Organometallics **2005,** *24,* 4734−4741

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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Received April 13, 2005

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 trigermanes 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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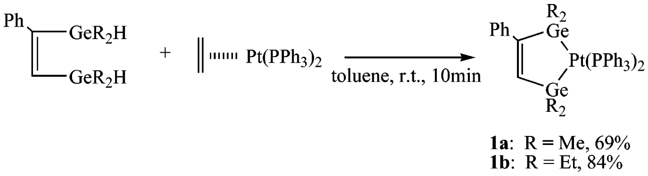
Results and Discussion

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(germyl)platinum(II) complexes and similar to those of the *cis*-isomer.[4c]

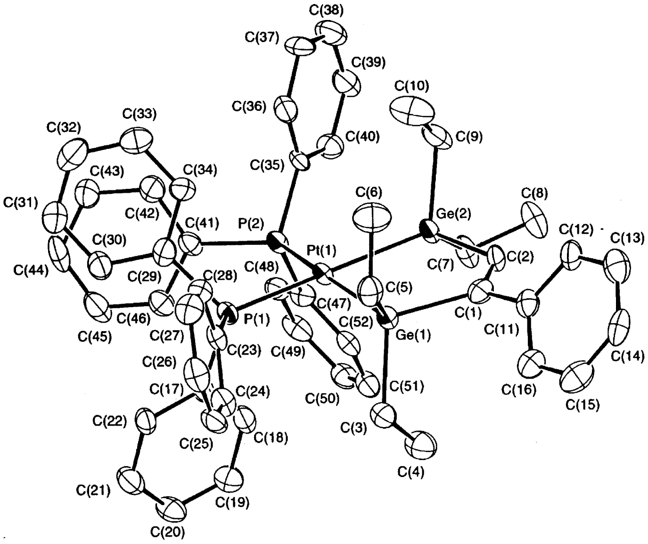
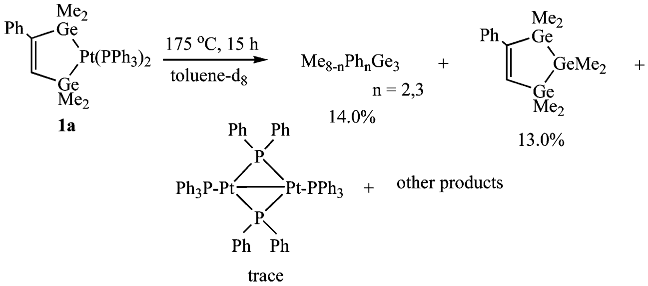


Figure 1. ORTEP view of **1b**. Thermal ellipsoids are drawn at 30% probability levels, and hydrogen atoms are omitted for clarity.

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)	

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 trigermanes (14%) and 1,2,3-trigermcyclopent-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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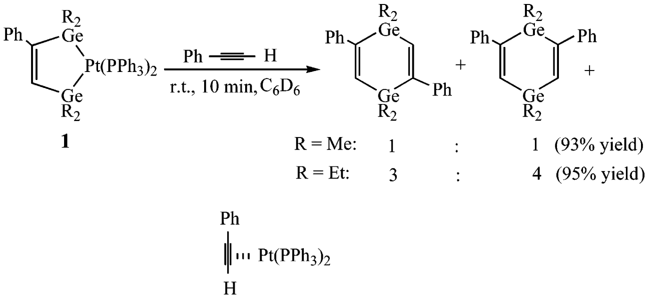
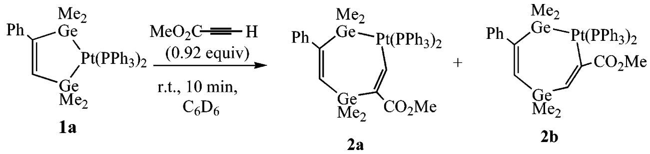
The presence of trigermanes and 1,2,3-trigermacyclopent-4-ene may have been due to the generation of a dimethylgermylene unit from **1a**.[12] The germylene then inserted into the activated Ge−Ge bond of 1,2-digermacyclobut-3-ene, produced by reductive elimination from **1a** with the regeneration of platinum species to afford 1,2,3-trigermacyclopent-4-ene. It is well known that the dimerization of germylenes 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-enes in toluene smoothly produced the corresponding 1,4-digermacyclohexa-2,5-dienes in moderate to good yield.[4c,5] 1,4-Digerma-2-buten-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]



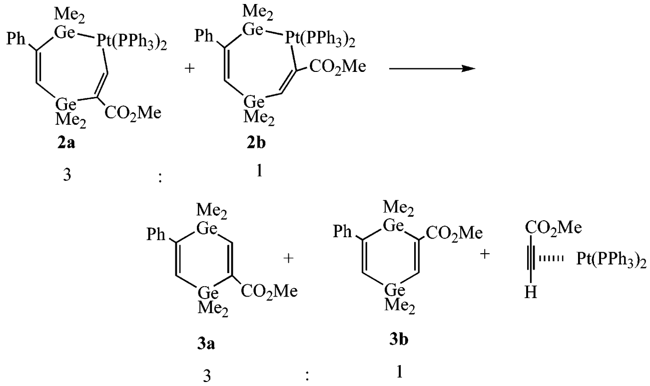
The reactions of **1b** with other terminal and internal alkynes such as 1-hexyne, methyl propiolate, and l-phenyl-1-propyne also gave the corresponding 1,4-digermacyclohexa-2,5-dienes in moderate to good yield. Internal alkynes such as diphenylacetylene, bis(trimethylsilyl)-acetylene, and dimethyl acetylenedicarboxylate 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_{Pt-P} = 2198 Hz, J_{P-P} = 17 Hz) and 29.9 ppm (J_{t-P} = 2219 Hz, J_{P-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_{Pt-P} = 2200 Hz, J_{P-P} = 15 Hz) and 25.3 ppm (d with two satellites, J_{Pt-P} = 1822 Hz, J_{P-P} = 15 Hz), and 22.5 ppm (d, J_{P-P} = 15 Hz) and 25.5 ppm (d, J_{P-P} = 15 Hz). The Pt satellites in **2b** could not be observed in the ^{31}P NMR spectrum due to its low intensity. The ^{1}H NMR spectrum of **2a** showed three singlets at −0.71 ppm (J_{Pt-H} = 14 Hz) due to the methyl group of the platinum-bound dimethylgermyl group (Pt-GeMe$_2$), at 1.03 ppm due to another dimethylgermyl group (GeMe$_2$), at 3.41 ppm due to the methyl ester group (CO$_2$Me), and multiplet signals in the range 6.80−7.80 ppm due to the phenyl groups and the olefinic proton. The ^{1}H NMR spectrum of **2b** showed three methyl signals at −0.44 ppm (J_{Pt-H} = 11 Hz) due to Pt-GeMe$_2$, at 1.15 ppm due to GeMe$_2$, at 3.43 ppm due to CO$_2$Me, 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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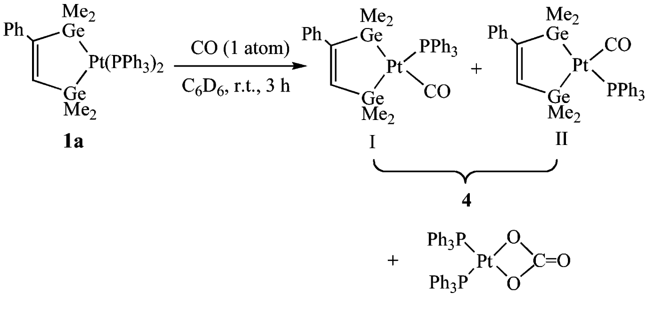
Reactions of Platinum(II) Complex 1a with Carbon Monoxide. Although many interesting reactions of bis(germyl)platinum(II) complexes toward unsaturated organic compounds via the Pt−Ge bond cleavage have been reported, there has been no study of the insertion of small molecules such as carbon monoxide into the Pt−Ge bond in these complexes. A large excess of carbon monoxide was bubbled into a C_6D_6 solution of **1a** at room temperature for 3 h. The product was identified to be the 1,4-digerma-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 ($[Pt(PPh_3)_2CO_3]$) was formed as a minor byproduct. The identify of all products was determined by IR and NMR spectroscopy. The structure of $[Pt(PPh_3)_2CO_3]$ 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 C_6D_6 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 ^{31}P NMR of **4** in C_6D_6 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]

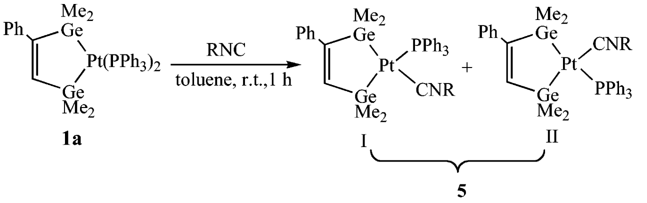


The preparation of $[Pt(PPh_3)_2CO_3]$ by the reaction of $[Pt(PPh_3)_4]$ with oxygen under a carbon dioxide atmosphere and its structural characterization by X-ray analysis have been reported by Dell'Amico and coworkers[15] and other groups.[16,17]

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-digerma-2-butene-1,4-diylplatinum(II) complexes (**5**) containing both phosphine and isocynanide 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 CD_2Cl_2 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

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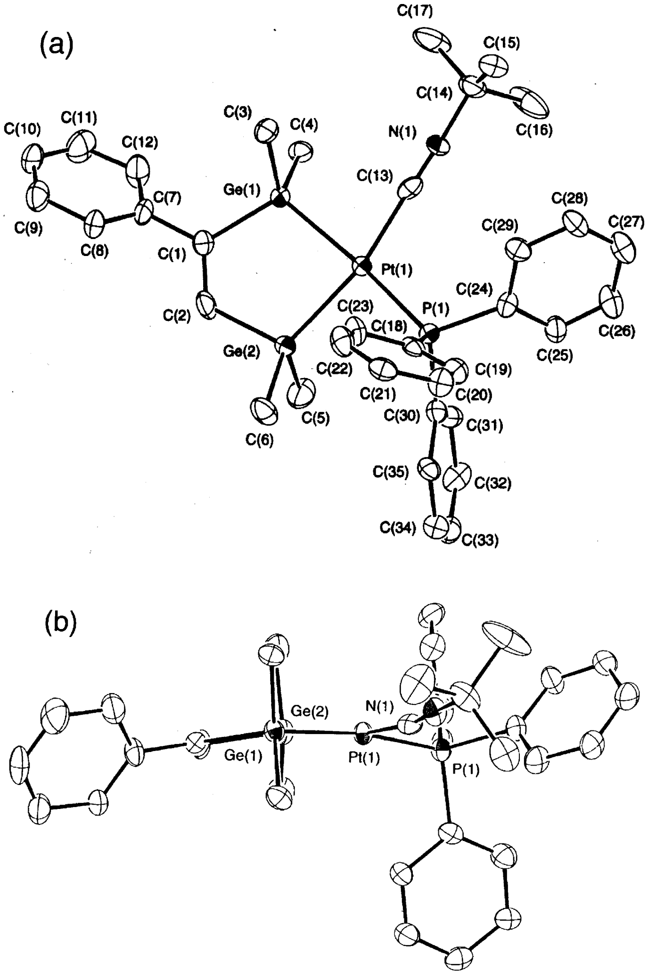

Figure 2. ORTEP view of **5a**-I: (a) top view, (b) side view. Thermal ellipsoids are drawn at 30% probability levels, and hydrogen atoms are omitted for clarity.

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)plantinum(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 N_2 or argon using standard Schlenk line techniques. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian Unity Inova-400 MHz. GC-MS spectra were measured with a JEOL JMS-DX 303 mass spectrometer. The UV and UV−vis spectra were recorded on a Shimadzu UV 2200 spectrometer. IR spectra were recorded on a Shimadzu FT IR 4200 spectrometer. Gas chromatographic analyses were performed with 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 ($\lambda = 0.71073$ Å) radiation. The structures were solved by direct methods using the program system SIR-92 and refined with all data on F^2 by means of SHELXL-97. A refinement was performed by a Silicon Graphics O_2 with maXus.

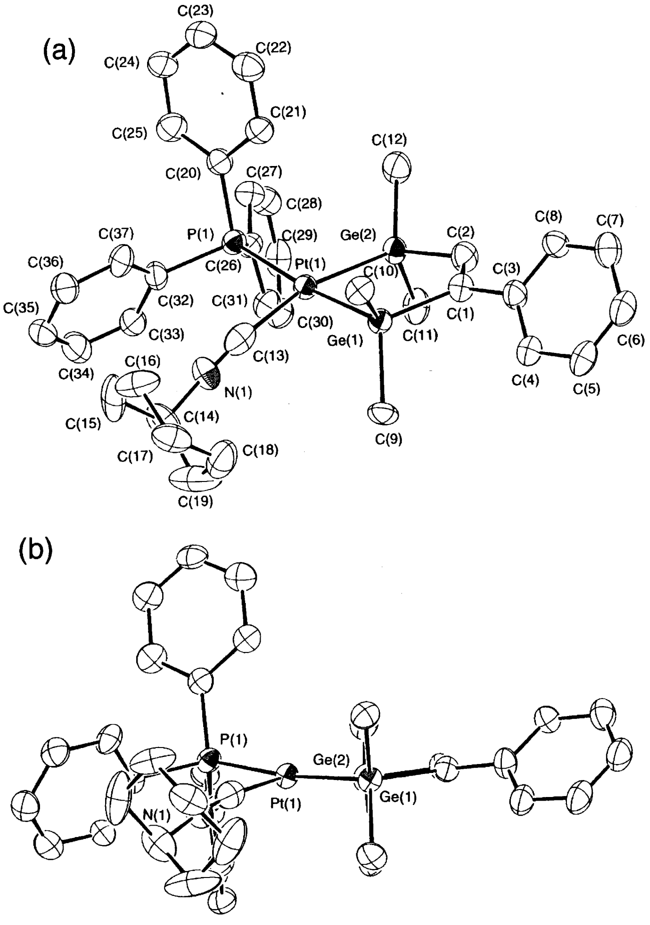

Figure 3. ORTEP view of **5b**: (a) top view, (b) side view. Thermal ellipsoids are drawn at 30% probability levels, and hydrogen atoms are omitted for clarity.

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) 2.35483)	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)platinum[13] 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 $LiAlH_4$ (0.39 g, 10.3 mmol) was stirred

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[18] Blake, D. M.; Roundhill, D. M. *Inorg. Synth.* **1978**, *18*, 120.

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

	1b	**5a**-I	**5b**
formula	$C_{52}H_{56}Ge_2P_2Pt$	$C_{35}H_{42}Ge_2NP_{Pt}$	$C_{37}H_{44}Ge_2NPPt$
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	$P\bar{1}$	Pn	Pn
unit cell dimens			
a (Å)	12.5340(16)	9.5910(4)	9.3510(6)
b (Å)	12.9030(17)	11.0280(5)	11.2320(7)
c (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)		
V (Å^3)	1234.8(5)	1707.72(12)	1735.34(17)
Z	2	2	2
radiation Mo Kα (Å)	0.71070	0.71070	0.71070
temperature (K)	120	120	120
D_{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
R_1 ($I > 2\sigma(I)$)	0.0398	0.0372	0.0472
wR_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): ^{1}H NMR (δ, C_6D_6) 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); ^{13}C NMR (δ, $CDCl_3$) 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 $C_{16}H_{28}Ge_2$: 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 μmol) and (η-ethylene)bis(triphenylphosphine)platinum (208 mg, 278 ηmol) 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 μmol, 84.4% yield). **1a**: ^{1}H NMR (δ, C_6D_6) 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=); ^{31}P NMR (δ, C_6D_6) 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); ^{13}C NMR (δ, CD_2Cl_2) 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 $C_{48}H_{48}Ge_2P_2Pt$: 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 μmol) with (η-ethylene)bis(triphenylphosphine)platinum (201 mg, 269 ηmol) 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 μmol, 69% yield). **1b**: ^{1}H NMR (δ, C_6D_6) 0.45−1.42 (m, 20H), 6.75−7.67 (m, 36H); ^{13}C NMR (δ, CD_2Cl_2) 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; ^{31}P NMR (δ, C_6D_6) 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 $C_{52}H_{56}Ge_2P_2Pt$: 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 μmol) 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 trigermanes, $Me_{8-n}Ph_nGe_3$ (n = 2, 3) (14%) and 1,2-3-trigermcyclopentene (13%), and a dinuclear platinum(II) complex, $[Pt_2(PPh_3)_2(PPh_2)_2]$ (trace). The germanium compounds were carefully characterized by ^{1}H, ^{13}C, ^{31}P NMR, and GC-MS data, which were compared with those of related germanium compounds. The identity of the dinuclear platinum(II) complex, $[Pt_2(PPh_3)_2(\mu\text{-}PPh_2)_2]$, 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] ^{1}H NMR (δ, $CDCl_3$) 0.35 (s, 12H), 0.39 (s, 6H), 6.75−7.45 (m, 6H); ^{13}C NMR (δ, $CDCl_3$) −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 trigermanes, $Me_{8-n}Ph_nGe_3$ (n = 2, 3):[7,8] ^{1}H NMR (δ, $CDCl_3$) 0.04 (s), 0.31 (s), 0.32 (s), 6.75−7.50 (m); ^{13}C NMR (δ, $CDCl_3$) −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$^+$ − $GeMe_3$, 20), 283 (M$^+$ − $GeMe_2Ph$, 10), 243 ($GeMePh_2^+$, 100), 181 ($GeMe_2Ph^+$, 50); GC-MS *m/z* (relative intensity) for n = 3, 462 (M$^+$, 462), 447 (M$^+$ − Me, 25), 283 (M$^+$ − $GeMe_2Ph$, 25), 243 (Ph_2MeGe^+, 15), 181 ($PhMe_2Ge^+$, 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 μmol) were added phenylacetylene (34 mg, 194 μmol) and C_6D_6 (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-teramethyl-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 μmol, 95% yield): ^{1}H NMR (δ, C_6D_6) 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); ^{13}C NMR (δ, $CDCl_3$) −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 μmol) 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_2C−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 μmol) and C_6D_6 (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-teraethyl-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 μmol, 95% total isolated yield):[5] ^{1}H NMR (δ, C_6D_6) 0.89−1.17 (m, 40H, EtGe), 6.90 (s, 2H, CH=), 6.97 (s, 2H, CH=), 7.07−7.35 (m, 20H, phenyl); ^{13}C NMR (δ, $CDCl_3$) 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, 129.99, 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 μmol) and **1b** (20 mg, 19 μmol): 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 μmol, 87% isolated yield): ^{1}H NMR (δ, C_6D_6) 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); ^{13}C NMR (δ, $CDCl_3$) 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 μmol) and **1b** (20 mg, 19 μmol): 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 μmol, 89% isolated yield): ^{1}H NMR (δ, C_6D_6) 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); ^{13}C NMR (δ, $CDCl_3$) 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 μmol) and **1b** (20 mg, 19 μmol): 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 μmol, 84% isolated yield): ^{1}H NMR (δ, C_6D_6) 0.79−1.39 (m, 40H, EtGe), 3.41 (s, 3H, CO_2Me), 3.42 (s, 3H, CO_2Me), 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); ^{13}C NMR (δ, $CDCl_3$) 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 Propionate. In an NMR tube with a septum seal were placed 1,4-digermabut-2-ene-1,4-diylplatinum (20 mg, 19 μmol), methyl propiolate (1.6 μL, 18 μmol), and C_6D_6 (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-dilylplatinum (**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**: ^{1}H NMR (δ, C_6D_6) −0.17 (s, J_{Pt-H} = 14 Hz, 6H, $PtGeCH_3$), 1.03 (s, 6H, $GeCH_3$), 3.41 (s, 3H, CO_2Me), 6.77−7.64 (m, 37H, phenyl, 1H, CH=); ^{31}P NMR (δ, C_6D_6) 24.1 (d with two satellites, J_{P-P} = 15 Hz, J_{Pt-P} = 2200 Hz), 25.3 (d with two satellites, J_{P-P} = 15 Hz, J_{Pt-P} = 1822 Hz). **2b**: ^{1}H NMR (δ, C_6D_6) −0.44 (s, J_{Pt-H} = 11 Hz, 6H, $PtGeCH_3$), 1.15 (s, 6H, $GeCH_3$), 3.43 (s, 3H, CO_2Me), 6.77−7.64 (m, 37H, phenyl, 1H, CH=); ^{31}P NMR (δ, C_6D_6) 22.5 (d with two satellites, J_{P-P} = 15 Hz), 25.8 (d with two satellites, J_{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 μmol), methyl propiolate (17 μL, 194 μmol), and C_6D_6 (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 μmol): ^{1}H NMR (δ, C_6D_6) 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); ^{13}C NMR (δ, $CDCl_3$) −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 $C_{16}H_{22}O_2Ge_2$: 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 μmol) in C_6D_6 (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 separative silica gel TLC with benzene. White crystals were obtained in 71% yield (11 mg, 14 μmol): ^{1}H NMR (δ, C_6D_6, 23 °C) 0.23 (s with two satelliteds, J_{Pt-H} = 15.7 Hz, 6H), 0.29 (s with two satellites, J_{Pt-H} = 18.7 Hz, 6H), 1.02 (d with two satellites, J_{P-H} = 2.3 Hz, J_{Pt-H} = 20.1 Hz, 6H), 1.09 (d with two satellites, J_{P-H} = 2.2 Hz, J_{Pt-H} = 20.1 Hz, 6H), 6.80−7.63 (m, 42H); ^{31}P NMR (δ, C_6D_6, 23 °C) 25.6 (s with two satellites, J_{Pt-P} = 2022 Hz), 26.4 (s with two satellites, J_{Pt-P} = 2044 Hz); ^{13}C NMR (δ, CD_2Cl_2, 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 $C_{31}H_{33}Ge_2OPPt$: C, 46,96; H, 4.20. Found: C, 72.25; H, 4.45.

Reactions of 1,4-Digermabut-2-ene-1,4-diylplatinum(II) (1a) with *tert*-Butyl Isocyanide. To a Schlenk flask containing **1a** (30 mg, 29 μmol) were added toluene (2 mL) and *tert*-butyl isocyanide (30 μL, 268 μmol), 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-dilylplatinum (20 mg, 23 μmol, 80% yield): ^{1}H NMR (δ, CD_2Cl_6, 23 °C) −0.32 (s with two satellites, $J_{Pt-H} = 14.6$ Hz, 6H), −0.30 (s with two satellites, $J_{Pt-H} = 14.6$ Hz, 6H), 0.41 (d with two satellites, $J_{P-H} = 2.2$ Hz, $J_{Pt-H} = 19.4$ Hz, 6H), 0.46 (d with two satellites, $J_{P-H} = 2.2$ Hz, $J_{Pt-H} = 19.0$ Hz, 6H), 1.15 (s, 9H), 1.16 (s, 9H), 6.74−7.62 (m, 42H); ^{31}P NMR (δ, CD_2Cl_2, 23 °C) 25.0 (s with two satellites, $J_{Pt-P} = 2035$ Hz), 25.8 (s with two satellites, $J_{Pt-P} = 2040$ Hz); ^{13}C NMR (δ, CD_2Cl_2, 23 °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 $C_{35}H_{42}Ge_2PNPt$: C, 47.63; H, 4.99. Found: C, 47.85; H, 4.70.

Reactions of 1,4-Digermabut-2-ene-1,4-diylplatinum(II) (1a) with Cyclohexyl Isocyanide. To a Schlenk flask containing **1a** (100 mg, 97 μmol) were added toluene (3 mL) and *tert*-butyl isocyanide (36 μL, 292 μmol), 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-dilylplatinum (42 mg, 48 μmol, 49% yield): ^{1}H NMR (δ, CD_2Cl_6, 23 °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 °C) 25.0 (br, s with two satellites, $J_{Pt-P} = 2022$ Hz); ^{13}C NMR (δ, CD_2Cl_2, 23 °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 $C_{37}H_{44}Ge_2PNPt$: C, 50.85; H, 5,07. Found: C, 50.55; H, 4.82.

Acknowledgment. We thank Miss Mariko Kanai for preliminary experiments of this study. This work was supported by a Grant-in-Aid for Priority Area Research on “Dynamic Complex” from the Ministry of Education, Culture, Science, Sports, and Technology, Japan.

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OM058021V