

# Digermylplatinum(II) Organometallic Rings

## $L_2PtGe(Me_2)EGeMe_2$ [ $E = N-, O, S, (\eta-C_5H_4)_2Fe$ ]

J. Barrau,\* G. Rima, V. Cassano, and J. Satgé

Laboratoire de chimie des Organominéraux, URA 477 du CNRS, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex, France

Received February 21, 1995\*

The synthesis, reactivity, and characterization of the digermylplatinum(II) linear complexes  $(ClMe_2Ge)_2Pt(PPh_3)_2$  (**1**) and  $(ClMe_2Ge)_2Pt(diphos)$  (**2**) and cyclic complexes  $(diphos)PtGe(Me_2)EGeMe_2$  [ $E = S$  (**3**),  $-NPh$  (**4**),  $(\eta^5-C_5H_4)Fe(\eta^5-C_5H_4)$  (**5**),  $O$  (**6**)] are reported. The chemistry of **2–6** is illustrated through their reactions with phenylacetylene and N-methyltriazolinedione. Complexes **3** and **6** give double germylation of these unsaturated systems, while **2**, by reaction with triazolinedione, gives the monogermylated complex  $Me_2GePt(Cl)diphos$  and the dimer of the germylated heterocycle  $Me_2GeNC(O)N(Me)C(O)N$ .

### Introduction

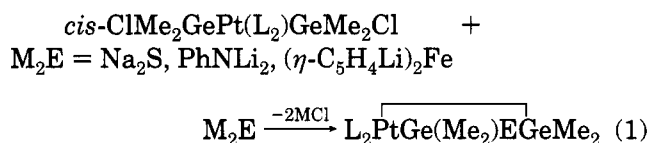
There recently has been a great interest in the use of transition-metal complexes to catalyze the formation and cleavage of metal 14–metal 14 bonds.<sup>1</sup> In continuation of our studies on cyclic silyl- or germyliron, -ruthenium, -dicobalt, and -platinum complexes,<sup>2,3</sup> we have explored the potential of new three-, four-, and five-membered cyclic germanium–transition-metal compounds in the context of (i) new germanium–transition-metal chemistry and (ii) stabilization of strained cyclic, transient divalent, or unsaturated germanium–transition-metal compounds. In this area the chemistry of silyl–transition-metal complexes<sup>4–10</sup> is more advanced than that of germyl–transition-metal complexes.

We report here the details of the synthesis and characterization of new digermylplatinum(II) four-membered cyclic compounds of type  $L_2PtGe(Me_2)EGeMe_2$  [ $E = N-, O, S, (\eta^5-C_5H_4)Fe(\eta^5-C_5H_4)$ ].

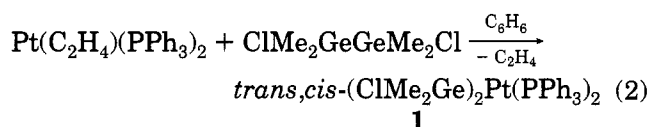
### Results and Discussion

For these syntheses, treatment of bis(chlorogermyl) derivatives with alkali-metal reagents, the classic route to germanium-containing heterocycles with Ge–E–Ge

linkages, was applied to a *cis*-bis(chlorogermyl)platinum complex (eq 1).



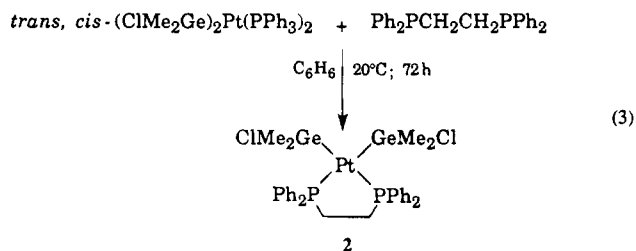
**1. *cis*-Bis(chlorogermyl)platinum Complexes.** When 1,2-dichlorotetramethyldigermene in benzene was treated with the platinum complex  $Pt(C_2H_4)(PPh_3)_2$ , a selective oxidative addition of the germanium–germanium bond gave a mixture of *cis*- and *trans*-bis(chlorogermyl)platinum complexes, **1** (eq 2). When the solution



was 0.05 M in platinum, the *trans*/*cis* ratio was 95/5. When the solution was more concentrated [0.2 M in Pt], the ratio was 80/20.

From dilute solution *cis* complex **1** was isolated by crystallization as yellow crystals. When these were dissolved in  $CD_2Cl_2$ , rapid isomerization occurred to give, at room temperature, a 90/10 *cis*/*trans* mixture after 30 min and a 70/30 equilibrium mixture after 3 h; this ratio did not change after several hours.

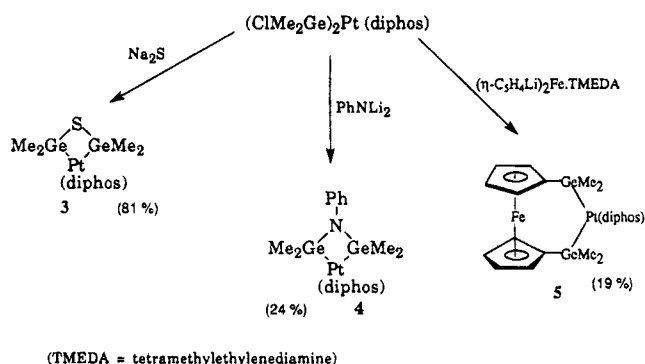
Treatment of the *cis* and *trans* complexes with 1,2-bis(diphenylphosphino)ethane (diphos) produced the *cis* complex **2** (eq 3). The latter was characterized by mass



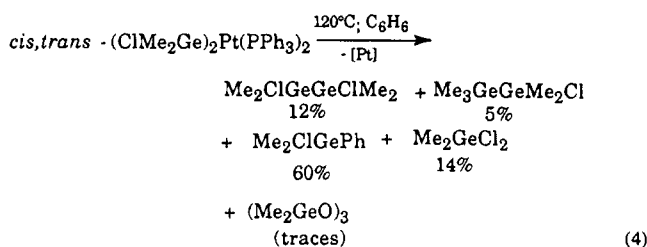
spectroscopy and NMR analyses.

- \* Abstract published in *Advance ACS Abstracts*, September 15, 1995.  
 (1) (a) Yamashita, H.; Tanaka, M.; Goto, M. *Organometallics* **1992**, *11*, 3227. (b) Pannell, K. H.; Cervantes, J.; Parkanyi, L.; Cervantes Lee, F. *Organometallics* **1990**, *9*, 859. (c) Pannell, K. H.; Brun, M. C.; Sharma, H.; Jones, K.; Sharma, S. *Organometallics* **1994**, *13*(4), 1075. (d) Finckh, W.; Tang, B. Z.; Lough, A.; Manners, I. *Organometallics* **1992**, *11*, 2904. (e) Ishikawa, M.; Naka, A.; Okazaki, S.; Sakamoto, H. *Organometallics* **1993**, *12*, 87 and references therein.  
 (2) Barrau, J. *Heteroat. Chem.* **1991**, *2*(6), 601.  
 (3) Barrau, J.; Rima, G.; Cassano, V.; Satgé, J. *Inorg. Chim. Acta* **1992**, *198–200*, 461.  
 (4) Belluco, V.; Croatto, V.; Uguagliati, P.; Pietropaolo, R. *Inorg. Chem.* **1967**, *6*, 718.  
 (5) Zybill, C.; West, R. *J. Chem. Soc., Chem. Comm.* **1986**, 8571.  
 (6) Campion, B. K.; Heyn, R. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1988**, *110*, 7558.  
 (7) Pham, E. K.; West, R. *J. Am. Chem. Soc.* **1989**, *111*, 7667.  
 (8) Koloski, T. S.; Carroll, P. J.; Berry, D. H. *J. Am. Chem. Soc.* **1990**, *112*, 6405.  
 (9) Pham, E. K.; West, R. *Organometallics* **1990**, *9*, 1517.  
 (10) Berry, D. H.; Chey, J.; Zipin, H. S.; Carroll, P. J. *J. Am. Chem. Soc.* **1990**, *112*, 452; *Tetrahedron* **1991**, *10*, 1189.

### Scheme 1



These bis(chlorogermyl)platinum complexes are stable at room temperature but decompose when heated. A study of the thermal decomposition of a mixture of *cis,trans*-(chlorogermyl)platinum complexes 1 showed that at 120 °C a complex mixture of chlorogermanium derivatives and metallic platinum is produced (eq 4).



No trace of the monogermylated platinum complex  $\text{ClMe}_2\text{GePt}(\text{PPh}_3)_2\text{Cl}$  or the dimethylgermylene-derived products was observed. Thus, this decomposition is different from that observed by Tanaka<sup>11</sup> for the analogous complex  $(\text{ClMe}_2\text{Ge})_2\text{Pt}(\text{PET}_3)_2$ . The difference must be due to the difference in the phosphino ligands, triethylphosphine in Tanaka's case and triphenylphosphine in ours. It is also noteworthy that the  $\text{Ge}-\text{Cl}$  bond of  $\text{Me}_2\text{GeCl}_2$  oxidatively adds to the  $\text{Pt}(0)$  complex  $\text{Pt}(\text{PET}_3)_3$ <sup>11</sup> but not to  $\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$ .

**2. (diphos)PtGe(Me<sub>2</sub>)EGeMe<sub>2</sub>.** The action of a dichlorodigermanium compound with a dialkali derivative, the classic route to germyl sulfides, amines, and ferrocenophanes, was used in further conversions of *cis*-bis(chlorodimethylgermyl)platinum complex **2**.

These cyclization reactions were carried out at room temperature, except for the case where  $E = NPh$ , and the expected complexes were isolated in variable yield depending on the nature of the dialkali derivative (Scheme 1).

Reactions of **3–5** with diverse reagents have been studied (Scheme 2). Bromine and iodomethane, as expected, cleave the platinum–germanium bond to give platinum complexes and the corresponding bis(bromodimethylgermyl) and bis(trimethylgermyl) sulfides (in the case of E = S). These cleavages probably proceed *via* octahedral platinum(IV) intermediates.<sup>12</sup>

Hydrolysis of the Ge-N bond of **4** afforded the four-membered digermoxane **6**.

**Scheme 2**

$$\begin{array}{c} \text{L}_2 \\ | \\ \text{Pt} \\ / \quad \backslash \\ \text{Me}_2\text{Ge} \quad \text{GeMe}_2 \\ \backslash \quad / \\ \text{E} \end{array}$$

Left pathway:  $\text{E} = \text{NPh}$   
 $+ \text{H}_2\text{O} \quad - \text{H}_2\text{NPh}$   
Product 6: 
$$\begin{array}{c} \text{L}_2 \\ | \\ \text{Pt} \\ / \quad \backslash \\ \text{Me}_2\text{Ge} \quad \text{GeMe}_2 \\ \backslash \quad / \\ \text{O} \end{array} \quad \mathbf{6}$$

Middle pathway:  $\text{E} = \text{S}$   
 $+ \text{MeI} \quad - [\text{Pt}]$   
Product:  $\text{Me}_3\text{GeSGeMe}_3$

Right pathway:  $\text{E} = \text{S}$   
 $+ \text{Br}_2 \quad - [\text{Pt}]$   
Intermediate: 
$$\left[ \begin{array}{c} \text{Me}_2\text{GeSGeMe}_2 \\ \text{Br} \quad \text{Br} \end{array} \right]$$
  
Products:  $\text{Me}_2\text{GeBr}_2 + (\text{Me}_2\text{GeS})_3$

Bottom reaction:  $\text{Me}_2\text{ClGePt}(\text{L}_2)\text{GeClMe}_2 \xrightarrow{\text{C}_6\text{H}_6 (\text{H}_2\text{O}), 180^\circ\text{C}}$

**Scheme 3**

$$\text{Me}_2\text{Ge} \begin{array}{c} \diagup \text{L}_2 \\ \text{Pt} \\ \diagdown \end{array} \text{GeMe}_2 \begin{array}{c} \diagdown \\ \text{E} \\ \diagup \end{array} \xrightarrow[\text{E}=\text{O}]{\text{PhC}\equiv\text{CH} \cdot [\text{Pt}], 100^\circ\text{C}} \text{Me}_2\text{Ge} \begin{array}{c} \diagup \\ \text{C}\equiv\text{C} \text{Ph} \\ \diagdown \end{array} \text{GeMe}_2 \begin{array}{c} \diagdown \\ \text{O} \\ \diagup \end{array}$$

**7 (59%)**

$$\text{E}=\text{S} \xrightarrow[20^\circ\text{C}]{\text{O}=\text{C} \begin{array}{c} \diagup \text{N}=\text{N} \\ \diagdown \text{N} \\ \text{Me} \end{array} \text{C}=\text{O}} \cdot [\text{Pt}] \downarrow$$

$$\text{Me} \begin{array}{c} \diagup \text{N} \\ \diagdown \end{array} \text{C}=\text{O} \begin{array}{c} \diagdown \text{N} \\ \diagup \end{array} \text{C}=\text{O} \begin{array}{c} \diagdown \text{N} \\ \diagup \end{array} \text{N} \begin{array}{c} \diagup \text{S} \\ \diagdown \end{array} \text{GeMe}_2 \begin{array}{c} \diagup \text{GeMe}_2 \\ \diagdown \end{array}$$

**8 (37%)**

$$\xleftarrow{\text{Na}_2\text{S}} \left[ \text{Me} \begin{array}{c} \diagup \text{N} \\ \diagdown \end{array} \text{C}=\text{O} \begin{array}{c} \diagdown \text{N} \\ \diagup \end{array} \text{C}=\text{O} \begin{array}{c} \diagdown \text{N} \\ \diagup \end{array} \text{N} \begin{array}{c} \diagup \text{S} \\ \diagdown \end{array} \text{GeMe}_2 \begin{array}{c} \diagup \text{GeMe}_2 \\ \diagdown \end{array} \right]^-$$

Upon treatment of  $\text{L}_2\text{PtGe}(\text{Me}_2)\text{EGeMe}_2$  with triazolidione and phenylacetylene, double germylation of the unsaturated systems occurred (Scheme 3). For example, the four-membered oxide **6** and sulfide **3** reacted instantaneously at room temperature with *N*-methyltriazolidione but only at 100 °C with phenylacetylene, producing, in each case, new digermanium heterocycles. These are *formally* adducts of the oxa- or thiadigermanirane with phenylacetylene or with *N*-methyltriazolidione. They were characterized by NMR, mass spectroscopy, and elemental analysis.

To confirm the structure of the thiadiazadigermolane **8**, an alternate synthesis, the direct cyclization of the bis(chlorodimethylgermyl)triazolidine **9** with sodium sulfide was sought. Thus, in order to obtain **9**, the reaction of bis(chlorodimethylgermyl)platinum(II)-diphos with 4-methyl-1,2,4-triazolinedione was carried out. The double germylation of this unsaturated system was not the main path observed for this reaction, the expected dihalodigermanium **9** being obtained in solution, in only low yield, as an unisolated intermediate only. Trapping with Na<sub>2</sub>S resulted in formation of **8** in approximately 10% yield.

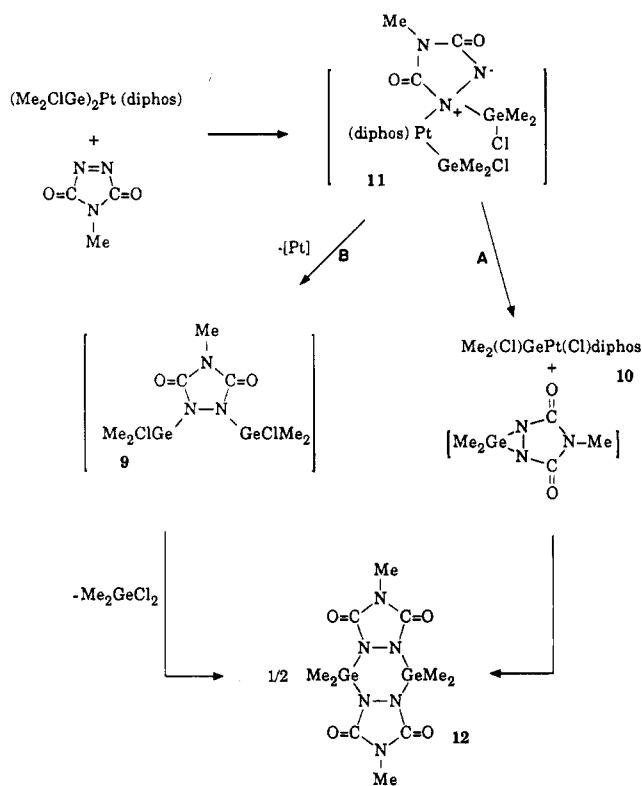
In effect, somewhat unexpected is the reaction of bis-(chlorodimethylgermyl)platinum-diphos) with triazolinedione to form dichlorodimethylgermanium, the tetraazadigerminane **12**, and, an interesting feature, the monogermylated platinum complex **10**.

The formation of dichlorodimethylgermanium and of platinum complex **10** suggests that the reaction pro-

(11) Yamashita, H.; Kobayashi, T.; Tanaka, M.; Samuels, J. A.; Streib, W. E. *Organometallics* **1992**, *11*, 2330.

(12) Hartley, F. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 6, Chapter 39, p 471, and references therein.

Scheme 4



ceeds in a stepwise fashion probably involving a zwitterionic intermediate **11**. The formation of the monogermylated platinum complex **10** is most likely explained by rearrangement of **11** with a shift of chlorine to platinum (path A). The formation of the dichlorodimethylgermane indicates the existence of path B involving extrusion of platinum from **11**, leading to the expected bis(chlorodimethylgermyl)triazolidine which decomposes slowly at room temperature to give dichlorodimethylgermanium and **12** (Scheme 4).

We now are investigating the chemistry of these four-membered heterocycles with various other unsaturated compounds. With judiciously selected ligands, these digermylplatinum(II) organometallic rings should have potential, especially as precursors of species containing germanium in low-coordination states.

## Experimental Section

**General Procedures.** All reactions and manipulations were carried out under an argon or nitrogen atmosphere with the use of Schlenk techniques. The solvents were dried and deoxygenated by standard methods. The  $^1\text{H}$  NMR spectra were recorded on an AC Bruker spectrometer operating at 80 MHz; the  $^{31}\text{P}$  spectra were measured on a Bruker AC-200 (spectrometer frequency 81.015 Hz). The  $^1\text{H}$  chemical shifts are given in ppm ( $\delta$ ) relative to  $\text{Me}_4\text{Si}$ .  $^{31}\text{P}$  spectra are externally referenced to 85%  $\text{H}_3\text{PO}_4$ . Gas-phase chromatography was effected on an HP 5890 series II apparatus (capillary column, HP1 methylsilicone gum, 10 m  $\times$  0.53 mm  $\times$  2.65  $\mu\text{m}$  film thickness) using nitrogen as carrier gas. Infrared spectra were obtained of samples in KBr pellets and were recorded on a Perkin-Elmer 1600 series FTIR instrument. Mass spectra were recorded on a Nermag R10-10H or a Hewlett Packard 5989 instrument operating in the electron impact mode at 70 eV, and samples were contained in glass capillaries under argon or in the chemical ionization mode ( $\text{CH}_4$ ). In all cases, the complex envelope of peaks obtained for polygermanes agreed with the isotopic distribution char-

acteristic of germanium.<sup>13</sup> Melting points were measured on an Electrothermal digital melting point apparatus in sealed glass capillaries. Elemental analyses were performed by the Microanalytic Laboratory of CNRS or ENSCT, Toulouse, France.

**(ClMe<sub>2</sub>Ge)<sub>2</sub>Pt(PPh<sub>3</sub>)<sub>2</sub>, 1.** A solution of  $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$  (0.40 g, 0.535 mmol) in  $\text{C}_6\text{H}_6$  (1.5 mL) was added to a solution of *sym*-dichlorotetramethyldigermene (0.148 g, 0.535 mmol) in  $\text{C}_6\text{H}_6$  (1 mL). The resulting yellow suspension was stirred for 1 h at room temperature. The resulting mixture was filtered, and the yellow filtrate was washed with  $\text{C}_6\text{H}_6$  (5 mL). Filtration gave 0.48 g (91%) of **1**; mp 195–200 °C. NMR analyses showed that the *cis*/*trans* ratio is 20/80. In a second identical experiment, starting from 1.27 g (1.70 mmol) of  $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$  in 10 mL of  $\text{C}_6\text{H}_6$  and 0.47 g (1.70 mmol) of *sym*-dichlorotetramethyldigermene, the NMR analyses of the resulting solution showed the formation of a mixture of *cis*- and *trans*-**1** with the ratio 5/95. From this mixture, *cis*-**1** crystallized after 12 h as pale yellow crystals. Dissolution of these crystals in  $\text{CH}_2\text{Cl}_2$  gave a mixture of *cis*- and *trans*-**1** in *cis*/*trans* ratio 90/10 after 30 min.

*trans*-**1**:  $^1\text{H}$  NMR ( $\text{C}_6\text{H}_6$ )  $\delta$  0.98 [s, with two satellites  $J(^1\text{H}-\text{C}-\text{Ge}-^{195}\text{Pt}) = 8.2$  Hz, 12H], 6.90 (m, 18H), 7.56 (m, 12H);  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{H}_6$ )  $\delta$  25.17 [s, with two satellites  $J(^{195}\text{Pt}-^{31}\text{P}) = 2327$  Hz]; IR (KBr)  $\nu(\text{Pt}-\text{P})$  422,  $\nu(\text{Ge}-\text{C})$  573,  $\rho(\text{Me})$  835; MS  $m/z$  818 ( $\text{M}^+ - \text{MeCl}$ ).

*cis*-**1**:  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  0.32 [d,  $J(^1\text{H}-\text{C}-\text{Ge}-\text{Pt}-^{31}\text{P}) = 1.7$  Hz with two satellites (d)  $J(^1\text{H}-\text{C}-\text{Ge}-^{195}\text{Pt}) = 10.1$  Hz, 12H];  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  21.31 [s, with two satellites  $J(^{195}\text{Pt}-^{31}\text{P}) = 2210$  Hz]; IR (KBr)  $\nu(\text{Pt}-\text{P})$  450,  $\nu(\text{Ge}-\text{C})$  573,  $\rho(\text{Me})$  835. Anal. Calcd for  $\text{C}_{40}\text{H}_{42}\text{Cl}_2\text{Ge}_2\text{P}_2\text{Pt}$  (mixture of *cis*/*trans*, 20/80): C, 48.23; H, 4.22. Found: C, 48.40; H, 4.20.

**(ClMe<sub>2</sub>Ge)<sub>2</sub>Pt(diphos), 2.** A solution of **1** (1.00 g, 1.00 mmol) and 1,2-bis(diphenylphosphino)ethane (0.40 g, 1.00 mmol) in  $\text{C}_6\text{H}_6$  (10 mL) was stirred for 3 days at room temperature. The precipitate was filtered and washed twice with  $\text{C}_6\text{H}_6$  (5 mL). Drying *in vacuo* gave **2** as yellow crystals (0.61 g; 70%).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  0.57 [d,  $J(^1\text{H}-\text{C}-\text{Ge}-\text{Pt}-^{31}\text{P}) = 1.3$  Hz, with two satellites (d)  $J(^1\text{H}-\text{C}-\text{Ge}-^{195}\text{Pt}) = 12.0$  Hz, 12H], 2.05 [d,  $J(^1\text{H}-\text{C}-^{195}\text{Pt}) = 19.9$  Hz, with two satellites (dd)  $J(^1\text{H}-\text{C}-\text{P}-^{195}\text{Pt}) = 18.5$  Hz, 4H], 7.53 (m, 12H), 7.75 (m, 8H);  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  55.36 [s, with two satellites  $J(^{195}\text{Pt}-^{31}\text{P}) = 2025$  Hz]; IR (KBr)  $\nu(\text{Ge}-\text{Pt})$  392,  $\nu(\text{Pt}-\text{P})$  441,  $\nu(\text{Ge}-\text{C})$  529,  $\rho(\text{Me})$  830. MS  $m/z$  833 ( $\text{M}^+ - \text{Cl}$ ). Anal. Calcd for  $\text{C}_{30}\text{H}_{36}\text{Ge}_2\text{Cl}_2\text{P}_2\text{Pt}$ : C, 41.39; H, 4.14. Found: C, 41.68; H, 4.08.

**Thermolysis of 1.** A benzene solution (1 mL) of **1** (0.05 g, 0.05 mmol) was heated at 120 °C for 4 h in a degassed sealed tube. Analyses by  $^1\text{H}$  NMR spectroscopy, GC (including coinjection with authentic samples), and GCMS showed  $\text{Me}_2\text{GePhCl}$  [ $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  0.37 (s, 6 H);  $m/z$  216 ( $\text{M}^+$ )],  $\text{Me}_2\text{GeCl}_2$  [ $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  0.59(s);  $m/z$  174 ( $\text{M}^+$ )],  $\text{Me}_2(\text{Cl})\text{GeGe}(\text{Cl})\text{Me}_2$  [ $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ) 0.62(s);  $m/z$  276 ( $\text{M}^+$ )],<sup>14</sup>  $\text{Me}_3\text{GeGe}(\text{Cl})\text{Me}_2$  [ $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ) 0.27(s, 9 H), 0.59 (s, 6 H);  $m/z$  256 ( $\text{M}^+$ )]<sup>14</sup> to be present in this solution in relative amounts of 60%, 14%, 12%, and 5%, respectively.

**Me<sub>2</sub>GeSGe(Me<sub>2</sub>)Pt(diphos), 3.** To a solution of 0.20 g (0.23 mmol) of **2** in 10 mL of  $\text{CH}_2\text{Cl}_2$  was added 0.60 g (7.6 mmol) of  $\text{Na}_2\text{S}$ . The resulting mixture was sonicated for 12 h. After the remaining  $\text{Na}_2\text{S}$  and resulting  $\text{NaCl}$  were filtered,  $\text{CH}_2\text{Cl}_2$  was evaporated. A 5 mL amount of  $\text{C}_6\text{H}_6$  was added to the residue. Pure **3** was obtained by filtration as a white solid (0.16 g, 81%), mp 243–245 °C (decomp).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  0.29 [d,  $J(^1\text{H}-\text{C}-\text{Ge}-\text{Pt}-^{31}\text{P}) = 1.7$  Hz, with two satellites (d)  $J(^1\text{H}-\text{C}-\text{Ge}-^{195}\text{Pt}) = 14.2$  Hz, 12H], 2.18 [d,  $J(^1\text{H}-\text{C}-^{31}\text{P}) = 18.1$  Hz, with two satellites (dd)  $J(^1\text{H}-\text{C}-\text{P}-^{195}\text{Pt}) = 15.2$  Hz, 4H], 7.47 (m, 12H), 7.73 (m, 8H);  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  55.22 [s, with two satellites  $J(^{195}\text{Pt}-^{31}\text{P}) =$

(13) Carrick, A.; Glockling, F. *J. Chem. Soc. A* **1966**, 623.

(14) Barrau, J.; Rima, G.; El-Amine, M.; Satgé, J. *Synth. React. Inorg. Met.-Org. Chem.* **1988**, *18*, 21.

1868 Hz]. MS  $m/z$  832 ( $M^+$ ). Anal. Calcd for  $C_{30}H_{36}Ge_2Pt_2S$ : C, 43.33; H, 4.33; S, 3.85. Found: C, 43.16; H, 4.29; S, 3.73.

**$Me_2GeN(Ph)Ge(Me_2)Pt$  (diphos), 4.** To a solution of 0.110 g (0.118 mmol) of **2** in 5 mL of  $C_6H_6$  was added dropwise a solution of 0.118 mmol of  $PhNLi_2$  [prepared from 0.011 g (0.118 mmol) of aniline and 0.15 mL of a solution 1.6 M of butyllithium; addition at  $-78^\circ C$  and heating to reflux for 36 h] in 2 mL of xylene at room temperature. The mixture was heated at reflux for 12 h. After filtration the solvent was removed under vacuum, yielding 0.025 g (24%) of **4** as an orange powder, mp  $116-118^\circ C$  (decomp).  $^1H$  NMR ( $CD_2Cl_2$ )  $\delta$  0.30 [d,  $J(^1H-C-Ge-Pt-^{31}P) = 1.5$  Hz, with two satellites (d)  $J(^1H-C-Ge-^{195}Pt) = 12.6$  Hz, 12H], 2.25 [d,  $J(^1H-C-^{31}P) = 17.7$  Hz, with two satellites (dd)  $J(^1H-C-P-^{195}Pt) = 14.4$  Hz, 4H], 7.48 (m, 12H), 7.53 (m, 8H);  $^{31}P\{^1H\}$  NMR ( $CD_2Cl_2$ )  $\delta$  58.10 [s, with two satellites  $J(^{195}Pt-^{31}P) = 1863$  Hz]. MS  $m/z$  875 ( $M^+ - Me$ ). Anal. Calcd for  $C_{36}H_{41}Ge_2NPt_2$ : C, 48.58; H, 4.64; N, 1.57. Found: C, 48.77; H, 1.65; N, 1.38.

**$Me_2Ge[(\eta^5-C_5H_4)Fe(\eta^5-C_5H_4)]Ge(Me_2)Pt$  (diphos), 5.** To a suspension of 1,1'-ferrocenylenedilithium-TMEDA<sup>15</sup> (0.06 g, 0.19 mmol) in pentane (5 mL) at  $-78^\circ C$  was added a cooled ( $-78^\circ C$ ) solution of **2** (0.17 g, 0.19 mmol) in diethyl ether (3 mL). The reaction mixture was warmed slowly to room temperature and then was stirred overnight. The reaction mixture was filtered, and the solvent was removed. Residual TMEDA was removed under vacuum ( $25^\circ C$ , 0.002 mmHg). The red orange residue was identified as **5** (0.035 g, 19%), mp  $166-168^\circ C$  (decomp).  $^1H$  NMR ( $C_6D_6$ )  $\delta$  0.29 [d,  $J(^1H-C-Ge-Pt-^{31}P) = 1.4$  Hz, with two satellites (d)  $J(^1H-C-Ge-^{195}Pt) = 11.4$  Hz, 12H], 2.31 [d,  $J(^1H-C-^{31}P) = 17.6$  Hz, with two satellites (dd)  $J(^1H-C-P-^{195}Pt) = 14.2$  Hz, 4H], 4.14 (m, 4H), 4.24 (m, 4H), 7.45 (m, 12H), 7.62 (m, 8H). Anal. Calcd for  $C_{40}H_{44}FeGe_2Pt_2$ : C, 48.88; H, 4.51. Found: C, 49.10; H, 4.39.

**$Me_2GeOGe(Me_2)Pt$  (diphos), 6.** Compound **2** (0.10 g, 0.11 mmol), 1 mL of benzene, and 0.1 mL of water were placed in a sealed tube and heated at  $180^\circ C$  for 12 h.  $^1H$  NMR, GC, and MS analysis of the reaction mixture showed the presence of **6** and  $(Me_2GeO)_3$  in 58% and 37% yield, respectively.  $^1H$  NMR ( $C_6D_6$ )  $\delta$  1.14 [d,  $J(^1H-C-Ge-Pt-^{31}P) = 1.3$  Hz, with two satellites (d)  $J(^1H-C-Ge-^{195}Pt) = 7.2$  Hz, 12H], 1.93 [d,  $J(^1H-C-^{31}P) = 20.1$  Hz, with two satellites (dd)  $J(^1H-C-P-^{195}Pt) = 15.1$  Hz, 4H], 7.06 (m, 12H), 7.74 (m, 8H);  $^{31}P\{^1H\}$  NMR ( $C_6D_6$ )  $\delta$  46.62 [s, with two satellites  $J(^{195}Pt-^{31}P) = 1760$  Hz]. MS  $m/z$  814 ( $M^+$ ).

Compound **4** (0.012 g, 0.013 mmol) was dissolved in  $CD_2Cl_2$  (0.5 mL) in an NMR tube. The opened NMR tube stood at ambient temperature for a few hours.  $^1H$  NMR, GC, and MS analysis of the reaction mixture after 2 h showed the presence of **6** and  $(Me_2GeO)_3$  in 69% and 31% yield, respectively.

Any attempt to obtain pure **6** by addition of pentane was unsuccessful.

**Reaction of 3 with  $Br_2$  and MeI.** Equimolar amounts of **3** and  $Br_2$  or MeI reacted in the presence of benzene at  $20^\circ C$  to give the results recorded in Scheme 2. In all cases, after elimination of inorganic platinum products by filtration, the remaining mixtures were analyzed by GC,  $^1H$  NMR, and GCMS.

The known compounds  $Me_2GeBr_2$ ,  $(Me_2GeS)_3$ , and  $(Me_3Ge)_2S$  were detected in 80% (both  $Me_2GeBr_2$  and  $(Me_2GeS)_3$ ) or 85% yield, respectively (comparisons with authentic samples).

**Reaction of 6 with Phenylacetylene.** A 0.10 g amount of a mixture of **6** (68%) and  $(Me_2GeO)_3$  (27%) and 0.12 g (1 mmol) of phenylacetylene in 1 mL of benzene were heated in a sealed glass tube at  $100^\circ C$  for 3 h. Analysis by  $^1H$  NMR and GCMS of the resulting mixture showed that the oxide

$Me_2GeCH=C(Ph)Ge(Me_2)O$ , **7**, had been formed in 59% yield (comparison with authentic sample obtained by hydrolysis of  $ClMe_2GeC(Ph)=CHGeMe_2Cl$ ).<sup>16</sup>  $^1H$  NMR ( $C_6D_6$ )  $\delta$  0.87 (s, 6H), 1.10 (s, 6H), 6.87 (s, 1H), 7.04–7.35 (m, 5H). MS  $m/z$  324 ( $M^+$ ).

**Reaction of 3 with 4-Methyl-1,2,4-triazolinedione.** To a solution of **3** (0.10 g, 0.12 mmol) in  $CH_2Cl_2$  (1 mL) was added dropwise 0.014 g (0.12 mmol) of 4-methyl-1,2,4-triazolinedione. After decolorization of the reaction mixture, the platinum products were filtered and the filtrate was evaporated to dryness. The solid residue was treated with 0.2 mL of benzene. Filtration and removal of the solvent under vacuum yielded 0.015 g of  $Me_2GeNC(O)N(Me)C(O)NGe(Me_2)S$ , **8** (37%)

as a yellow powder, mp  $154-156^\circ C$ .  $^1H$  NMR ( $C_6D_6$ )  $\delta$  0.54 (s, 12H), 2.90 (s, 3H). MS  $m/z$  351 ( $M^+$ ). Anal. Calcd for  $C_7H_{15}Ge_2N_3O_2$ : C, 26.41; H, 4.75. Found: C, 26.53; H, 4.57.

**Reaction of 2 with 4-Methyl-1,2,4-triazolinedione.** A solution of 4-methyl-1,2,4-triazolinedione (0.013 g, 0.115 mmol) in  $C_6H_6$  (1 mL) was added to a solution of **2** (0.10 g, 0.115 mmol). After decolorization of the reaction mixture, the mixture was analyzed by  $^1H$  NMR spectroscopy. Appearance of new signals in the range of  $\delta(Me_2Ge)$  at  $\delta$  0.26 (d), 0.84 (s), 1.01 (s), and 1.12 (s) were observed, establishing that **10**, **12**, and  $Me_2GeCl_2$  had been formed (comparisons with authentic samples); the signal at  $\delta$  1.01 could be consistent with the proposed intermediate structure **9**. After 2 h at room temperature, the resulting mixture was filtered; the white residue was washed with  $C_6H_6$  (1 mL); filtration gave 0.06 g (68%) of **10**. Removal of solvent from the filtrate under vacuum yielded compound **12** as an analytically pure white powder.

Data for **10**: mp  $309-312^\circ C$ ;  $^1H$  NMR ( $CD_2Cl_2$ )  $\delta$  0.26 [d,  $J(^1H-C-Ge-Pt-^{31}P) = 0.8$  Hz with two satellites (d)  $J(^1H-C-Ge-^{195}Pt) = 12.6$  Hz, 6H], 2.26 [d,  $J(^1H-C-^{31}P) = 18.9$  Hz, with two satellites (dd)  $J(^1H-C-P-^{195}Pt) = 17.1$  Hz, 4H], 7.47 (m, 12H), 7.71 (m, 8H);  $^{31}P\{^1H\}$  NMR ( $CD_2Cl_2$ )  $\delta$  53.10 [s, with two satellites  $J(^{195}Pt-^{31}P) = 1990$  Hz]; MS  $m/z$  731 ( $M^+ - Cl$ ). Anal. Calcd for  $C_{28}H_{30}Cl_2Ge_2Pt_2$ : C, 43.82; H, 3.91; Cl, 9.26. Found: C, 43.74; H, 3.86; Cl, 9.20.

For **12**: mp  $167-169^\circ C$ ;  $^1H$  NMR ( $CD_2Cl_2$ )  $\delta$  0.84 (s, 12H), 2.72 (s, 6H); IR ( $C_6D_6$ )  $\nu(CO)$  1710, 1670. MS  $m/z$  432 ( $M^+$ ). Anal. Calcd for  $C_{10}H_{18}N_6O_4Ge_2$ : C, 27.82; H, 4.17; N, 19.48. Found: C, 26.92; H, 4.21; N, 19.27.

Immediately after a mixture of 4-methyl-1,2,4-triazolinedione (0.013 g, 0.115 mmol) and **2** (0.10 g, 0.115 mmol) in  $CH_2Cl_2$  (1 mL) was decolorized, 0.10 g (1.28 mmol) of  $Na_2S$  was added. The resulting mixture was sonicated for 1 h. After the remaining  $Na_2S$  and resulting NaCl were filtered, and  $^1H$  NMR and MS showed formation of **8** (~10%),  $(Me_2GeS)_3$  (15%), and unidentified products (yields estimated by  $^1H$  NMR).

OM950149X

(15) Rausch, M. I.; Cappanelli, D. J. *J. Organomet. Chem.* **1967**, *10*, 127.

(16) Hayashi, T.; Yamashita, H.; Sakakura, T.; Uchimar, Y.; Tanaka, M. *Chem. Lett.* **1991**, 245.