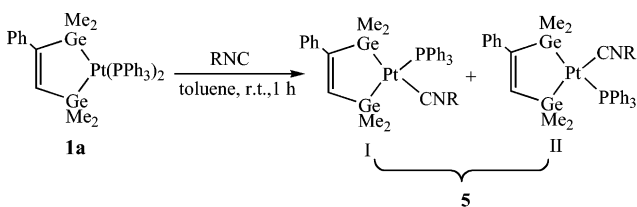
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Ozawa and co-workers have reported the insertion of CO into the Pt–C bond of alkyl(silyl)platinum(II) complexes.³ⁿ As far as we know, there have been no reports of CO insertion into the Pt–group 14 element bonds.

Reactions of Platinum(II) Complex **1a with Organic Isocyanides.** The reactivity of platinum(II) complex **1a** with organic isocyanides (CNR), which are isoelectronic with CO, was examined. Reactions of **1a** with 1 molar equiv of CNR (R = *tert*-Bu and cyclohexyl) in toluene at room temperature for 1 h gave new 1,4-digermma-2-butene-1,4-diylplatinum(II) complexes (**5**) containing both phosphine and isocyanide ligands. Evaporation of toluene and unreacted isocyanide followed by preparative TLC on silica gel gave platinum(II) complexes **5** as colorless crystals in 49–80% isolated yield, which are very stable at room temperature in air. Complex **5** was formed regardless of the amount of isocyanide used. The structures of **5** were determined by IR and NMR analysis coupled with X-ray diffraction analysis.

The NMR spectrum of **5a** in CD₂Cl₂ at 23 °C showed the presence of isomers I and II in an approximately 3:1 ratio. On the other hand NMR examination of **5b** showed a single isomer I.



R = *t*-butyl (**5a**), 80%; R = cyclohexyl (**5b**), 49%;

Very recently, reactions of bis(silyl)platinum(II) complexes with organic isocyanides have been reported by Kim and co-workers^{3v} to give the corresponding bis(silyl)platinum(II) complexes containing both phosphine and isocyanide ligands. NMR spectra of new bis(silyl)platinum(II) complexes containing both phosphine and isocyanide ligands broaden at room temperature due to *cis*–*trans* isomerism.

The molecular structures of **5a**-I and **5b** have been determined by X-ray diffraction, as shown in Figures 2 and 3. Platinum(II) complexes containing both phosphine and isocyanide ligands, **5a**-I and **5b**, could be isolated as colorless crystals by recrystallization from benzene at room temperature for a few days. The crystal data and refinement data are summarized in the Experimental Section. Selected bond lengths and angles are tabulated in Table 2.

Both **5a**-I and **5b** have distorted square-planar *cis* geometries, with the dihedral angles between the planes composed of Ge(1)–Pt(1)–Ge(2) and P(1)–Pt(1)–C(13) being 9.11° and 14.02°, respectively. The deformation from planarity is considered to be caused by a steric repulsion between the bulky ligands. The two germyl groups are bound to the platinum center, with the bite angle, Ge(1)–Pt(1)–Ge(2), being 81.77° for **5a** and 83.09° for **5b**. In contrast, the bite angles, P(1)–Pt(1)–C(13), for **5a** and **5b** are 99.9° and 93.6°, respectively. The bond lengths of Pt–Ge (2.4515(8) and 2.4430(11) Å for **5a** and 2.424(10) and 2.4265(14) Å for **5b**) are similar to those of *cis*-bis(germyl)platinums(II) and are

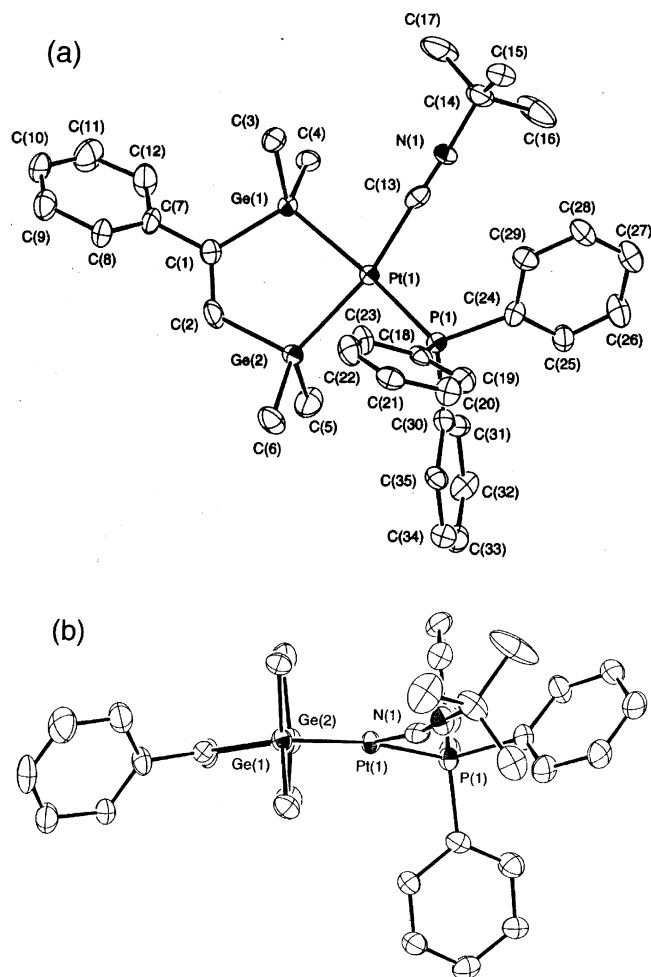


Figure 2. ORTEP view of **5a-I**: (a) top view, (b) side view. Thermal ellipsoids are drawn at 30% probability levels, and hydrogen atoms are omitted for clarity.

shorter than those of *trans*-bis(germyl)platinums(II). The bond lengths of P(1)–Pt(1) (2.2981(19) Å for **5a** and 2.354(3) Å for **5b**) are similar to those of *cis*- and *trans*-bis(germyl)platinum(*tert*-phosphine)platinum(II) complexes.^{4e} The Pt–C bond lengths (1.984(12) Å for **5a** and 2.02(2) Å for **5b**) are similar to those in bis(silyl)platinum(II) containing isocyanide and slightly longer than those found in other platinum-isocyanide complexes.^{3v} These results are due to the high *trans* influence of the germyl ligand.

Experimental Section

General Methods. All manipulations of air-sensitive compounds were performed under N₂ or argon using standard Schlenk line techniques. ¹H, ¹³C, and ³¹P 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 a 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 Mo Kα (λ = 0.71073 Å) radiation. The structures were solved by direct methods using the program system SIR-92 and refined with all data on F² by means of SHELXL-97. A refinement was performed by a Silicon Graphics O₂ with maXus.

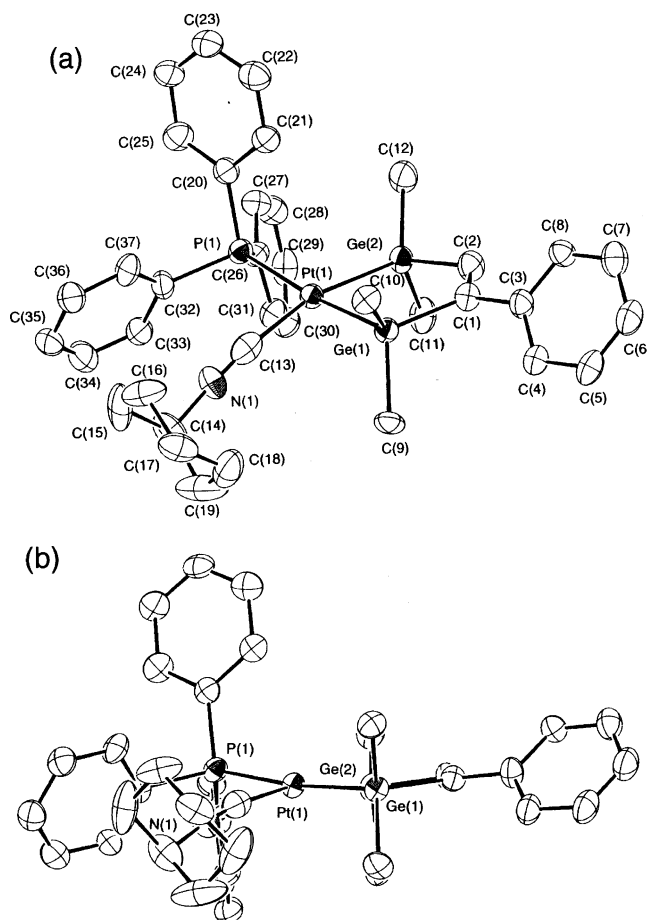


Figure 3. ORTEP view of **5b**: (a) top view, (b) side view. Thermal ellipsoids are drawn at 30% probability levels, and hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) of 1,4-Digerma-2-buten-1,4-diylplatinum(II) Containing Both Phosphine and Isocyanide Ligands, 5a-I and 5b

5a-I	
Pt(1)–Ge(1) 2.4515(8)	Pt(1)–Ge(2) 2.4430(11)
Pt(1)–P(1) 2.2981(19)	Pt(1)–C(13) 1.984(12)
Ge(1)–C(1) 1.982(8)	Ge(2)–C(2) 1.995(5)
C(1)–C(2) 1.342(13)	Ge(1)–Pt(1)–C(13) 83.9(3)
P(1)–Pt(1)–C(13) 99.9(3)	Ge(2)–Pt(1)–P(1) 95.15(5)
Ge(1)–Pt(1)–Ge(2) 81.77(3)	
5b	
Pt(1)–Ge(1) 2.4241(10)	Pt(1)–Ge(2) 2.4265(14)
Pt(1)–P(1) 2.3548(3)	Pt(1)–C(13) 2.02(2)
Ge(1)–C(1) 1.972(11)	Ge(2)–C(2) 1.915(11)
C(1)–C(2) 1.381(16)	Ge(1)–Pt(1)–C(13) 89.9(3)
P(1)–Pt(1)–C(13) 93.6(3)	Ge(2)–Pt(1)–P(1) 94.74(7)
Ge(1)–Pt(1)–Ge(2) 83.09(4)	

Materials. Solvents were dried by refluxing over sodium benzophenone ketyl under a nitrogen atmosphere and were distilled just before use. Alkynes and organic isocyanides were commercially available. 1,4-Digermacyclohexa-2,5-dienes,⁵ (*Z*)-α,β-(dimethylgermyl)styrene,⁵ (*η*-ethylene)bis(triphenylphosphine)platinum,¹⁸ and (*η*-phenylacetylene)bis(triphenylphosphine)platinum¹³ were prepared according to reported procedures.

Preparation of (*Z*)-α,β-(Diethylgermyl)styrene. A diethyl ether solution (40 mL) of bis(chlorodiethylgermyl)styrene (3.76 g, 10.3 mmol) and LiAlH₄ (0.39 g, 10.3 mmol) was stirred

Table 3. Crystallographic Data for 1b, 5a-I, and 5b

	1b	5a-I	5b
formula	C ₅₂ H ₅₆ Ge ₂ P ₂ Pt	C ₃₅ H ₄₂ Ge ₂ NPt	C ₃₇ H ₄₄ Ge ₂ NPt
molecular wt	1083.18	847.94	873.97
cryst size (mm)	0.35 × 0.30 × 0.25	0.20 × 0.20 × 0.20	0.10 × 0.06 × 0.06
cryst syst	triclinic	monoclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>Pn</i>	<i>Pn</i>
unit cell dimens			
<i>a</i> (Å)	12.5340(16)	9.5910(4)	9.3510(6)
<i>b</i> (Å)	12.9030(17)	11.0280(5)	11.2320(7)
<i>c</i> (Å)	17.1630(13)	16.7050(5)	17.0280(7)
α (deg)	106.463(7)		
β (deg)	94.423(7)		
γ (deg)	115.172(5)		
<i>V</i> (Å ³)	1234.8(5)	1707.72(12)	1735.34(17)
<i>Z</i>	2	2	2
radiation Mo K α (Å)	0.71070	0.71070	0.71070
temperature (K)	120	120	120
<i>D</i> _{calc} (g cm ⁻³)	1.534	1.649	1.673
no. of unique reflns	6158	4037	4109
goodness-of-fit	0.952	1.050	1.243
<i>R</i> ₁ (<i>I</i> > 2 σ (<i>I</i>))	0.0398	0.0372	0.0472
<i>wR</i> ₂	0.1109	0.1070	0.1309

at 40 °C for 3 h. After hydrolysis with water, pure (*Z*)- α,β -bis-(diethylgermyl)styrene was obtained by silica gel chromatography on a short column packed with silica gel, eluting with hexane (1.6 g, 4.4 mmol, 43% yield): ¹H NMR (δ , C₆D₆) 0.86–1.18 (m, 20H), 4.45–4.59 (m, 1H), 4.67 (quint., *J* = 3.5 Hz), 6.81 (d, *J* = 6.2 Hz, 1H), 7.04–7.23 (m, 5H); ¹³C NMR (δ , CDCl₃) 5.9, 6.8, 10.2, 10.5, 126.1, 126.2, 128.0, 142.7, 147.9, 160.5; GC-MS *m/z* (relative intensity) 366 (M⁺, 8), 337 (100), 236 (33). Anal. Calcd for C₁₆H₂₈Ge₂: C, 52.57; H, 7.72. Found: C, 52.78; H, 7.95.

Preparation of Bis(triphenylphosphine)-2-phenyl-2-butene-1,1,4,4-tetramethyl-1,4-digerma-1,4-diylplatinum (1a). A solution of bis(dimethylgermyl)styrene (161 mg, 521 μ mol) and (η -ethylene)bis(triphenylphosphine)platinum (208 mg, 278 μ mol) in degassed toluene (4 mL) was placed in a 25 mL Schlenk tube. After the mixture had been stirred at room temperature for 10 min, the toluene was removed under reduced pressure. Washing the residue with hexane gave pure bis(triphenylphosphine)-2-phenyl-2-butene-1,1,4,4-tetramethyl-1,4-digerma-1,4-diylplatinum (**1a**) (241 mg, 235 μ mol, 84.4% yield). **1a**: ¹H NMR (δ , C₆D₆) 0.41 (s with two satellites, *J*_{Pt-H} = 15 Hz, 6H), 0.47 (s with two satellites, *J*_{Pt-H} = 15 Hz, 6H), 6.77–7.64 (m, 35H, phenyl, 1H, CH=); ³¹P NMR (δ , C₆D₆) 29.0 (d with two satellites, *J*_{Pt-P} = 2198 Hz, *J*_{P-P} = 17 Hz), 29.9 (d with two satellites, *J*_{Pt-P} = 2219 Hz, *J*_{P-P} = 17 Hz); ¹³C NMR (δ , CD₂Cl₂) 4.1, 5.8, 124.8, 126.7, 127.5, 127.7, 127.8, 128.4, 129.5, 134.1, 134.2, 134.4, 135.2, 135.7, 146.5, 152.1. Anal. Calcd for C₄₈H₄₈Ge₂P₂Pt: C, 56.13; H, 4.71. Found: C, 56.22; H, 4.92.

Preparation of Bis(triphenylphosphine)-2-phenyl-2-butene-1,1,4,4-tetraethyl-1,4-digerma-1,4-diylplatinum (1b). The same procedure was used in the reaction of bis-(diethylgermyl)styrene (169 mg, 462 μ mol) with (η -ethylene)-bis(triphenylphosphine)platinum (201 mg, 269 μ mol) in toluene (4 mL). Pure bis(triphenylphosphine)-2-phenyl-2-butene-1,1,4,4-tetraethyl-1,4-digerma-1,4-diylplatinum (**1b**) was isolated (200 mg, 185 μ mol, 69% yield). **1b**: ¹H NMR (δ , C₆D₆) 0.45–1.42 (m, 20H), 6.75–7.67 (m, 36H); ¹³C NMR (δ , CD₂Cl₂) 11.6, 11.8, 12.6, 12.8, 124.4, 126.5, 127.2, 127.4, 127.4, 129.2, 129.4, 131.7, 134.1, 134.1, 135.5, 147.9, 150.5, 165.1; ³¹P NMR (δ , C₆D₆) 28.8 (d with two satellites, *J*_{Pt-P} = 2144 Hz, *J*_{P-P} = 20 Hz), 25.8 (d with satellites, *J*_{Pt-P} = 2091 Hz, *J*_{P-P} = 20 Hz). Anal. Calcd for C₅₂H₅₆Ge₂P₂Pt: C, 56.72; H, 5.13. Found: C, 56.98; H, 5.33.

Thermolysis of Bis(triphenylphosphine)-2-phenyl-2-butene-1,1,4,4-tetramethyl-1,4-digerma-1,4-diylplatinum (1a). A mixture of **1a** (86 mg, 84 μ mol) in *o*-xylene (1.1 mL) was heated under argon in a sealed NMR tube at 175 °C for 15 h. Evaporation of *o*-xylene followed by preparative TLC on silica gel eluted with benzene gave two kinds of linear

trigermans, Me_{8-n}Ph_nGe₃ (*n* = 2, 3) (14%) and 1,2-3-trigermacyclopentene (13%), and a dinuclear platinum(II) complex, [Pt₂(PPh₃)₂(PPh₂)₂] (trace). The germanium compounds were carefully characterized by ¹H, ¹³C, ³¹P NMR, and GC-MS data, which were compared with those of related germanium compounds. The identity of the dinuclear platinum(II) complex, [Pt₂(PPh₃)₂(μ -PPh₂)₂], was determined by NMR and X-ray diffraction methods. 1,1,2,2,3,3-Hexamethyl-4-phenyl-1,2,3-germacyclopenta-4-ene:^{9,10} ¹H NMR (δ , CDCl₃) 0.35 (s, 12H), 0.39 (s, 6H), 6.75–7.45 (m, 6H); ¹³C NMR (δ , CDCl₃) -1.01, -0.07, 0.27, 126.52, 127.74, 128.53, 140.88, 149.72, 161.74; GC-MS *m/z* (relative intensity) 410 (M⁺, 59), 395 (80), 308 (45), 293, 206 (50), 175 (50), 119 (100). Linear trigermans, Me_{8-n}Ph_nGe₃ (*n* = 2, 3):^{7,8} ¹H NMR (δ , CDCl₃) 0.04 (s), 0.31 (s), 0.32 (s), 6.75–7.50 (m); ¹³C NMR (δ , CDCl₃) -1.1, -0.47, 0.25, 1.04, 126.52, 127.74, 128.53, 140.88; GC-MS *m/z* (relative intensity) for *n* = 2, 462 (M⁺, 5), 447 (M⁺ - Me, 30), 345 (M⁺ - GeMe₃, 20), 283 (M⁺ - GeMe₂Ph, 10), 243 (GeMePh₂⁺, 100), 181 (GeMe₃Ph⁺, 50); GC-MS *m/z* (relative intensity) for *n* = 3, 462 (M⁺, 462), 447 (M⁺ - Me, 25), 283 (M⁺ - GeMe₂-Ph, 25), 243 (Ph₂MeGe⁺, 15), 181 (PhMe₂Ge⁺, 100).

Reactions of Bis(triphenylphosphine)-2-phenyl-2-butene-1,1,4,4-tetramethyl-1,4-digerma-1,4-diylplatinum (1a) with Phenylacetylene. To an NMR tube containing 1,4-digermabut-2-ene-1,4-diylplatinum (20 mg, 19 μ mol) were added phenylacetylene (34 mg, 194 μ mol) and C₆D₆ (0.7 mL) under argon. The solution was degassed under vacuum and stirred at room temperature for 10 min. GC and GC-MS analyses of the reaction mixture showed that **1a** was completely consumed to give the corresponding 1,4-digermacyclohexa-2,5-dienes.^{4c} The crude solution was chromatographed on silica gel TLC to give a 1:1 mixture of 1,1,4,4-tetramethyl-2,5-diphenyl-1,4-digermacyclohexa-2,5-diene and 1,1,4,4-tetramethyl-2,6-diphenyl-1,4-digermacyclohexa-2,5-diene (8 mg, 15 μ mol, 95% yield): ¹H NMR (δ , C₆D₆) 0.40 (s, 6H), 0.43 (s, 6H), 6.82 (s, 1H), 6.90 (s, 1H), 7.20–7.37 (m, 10H), 7.20–7.37 (m, 10H); ¹³C NMR (δ , CDCl₃) -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; MS *m/z* (relative intensity) 410 (M⁺, 22), 395 (21), 308 (17), 293 (30), 206 (19), 191 (27), 173 (41), 119 (100), 89 (100).

Reactions of Bis(triphenylphosphine)-2-phenyl-2-butene-1,1,4,4-tetraethyl-1,4-digerma-1,4-diylplatinum (1b) with Alkynes. The platinum-catalyzed insertion reactions of alkynes into the Ge–Ge bond of **1b** are summarized in Table 4.

As a representative example, the reaction of **1b** with phenylacetylene is described. To an NMR tube containing 1,4-digermabut-2-ene-1,4-diylplatinum (20 mg, 19 μ mol) were

Table 4. Reactions of 1,2-Digerma-2-buten-1,4-diylplatinum(II) (1b) with Alkynes

run	1,2-digerma-2-buten-1,4-diylplatinum	alkyne	conditions	yield/%	product ratio (2-isomer:3-isomer)
1	1b	Bu-C≡C-H	rt, 98 h	87	1:1
2	1b	Ph-C≡C-H	rt, 10 min	95	3:4
3	1b	MeO ₂ C-C≡C-H	rt, 12 h	84	1:1
4	1b	Ph-C≡C-Me	rt, 160 h	89	1:1

added phenylacetylene (34 mg, 194 μ mol) and C₆D₆ (0.7 mL) under an argon atmosphere. The solution was degassed under vacuum and stirred at room temperature for 10 min. GC and GC-MS analyses of the reaction mixture showed that **1b** was completely consumed to give corresponding 1,4-digermacyclohexa-2,5-dienes. The crude solution was chromatographed on silica gel TLC to give a 3:4 mixture of 1,1,4,4-tetraethyl-2,5-diphenyl-1,4-digermacyclohexa-2,5-diene and 1,1,4,4-tetraethyl-2,6-diphenyl-1,4-digermacyclohexa-2,5-diene (8 mg, 16 μ mol, 95% total isolated yield): ¹H NMR (δ , C₆D₆) 0.89–1.17 (m, 40H, EtGe), 6.90 (s, 2H, CH=), 6.97 (s, 2H, CH=), 7.07–7.35 (m, 20H, phenyl); ¹³C NMR (δ , CDCl₃) 7.23, 7.40, 7.97, 9.14, 9.39, 9.45, 11.23, 12.42, 125.90, 125.91, 126.06, 126.07, 126.15, 126.23, 126.44, 127.56, 128.10, 128.11, 128.21, 128.22, 128.28, 128.64, 128.99, 130.23, 133.19, 140.00, 142.63, 142.70, 146.39, 147.30, 159.07, 160.11; MS *m/z* (relative intensity) 466 (M⁺, 7), 437 (100), 408 (18), 161 (18), 132 (16). 1-Heynes (16.0 mg, 194 μ mol) and **1b** (20 mg, 19 μ mol): 1,1,4,4-Tetraethyl-2-butyl-5-phenyl-1,4-digermacyclohexa-2,5-diene and 1,1,4,4-tetraethyl-3-butyl-5-phenyl-1,4-digermacyclohexa-2,5-diene (8 mg, 17 μ mol, 87% isolated yield): ¹H NMR (δ , C₆D₆) 0.84–1.24 (m, 40H, EtGe), 1.24–1.53 (m, 18H, C–Bu), 6.57 (s, 1H, CH=), 6.62 (s, 1H, CH=), 6.91 (s, 1H, CH=), 6.93 (s, 1H, CH=), 7.02–7.36 (m, 10H, phenyl); ¹³C NMR (δ , CDCl₃) 7.10, 7.41, 8.11, 8.42, 9.65, 10.66, 12.66, 14.46, 22.87, 30.06, 30.84, 31.08, 31.46, 38.16, 40.53, 41.47, 125.89, 125.96, 126.08, 126.22, 128.03, 128.09, 128.25, 128.62, 129.97, 133.07, 136.45, 137.18, 137.42, 142.60, 143.04, 147.36; MS *m/z* (relative intensity) 417 (100), 386 (13), 335 (23), 316 (10), 161 (11). 1-Phenyl-1-propyne (24 mg, 200 μ mol) and **1b** (20 mg, 19 μ mol): 1,1,4,4-Tetraethyl-2-methyl-3,5-diphenyl-1,4-digermacyclohexa-2,5-diene and 1,1,4,4-tetraethyl-3-methyl-2,5-diphenyl-1,4-digermacyclohexa-2,5-diene (8 mg, 18 μ mol, 89% isolated yield): ¹H NMR (δ , C₆D₆) 0.83–1.38 (m, 40H, EtGe), 1.53 (s, 3H, C–Me), 6.93 (s, 1H, CH=), 6.95 (s, 1H, CH=), 7.01–7.35 (m, 10H, phenyl); ¹³C NMR (δ , CDCl₃) 6.18, 6.35, 6.42, 6.49, 9.10, 9.34, 9.36, 9.50, 19.87, 20.03, 125.16, 125.21, 125.95, 126.26, 126.31, 127.10, 127.20, 127.25, 128.01, 128.03, 128.12, 128.15, 128.24, 128.29, 128.31, 130.00, 133.20, 142.99, 143.12, 143.45, 143.72, 146.88, 148.05, 159.65; MS *m/z* (relative intensity) 480 (M⁺, 8), 451 (100), 436 (18), 407 (18), 350 (19), 335 (43), 306 (8), 205 (16), 160 (32). Methyl propiolate (17 mg, 200 μ mol) and **1b** (20 mg, 19 μ mol): 1,1,4,4-Tetraethyl-2-methylcarboxylate-5-phenyl-1,4-digermacyclohexa-2,5-diene and 1,1,4,4-tetraethyl-2-methylcarboxylate-6-phenyl-1,4-digermacyclohexa-2,5-diene (7 mg, 16 μ mol, 84% isolated yield): ¹H NMR (δ , C₆D₆) 0.79–1.39 (m, 40H, EtGe), 3.41 (s, 3H, CO₂Me), 3.42 (s, 3H, CO₂Me), 6.76 (s, 1H, CH=), 6.91 (s, 1H, CH=), 8.34 (s, 1H, CH=), 8.36 (s, 1H, CH=), 6.94–7.35 (m, 10H, phenyl); ¹³C NMR (δ , CDCl₃) 6.97, 7.38, 7.60, 7.79, 8.07, 9.27, 9.33, 9.39, 51.79, 52.01, 125.85, 125.99, 126.39, 126.59, 128.15, 128.27, 129.99, 140.88, 143.22, 147.14, 149.14, 158.87, 159.81, 160.33, 160.68, 67.42, 243.14, 143.15; MS *m/z* (relative intensity) 448 (M⁺, 9), 419 (54), 390 (100), 361 (23), 332 (21), 317 (11), 259 (9), 230 (7).

NMR Study of Reactions of Bis(triphenylphosphine)-2-phenyl-2-butene-1,1,4,4-tetramethyl-1,4-digerma-1,4-diylplatinum (1a) with Methyl Propiolate. In an NMR tube with a septum seal were placed 1,4-digermabut-2-ene-1,4-diylplatinum (20 mg, 19 μ mol), methyl propiolate (1.6 μ L, 18 μ mol), and C₆D₆ (0.7 mL). The solution was degassed and sealed under vacuum. The progress of the reaction was monitored at room temperature for 10 min by means of NMR spectroscopy. The NMR signals assigned to 1,4-digerma-1,4-

diylplatinum (**1a**) and methyl propiolate decayed, making possible immediate observation of a buildup of new NMR signals of the products of the methyl propiolate insertion into the Ge–Ge bond of **1a** (**2a,b**). NMR signals of the methyl propionate insertion products **2a,b** gradually disappeared, and other signals assigned to 1,4-digermacyclohexa-2,5-dienes (**3a,b**) appeared, which were observed as final products. (η -Methyl propiolate)bis(triphenylphosphine)platinum was also detected by NMR analysis.¹³ Cyclic germyl(vinylgermyl)-platinum **2a**: ¹H NMR (δ , C₆D₆) –0.17 (s, $J_{\text{Pt-H}} = 14$ Hz, 6H, PtGeCH₃), 1.03 (s, 6H, GeCH₃), 3.41 (s, 3H, CO₂Me), 6.77–7.64 (m, 37H, phenyl, 1H, CH=); ³¹P NMR (δ , C₆D₆) 24.1 (d with two satellites, $J_{\text{P-P}} = 15$ Hz, $J_{\text{Pt-P}} = 2200$ Hz), 25.3 (d with two satellites, $J_{\text{P-P}} = 15$ Hz, $J_{\text{Pt-P}} = 1822$ Hz). **2b**: ¹H NMR (δ , C₆D₆) –0.44 (s, $J_{\text{Pt-H}} = 11$ Hz, 6H, PtGeCH₃), 1.15 (s, 6H, GeCH₃), 3.43 (s, 3H, CO₂Me), 6.77–7.64 (m, 37H, phenyl, 1H, CH=); ³¹P NMR (δ , C₆D₆) 22.5 (d with two satellites, $J_{\text{P-P}} = 15$ Hz), 25.8 (d with two satellites, $J_{\text{P-P}} = 15$ Hz).

Reactions of Bis(triphenylphosphine)-2-phenyl-2-butene-1,1,4,4-tetramethyl-1,4-digerma-1,4-diylplatinum (1a) with Methyl Propiolate. In an NMR tube with a septum seal were placed 1,4-digermabut-2-ene-1,4-diylplatinum (20 mg, 19 μ mol), methyl propiolate (17 μ L, 194 μ mol), and C₆D₆ (0.7 mL) at ambient temperature. The solution was degassed and sealed under vacuum. The progress of the reaction was examined by means of NMR spectroscopy. The reaction mixture was separated by preparative silica gel TLC eluting with a 5:2 mixture of hexane/benzene. A 3:1 mixture of 1,1,4,4-tetramethyl-2-carboxylate-5-phenyl-1,4-digermacyclohexa-2,5-diene and 1,1,4,4-tetramethyl-3-carboxylate-5-phenyl-1,4-digermacyclohexa-2,5-diene was obtained in 87% yield (8 mg, 17 μ mol): ¹H NMR (δ , C₆D₆) 0.34 (s, 6H), 0.41 (s, 6H), 0.50 (s, 6H), 0.59 (s, 6H), 3.73 (s, 3H), 3.74 (s, 3H), 6.65 (s, 1H), 6.76 (s, 1H) <7.95 (s, 1H), 7.97 (s, 1H), 7.13–7.46 (m, 10H); ¹³C NMR (δ , CDCl₃) –1.39, –0.5, 0, 2.48, 51.84, 52.11, 125.96, 126.08, 126.20, 126.49, 126.70, 128.15, 128.27, 128.70, 141.41, 143.98, 146.25, 150.57, 158.68, 160.12, 160.43, 161.62, 239.64, 139.64; MS *m/z* (relative intensity) 392 (M⁺, 49), 377 (10), 346 (27), 316 (14), 259 (100), 244 (23), 133 (18), 118 (46), 103 (36). Anal. Calcd for C₁₆H₂₂O₂Ge₂: C, 49.08; H, 5.66. Found: C, 49.25; H, 5.43.

Reactions of 1,4-Digermabut-2-ene-1,4-diylplatinum-(II) (1a) with Carbon Monoxide. A solution of **1a** (20 mg, 19.5 μ mol) in C₆D₆ (2.2 mL) was stirred under carbon monoxide (1 atm) at room temperature for 22 h. The solution was concentrated to dryness under reduced pressure to give the crude product, which was dissolved in benzene. The reaction mixture was eluted by preparative silica gel TLC with benzene. White crystals were obtained in 71% yield (11 mg, 14 μ mol): ¹H NMR (δ , C₆D₆, 23 °C) 0.23 (s with two satellites, $J_{\text{Pt-H}} = 15.7$ Hz, 6H), 0.29 (s with two satellites, $J_{\text{Pt-H}} = 18.7$ Hz, 6H), 1.02 (d with two satellites, $J_{\text{P-H}} = 2.3$ Hz, $J_{\text{Pt-H}} = 20.1$ Hz, 6H), 1.09 (d with two satellites, $J_{\text{P-H}} = 2.2$ Hz, $J_{\text{Pt-H}} = 20.1$ Hz, 6H), 6.80–7.63 (m, 42H); ³¹P NMR (δ , C₆D₆, 23 °C) 25.6 (s with two satellites, $J_{\text{Pt-P}} = 2022$ Hz), 26.4 (s with two satellites, $J_{\text{Pt-P}} = 2044$ Hz); ¹³C NMR (δ , CD₂Cl₂, 23 °C) 3.39, 4.20, 5.04, 5.95, 125.52, 125.81, 126.72, 126.75, 127.74, 128.06, 128.40, 128.63, 128.63, 128.77, 128.77, 129.07, 130.76, 130.79, 133.59, 133.67, 133.77, 133.93, 134.04, 134.18, 222.04, 239.89; IR (cm^{–1}) 2038.6(CO). Anal. Calcd for C₃₁H₃₃Ge₂OPPt: C, 46.96; H, 4.20. Found: C, 72.25; H, 4.45.

Reactions of 1,4-Digermabuta-2-ene-1,4-diylplatinum-(II) (1a) with *tert*-Butyl Isocyanide. To a Schlenk flask containing **1a** (30 mg, 29 μ mol) were added toluene (2 mL) and *tert*-butyl isocyanide (30 μ L, 268 μ mol), in that order. After it had been stirred for 1 h at room temperature, the reaction mixture was completely evaporated under vacuum, and the resulting residue became solid when benzene was added. The solids were filtered and washed with hexane. Recrystallization from benzene gave white crystals of (*tert*-butylisocyanide)-(triphenylphosphine)-2-phenyl-1,1,4,4-tetramethyl-1,4-digermabuta-2-ene-1,4-diylplatinum (20 mg, 23 μ mol, 80% yield): ^1H NMR (δ , CD_2Cl_2 , 23 $^\circ\text{C}$) -0.32 (s with two satellites, $J_{\text{Pt-H}} = 14.6$ Hz, 6H), -0.30 (s with two satellites, $J_{\text{Pt-H}} = 14.6$ Hz, 6H), 0.41 (d with two satellites, $J_{\text{P-H}} = 2.2$ Hz, $J_{\text{Pt-H}} = 19.4$ Hz, 6H), 0.46 (d with two satellites, $J_{\text{P-H}} = 2.2$ Hz, $J_{\text{Pt-H}} = 19.0$ Hz, 6H), 1.15 (s, 9H), 1.16 (s, 9H), 6.74 – 7.62 (m, 42H); ^{31}P NMR (δ , CD_2Cl_2 , 23 $^\circ\text{C}$) 25.0 (s with two satellites, $J_{\text{Pt-P}} = 2035$ Hz), 25.8 (s with two satellites, $J_{\text{Pt-P}} = 2040$ Hz); ^{13}C NMR (δ , CD_2Cl_2 , 23 $^\circ\text{C}$) 3.03 , 3.87 , 4.77 , 5.65 , 29.8 , 29.9 , 29.9 , 30.01 , 125.24 , 126.73 , 126.78 , 126.82 , 127.53 , 127.86 , 128.22 , 128.34 , 128.51 , 128.67 , 130.01 , 131.93 , 131.96 , 132.09 , 133.87 , 133.98 , 134.00 , 134.14 , 134.16 , 134.24 , 153.88 , 153.97 ; IR (cm^{-1}) 2158.2 ν (CN). Anal. Calcd for $\text{C}_{35}\text{H}_{42}\text{Ge}_2\text{PNPt}$: C, 47.63; H, 4.99. Found: C, 47.85; H, 4.70.

Reactions of 1,4-Digermabuta-2-ene-1,4-diylplatinum-(II) (1a) with Cyclohexyl Isocyanide. To a Schlenk flask containing **1a** (100 mg, 97 μ mol) were added toluene (3 mL) and *tert*-butyl isocyanide (36 μ L, 292 μ mol), in that order. After

it had been stirred for 1 h at room temperature, the reaction mixture was completely evaporated under vacuum. The resulting residue became solid on addition of benzene. The solids were filtered and washed with hexane. Recrystallization from benzene gave white crystals of (*tert*-cyclohexylisocyanide)-(triphenylphosphine)-2-phenyl-1,1,4,4-tetramethyl-1,4-digermabuta-2-ene-1,4-diylplatinum (42 mg, 48 μ mol, 49% yield): ^1H NMR (δ , CD_2Cl_2 , 23 $^\circ\text{C}$) -0.29 (br, 6H), 0.44 (br, 6H), 1.05 – 1.73 (m, 10H), 3.38 (br, 1H), 6.67 – 7.65 (m, 21H); ^{31}P NMR (δ , CD_2Cl_2 , -50 $^\circ\text{C}$) 25.0 (br, s with two satellites, $J_{\text{Pt-P}} = 2022$ Hz); ^{13}C NMR (δ , CD_2Cl_2 , 23 $^\circ\text{C}$) 3.16 (br), 5.81 (br), 23.27 , 25.11 , 32.24 , 25.11 , 32.24 , 54.56 , 125.14 , 126.78 , 126.82 , 128.24 , 128.37 , 130.03 , 133.98 , 134.15 , 134.97 , 135.48 , 153.88 (br). Anal. Calcd for $\text{C}_{37}\text{H}_{44}\text{Ge}_2\text{PNPt}$: C, 50.85; H, 5.07. Found: C, 50.55; H, 4.82.

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