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Synthesis and reactivity of digermylplatinum(II) complexes $Me_2Ge(CH_2)_nGe(Me_2)PtL_2$ ($n=0, 1, 2$)

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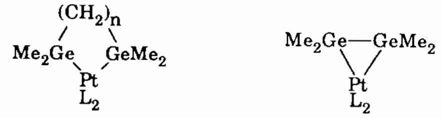
Abstract

This work concerns the synthesis of [bis(dimethylgermyl)alkane]bis(triphenylphosphine)platine(II) and -(diphos)platine(II) $Me_2Ge(CH_2)_nGe(Me_2)PtL_2$ ($n=2$, $L=PPh_3$ (**1**), diphos (**2**); $n=1$, $L=PPh_3$ (**3**), diphos (**4**) and (tetramethyldigermyl)bis(triphenylphosphine)platine(II) and -(diphos)platine(II) $Me_2GeGe(Me_2)PtL_2$ ($L=PPh_3$ (**5**), diphos (**6**). **3** and **5** are obtained by cyclization of bis(dimethylgermyl)alkanes $Me_2(H)Ge(CH_2)_nGe(H)Me_2$ ($n=1$ or 2) or 1,1,2,2-tetramethyldigermane $Me_2(H)GeGe(H)Me_2$ with $(Ph_3P)_2PtC_2H_4$. The polymeric structures $[Me_2Ge(CH)_2)_nGe(Me_2)Pt(PPh_3)_2]_m$ ($n=1$ or 2) react with diphos to give the monomer complexes **2** or **4**. IR and NMR examinations are reported. Various cleavage reactions with halogens and organic halides are described. Reactions of **2** with phenylacetylene and 1,2,4-triazolinediones afford new heterocycles arising from formal addition of these unsaturated systems across the Ge–Ge bond of the tetramethyldigermetane $Me_2Ge(CH_2)_2GeMe_2$.

Introduction

The interactions of transition metal complexes with atom M of organometallic compounds of Group 14 elements have been the subject of considerable scrutiny [1–7]. However, quite a few reports on the study of silyl or germyl cyclic complexes having M–X–M–M'Ln (M' = transition metal) linkages have appeared [8–17]. After our studies on the bis(dimethylgermyl) or (dimethylgermyl)(dimethylsilyl) alkane iron or ruthenium tetracarbonyls and dicobalt heptacarbonyls [16, 17], we sought to explore the potential of new three-, four- or five-membered heterocycles in the context of new heterocyclic chemistry and stabilization of transient divalent [R_2M] or unsaturated [$R_2M=X$] organometallic compounds in transition metal environments. To our knowledge few doubly bonded M atom derivatives have been stabilized by complexation with transition metals; in this 14 metal series the stable η^2-silene or -disilene complexes $(R_2Si=ER_2)M'Ln$ (M' = W, Mo, Pt, Hg; $ER_2 = SiMe_2$, $SiMes_2$, CH_2) are the only known structures [18–24].

We report herein the syntheses and some properties of the new polynuclear heterocyclic complexes **1–6**.



n=2 $L=PPh_3$ **1**; diphos **2**

n=1 $L=PPh_3$ **3**; diphos **4**

$L=PPh_3$ **5**

L = diphos **6**

[diphos = $Ph_2PCH_2CH_2PPh_2$]

Experimental

General procedures

All reactions were performed under an atmosphere of nitrogen or argon. Air sensitive compounds were handled by using standard Schlenk and high vacuum-line techniques. All solvents were distilled from appropriate drying agents. ^1H NMR spectra were recorded on a Bruker AC 80 spectrometer operating at 80 MHz (chemical shifts are reported in parts per million relative to internal Me_4Si as reference) and ^{13}C spectra on a AC 200 MHz spectrometer. ^{31}P NMR spectra were measured at 81.015 MHz by using a Bruker AC 200 MHz spectrometer and 86% H_3PO_4 as an external reference. Gas-phase chromatography was carried out on an HP 5890 series II apparatus using nitrogen as the carrier gas and HP 1 (methyl silicone gum) 5 m × 0.53 mm × 2.65 μm film thickness. IR spectra were

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recorded on a Perkin-Elmer IRFT series 1600. Mass spectra were recorded on a Nermag R10.10 H spectrometer operating in the chemical ionization mode (CH_4) and on a Hewlett Packard 5989 spectrometer in the electron impact mode (70 eV), In all cases the complex envelope of peaks obtained for polygermanes agreed with the expected isotopic distribution based on the number of isotopes of germanium and of platinum. Microanalyses were performed by the Microanalytical Laboratory of the CNRS or ENSCT, Toulouse, France.

1,1,2,2-Tetramethyldigermane, $Me_2(H)GeGe(H)Me_2$

A mixture of 1,2-dichloro-1,1,2,2-tetramethyldigermane [25] (1.01 g, 3.66 mmol) and Bu_3SnH (2.65 g, 9.11 mmol) is stirred for 5 h (the reaction was followed by GC). 0.53 g of $Me_2(H)GeGe(H)Me_2$ is extracted under reduced pressure (10^{-2} mmHg) and trapped at −195 °C (70% yield).

^{1}H NMR (C_6H_5): δ 0.24 (d, ^3J(H–H) = 3 Hz, 12H), 3.78 (m, 2H).

$[Me_2\overline{GeCH_2CH_2Ge(Me_2)Pt}(PPh_3)_2]_m$ (7)

In a Schlenk flask 1,2-bis(dimethylgermyl)ethane [26] (0.18 g, 0.76 mmol) is added via syringe to a solution of $(Ph_3P)_2PtC_2H_4$ (0.57 g, 0.76 mmol). The reaction mixture turns orange with noticeable evolution of gas, presumably H_2 and C_2H_4. After 12 h stirring under argon, solvent removal followed by work up in pentane affords **7** as a pale yellow solid powder in 91% yield (0.66 g).

7: m.p. 220–222 °C dec. *Anal.* Calc. for $(C_{42}H_{46}Ge_2P_2Pt)_m$: C, 52.92; H, 4.83. Found C, 53.28; H, 4.85%.

[1,2-Bis(dimethylgermyl)ethane](diphos)platine(II), $Me_2\overline{GeCH_2CH_2Ge(Me_2)Pt}(diphos)$ (2)

To a Schlenk flask containing 0.30 g of **7**, a C_6H_6 solution (2 ml) of diphos (0.12 g, 0.31 mmol) is added. The reaction mixture is heated at 120 °C for 2 h. The orange solution is concentrated under vacuum and pentane is added. The solid **2** which separates is filtered, washed with pentane and dried under vacuum (0.23 g, 92% yield).

2: m.p. 245–246 °C dec. NMR analyses, see 'Results and discussion'; mass spectrum *m/z* 829 ($M^{\cdot+}+1$).

[bis(dimethylgermyl)methane]bis(triphenylphosphine)platine(II), $Me_2\overline{GeCH_2(Me_2)Pt}(PPh_3)_2$ (3) and $[Me_2\overline{GeCH_2Ge(Me_2)Pt}(PPh_3)_2]_m$ (8)

To a solution of $(Ph_3P)_2PtC_2H_4$ (0.44 g, 0.59 mmol) in benzene (3 ml) is added via syringe $Me_2(H)GeCH_2Ge(H)Me_2$ [27] (0.13 g, 0.59 mmol). Rapid evolution of H_2 and C_2H_4 is observed. This solution is stirred at room temperature for 4 h. The pale yellow solid formed (0.22 g) filtered off and washed with pentane (5 ml) is identified as **8**. The red–brown filtrate is concentrated under reduced pressure, a yellow-brown solid precipitates and is washed with pentane (10 ml). Recrystallization from benzene/pentane gave 0.25 g of **3** as a yellow solid (m.p. 99 °C dec.) (45% yield).

8: m.p. 195–197 °C dec. *Anal.* Calc. for $C_{41}H_{44}Ge_2P_2Pt$: C, 52.44; H, 4.68. Found: C, 51.71; H, 4.41%.

3: ^{1}H NMR: 0.43 [d, J(^{31}P–Pt–Ge–C–^{1}H) = 0.9 Hz, 12H; with two satellites (d.d, J(^{195}Pt–Ge–C–^{1}H) = 5.1 Hz)], 0.15 [m, J(^{195}Pt–Ge–C–^{1}H) = 5.4 Hz, J(^{31}P–Pt–Ge–C–^{1}H) = 0.5 Hz, 2H]. Mass spectrum *m/z* 941 ($M^{\cdot+}+1$).

[Bis(dimethylgermyl)methane](diphos)platine(II), $Me_2\overline{GeCH_2Ge(Me_2)Pt}(diphos)$ (4)

Compound **4** is prepared as an extremely air-sensitive yellow solid in 55% yield from **8** or **3** (0.25 mmol) and diphos (0.10 g, 0.25 mmol) under conditions described above for **2**.

4: ^{1}H NMR (C_6D_6): 0.43 [pseudotriplet, J(^{1}H–C–Ge–^{195}Pt) = 11.6 Hz, 12H], 1.82 [d, J(^{1}H–C–^{31}P) = 18 Hz, J(^{1}H–C–P–^{195}Pt) = 15 Hz, 4H], 0.16 [m, J(^{195}Pt–Ge–C–^{1}H) = 5.5 Hz, J(^{31}P–Pt–Ge–C–^{1}H) = 0.5 Hz, 2H].

(Tetramethyldigermyl)bis(triphenylphosphine)platine(II), $Me_2\overline{GeGe(Me_2)Pt}(PPh_3)_2$ (5)

By a procedure analogous to that described for **3** and **8**, **5** is prepared in *c*. 56% yield (0.25 g) from $Me_2(H)GeGe(H)Me_2$ (0.10 g, 0.48 mmol) and $(Ph_3P)_2PtC_2H_4$ (0.36 g, 0.48 mmol) in 3 ml of C_6H_6. 0.12 g of pale yellow polymer of **5** is also obtained in this reaction.

5: m.p. 98 °C dec. ^{1}H NMR: 0.53 [broad pseudotriplet, J(^{195}Pt–Ge–C–^{1}H) = 14 Hz, 12H], 7.8 (m, 12H), 7.05 (m, 18H). ^{31}P{^{1}H} NMR (C_6D_6) 24.8 (s, J(Pt–P) = 1964 Hz). Mass spectrum *m/z* 927 ($M^{\cdot+}+1$). *Anal.* Calc. for $C_{40}H_{42}Ge_2P_2Pt$: C, 51.93; H, 4.51. Found: C, 50.97; H, 4.16%.

$Me_2\overline{GeOGe(Me_2)Pt}(PPh_3)_2$ (9)

Dry oxygen is bubbled through a C_6D_6 solution (0.5 ml) of **5** (0.05 g) for 0.5 h. Analyses by ^{1}H, ^{31}P NMR and IR spectroscopies show the formation of **9**, in addition to traces (< 10%) of $Me_2\overline{GeGe(Me_2)OGe(Me_2)Ge(Me)_2O}$ [26].

9: ^{1}H NMR (C_6D_6); 0.57 [pseudotriplet, 12H, J(^{1}H–C–Ge–^{195}Pt = 11.5 Hz], 7.76 (m, 12H), 7.05 (m, 18H). ^{31}P{^{1}H} NMR (C_6D_6): 24.32 [s, J(^{195}Pt–^{31}P) = 1201 Hz]. IR: νGe–O–Ge 850 cm^{-1}. Mass spectrum *m/z* 943 ($M^{\cdot+}+1$).

(Tetramethyldigermyl)(diphos)platine(II), $Me_2\overline{GeGe(Me_2)Pt}(diphos)$ (6)

To a Schlenk flask containing the pale yellow solid formed by the precedent reaction or containing 0.13 mmol of **5** a C_6H_6 solution of diphos (0.06 g, 0.15 mmol) is added. The reaction mixture is heated at 120 °C for 2 h. Analyses by ^1H, ^{31}P NMR show the formation of **6** in 85% yield.

^1H NMR: 0.68 [pseudotriplet, $J(^1H\text{–}C\text{–}Ge\text{–}^{195}Pt) = 10.4$ Hz, $J(^{31}P\text{–}Pt\text{–}Ge\text{–}C\text{–}^1H) \sim 0.5$ Hz), 12H], 1.66 [d, $J(^1H\text{–}C\text{–}^{31}P) = 17.8$ Hz, $J(^1H\text{–}C\text{–}P\text{–}^{195}Pt) = 14.8$ Hz, 4H].

Reaction of pyridine with 7

A mixture of **7** (0.1 g, 0.1 mmol) with pyridine (0.98 g, 12 mmol) is heated for 4 h at 100 °C in a sealed tube under argon. The excess of pyridine is removed at reduced pressure (10^{-2} mm Hg) to give a yellow wax which neither component could be induced to crystallize; ^1H, ^{13}C and ^{31}P ^1H NMR show that **10** has been formed.

10: ^1H NMR (C_6D_6): 0.37 [pseudotriplet $J(^1H\text{–}C\text{–}Ge\text{–}^{195}Pt)$ 12H], 0.93 (m, 4H), 6.93–7.95 (m, 40H). $^{31}P\{^1H\}$ NMR (C_6D_6) 24.12. ^{13}C NMR ($CDCl_3$) 1.042 (CH_3), 29.72 (CH_2), 128.5, 128.6, 133.7, 137.4 (C_6H_5), 124.2, 136.2, 149.6 (NC_5H_5).

Reactions of 2, 7 or 10 with halogens and organic halides

Equimolar amounts of **2** or **7**, or **10** and reagents listed in Tables 1 or 2 react in the presence of benzene at 20 °C to give the results recorded in the same Tables. In all cases after elimination of inorganic platine products by filtration, the dihalo products $Me_2(X)GeCH_2CH_2Ge(X)Me_2$ were isolated by crystallization from pentane (concentration of the solution under 10 mm Hg and addition of a few milliliters of pentane) or detected by GC and NMR comparisons with authentic samples. The other various products were identified directly in the benzene solution by ^1H NMR, IR and MS.

Reaction of 2 with PhC≡CH

To **2** (0.20 g, 0.24 mmol) in anhydrous C_6H_6 (2 ml) is added dropwise PhC≡CH (0.05 g, 0.50 mmol). The mixture is stirred for 12 h at 65 °C. ^1H NMR spectroscopy and GCMS reveal that **12** has been formed (92% yield).

12: ^1H NMR ($CDCl_3$): 0.07 (s, 6H), 0.26 (s, 6H), 0.88 (m, 4H), 6.7 (s, 1H), 7.1–7.67 (m, 5H). Mass spectrum *m/z* 336 ($M^{\cdot+}$).

Reaction of **2** with 1,2,4-triazolinediones

N-Methyl or *N*-phenyl 1,2,4-triazolinedione (0.50 mmol) is added dropwise to **2** (0.20 g, 0.24 mmol) dissolved in C_6H_6 (2 ml). After decolorization of the reaction mixture ^1H NMR spectroscopy and GCMS show that **13** or **14** has been formed in *c.* 95% yield.

13: m.p. 164–166 °C. *Anal.* Calc. for $C_{14}H_{21}Ge_2O_2N_3$: C, 41.15; H, 5.14; N, 10.28. Found: C, 41.32; H, 5.19; N, 9.99%. ^1H NMR (C_6D_6): 0.51 (s, 12H), 0.84 (s, 4H), 6.9–7.3 (m, 5H). IR (C_6D_6): 1676, 1728 cm^{-1}. Mass spectrum *m/z* 409 ($M^{\cdot+}$).

14: m.p. 145–146 °C. *Anal.* Calc. for $C_9H_{19}Ge_2O_2N_3$: C, 31.19; H, 5.48; N, 12.13. Found: C, 31.33; H, 5.21; N, 12.01%. ^1H NMR (C_6D_6): 0.48 (s, 12H), 0.81 (s, 4H), 2.9 (s, 3H). IR ($CDCl_3$: 1651, 1717 cm^{-1}. Mass spectrum *m/z* 347 ($M^{\cdot+}$).

TABLE 1. Reactions of **2** or **7** with halogens and organic or inorganic halides

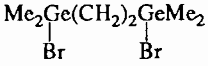
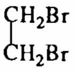
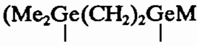
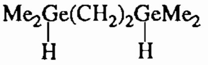
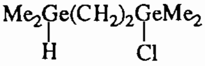
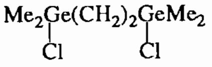
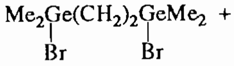
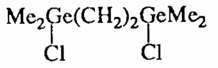
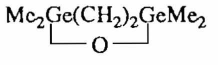
Reagent		**2** or **7**	Product (yield)
Br_2	0.027 g (0.17 mmol)	0.08 g (0.08 mmol)	 $Me_2\underset{\mathrm{Br}}{Ge}(CH_2)_2\underset{\mathrm{Br}}{Ge}Me_2$ + $(Ph_3P)_2PtBr_2$ (95%)
 $CH_2Br\text{–}CH_2Br$	0.01 g (0.05 mmol)	0.05 g (0.05 mmol)	 $(Me_2\underset{\vert}{Ge}(CH_2)_2\underset{\vert}{Ge}Me_2)_3$ + $(Ph_3P)_2PtBr_2$ + unidentified products (45%)
CH_3I	0.02 g (0.14 mmol)	0.07 g (0.07 mmol)	$Me_3Ge(CH_2)_2GeMe_3$ + $(Ph_3P)_2PtI_2$ (45%)
HCl, Et_2O (6 N)	3 ml	0.02 g (0.02 mmol)	 $Me_2\underset{\mathrm{H}}{Ge}(CH_2)_2\underset{\mathrm{H}}{Ge}Me_2$ +  $Me_2\underset{\mathrm{H}}{Ge}(CH_2)_2\underset{\mathrm{Cl}}{Ge}Me_2$ (traces <5%) (15%)  + $Me_2\underset{\mathrm{Cl}}{Ge}(CH_2)_2\underset{\mathrm{Cl}}{Ge}Me_2$ + $[(Ph_3P)_2PtH_2]$ (70%)

TABLE 2. Reaction of **10** with halogens, inorganic halides and water

Reagent		**10**	Product (yield)
Br_2	0.034 g (0.2 mmol)	0.111 g (0.1 mmol)	 $\underset{Br}{Me_2Ge}(CH_2)_2\underset{Br}{GeMe_2} + (Ph_3P)_2PtBr_2$ (95%)
HCl, Et_2O (6 N)	3.5 ml	0.03 g (0.027 mmol)	 $\underset{Cl}{Me_2Ge}(CH_2)_2\underset{Cl}{GeMe_2} + [(Ph_3P)_2PtH_2]$ (90%)
H_2O	0.2 ml	0.02 g (0.018 mmol)	 $\underbrace{Me_2Ge(CH_2)_2GeMe_2}_{O} + [(Ph_3P)_2PtH_2]$ (98%)

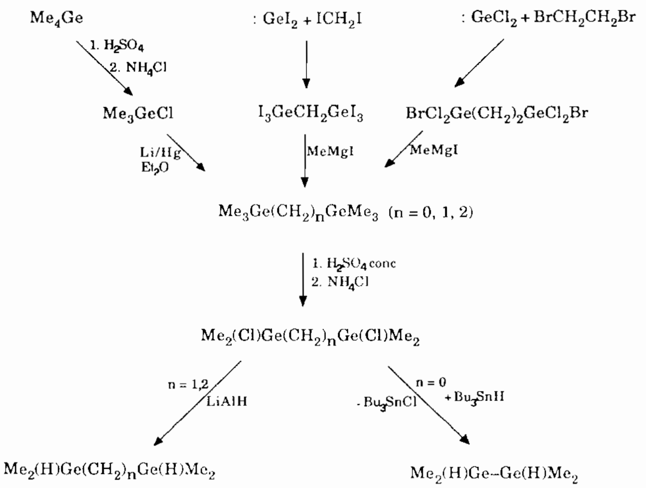
Results and discussion

Reaction of haloplatinum complexes with alkalimetal- or mercury-germyl species and oxidative addition of hydridogermanes to low coordination number–oxidation state platinum complexes have been successful routes to the formation of Pt–Ge bonds [28]. We used the latter method with the germanium hydrides $Me_2(H)Ge(CH_2)_nGe(H)Me_2$ ($n=0$, 1, 2) and the platinum(0) complex $[PtL_2(C_2H_4)]$ ($L=PPh_3$).

Synthesis of starting germanium hydrides $Me_2(H)Ge(CH_2)_nGe(H)Me_2$ ($n=0$, 1, 2)

The $Me_2(H)Ge(CH_2)_nGe(H)Me_2$ ($n=1$, 2) hydrides were prepared as previously described [26, 27], by insertion of dihalogermylenes in the dihaloalkanes $X(CH_2)_nX$, methylation, monochlorination on each germanium atom and reduction by $LiAlH_4$ as summarized in Scheme 1.

$Me_2(H)GeGe(H)Me_2$ is obtained by reduction of the dichloride $Me_2(Cl)GeGe(Cl)Me_2$ by Bu_3SnH. The starting material hexamethyldigermane can be readily prepared by a Würtz reaction using alkali metal or, better, Li–Hg amalgam for coupling of chlorotrimethylgermane. It is noteworthy that 1,1,2,2-tetramethyldigermane is a thermally unstable compound which decomposes near 70 °C with formation of dimethylgermylene Me_2Ge, according to Scheme 2.

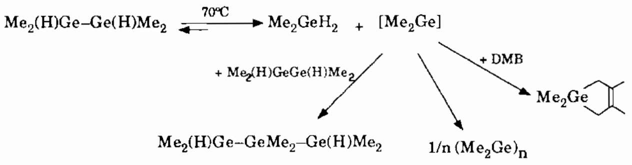


Scheme 1.

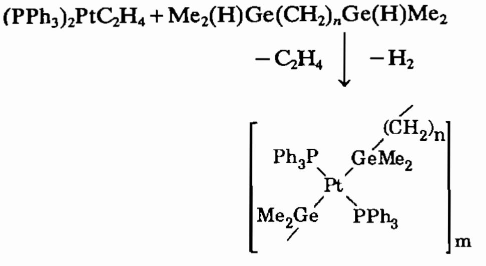
Dimethylgermylene which polymerizes in the absence of a reagent is easily characterized by condensation with a conjugated diene such as dimethylbutadiene (DMB) [29].

Synthesis of complexes 1–6

We attempted to prepare complexes **1** and **3** by oxidative addition of the corresponding digermanes $Me_2(H)Ge(CH_2)_nGe(H)Me_2$ ($n=1$, 2) to the platinum complex $[(PPh_3)_2PtC_2H_4]$ in C_6H_6 solution at room temperature. As expected rapid ethylene and hydrogen loss is observed; the reactions lead to pale yellow solids, practically insoluble in common organic solvents, stable in air, corresponding probably to the polymeric (or oligomeric) structures $[Me_2Ge(CH_2)_nGe(Me_2)\text{-}Pt(PPh_3)_2]_m$ ($n=2$ (**7**), 1 (**8**)). These reactions are analogous to those observed for various silylated platinum complexes [30] and probably involve in the first step unstable hydrido(germyl)platinum complexes; rapid hydrogen loss forms the Ge–Pt bond.



Scheme 2.

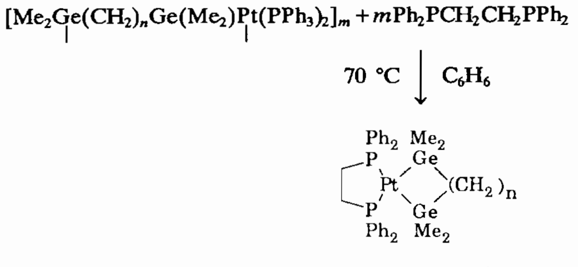


$n=2$ (**7**), 1 (**8**)

7 and **8** are likely to have a planar square structure of four groups around the platinum metal with a *trans* configuration of the phosphine ligands. This structure is suggested by the IR spectra of these solid forms. Both have a single sharp, medium band at 417 cm^{-1} assigned to ν(Pt–P) and the characteristic bands of the Me$_3$Ge group [ρ(Me) at 813 cm^{-1} and ν(Ge–C) in the range 559–505 cm^{-1}, two bands]. Usually *trans* complexes of platinum show one medium to strong band in the range 418–406 cm^{-1} [31].

Treatment of complexes **7** and **8** with the chelating 1,2-bis(diphenylphosphino)ethane (diphos) produces the monomer doubly chelated complexes **2** and **4** (Scheme 3). While the complexes **7** and **8** were only characterized by IR and elemental analyses, the complexes **2** and **4** were identified by their ^{1}H, ^{31}P NMR spectroscopic characteristics and by mass spectrometric and elemental analyses. For example in the ^{1}H NMR spectrum the Me$_2$Ge resonance of **2** consists of a doublet [$\delta=0.38$ ppm, $J(^{31}\text{P–Pt–Ge–C–}^1\text{H})=2.4$ Hz] flanked by two satellites doublets produced by coupling with the ^{195}Pt nucleus with a separation $J(^{195}\text{Pt–Ge–C–}^1\text{H})=16.8$ Hz. The CH$_2$Ge consists also of a pseudotriplet (1 singlet and 2 satellites) [$\delta=1.44$ ppm, $J(^{195}\text{Pt–Ge–C–}^1\text{H})=10.6$ Hz, $J(^{31}\text{P–Pt–Ge–C–}^1\text{H})=0.5$ Hz] and the CH$_2$–P resonance consists of a doublet [$\delta=1.80$ ppm, $J(^1\text{H–C–}^{31}\text{P})=18.2$ Hz] with satellites (d.d) of the correct intensity (~1, 4, 1) $J(^1\text{H–C–P–}^{195}\text{Pt})=14.5$ Hz.

The tetramethyldigermane Me$_2$(H)GeGe(H)Me$_2$ reacts also, at room temperature in C$_6$D$_6$ with [(Ph$_3$P)$_2$PtC$_2$H$_4$]. Loss of C$_2$H$_4$ and H$_2$ is very fast and the monomeric three-membered heterocycle **5**, soluble in C$_6$H$_6$ with high moisture- and oxygen-sensitivity is characterized by ^{1}H and ^{31}P NMR analysis [^{1}H NMR: δ GeMe$_2=0.53$(s) ppm flanked by the two expected satellites $J(^1\text{H–C–Ge–}^{195}\text{Pt})=14$ Hz; ^{31}P NMR $\delta=24.8$ ppm $J(^{195}\text{Pt–}^{31}\text{P})=1964$ Hz] and chemically by oxygen insertion reaction in the Ge–Ge bond and hydrolysis (Scheme 4). On treatment with 1,2-bis(diphenylphosphino)ethane the doubly chelated complex **6** is obtained.



$n=2$ (**2**), 1 (**4**)

Scheme 3.

Reactivity of 1–8

All these germylated platinum complexes have high potential in organometallic synthesis and for example can lead to new organogermanium heterocycles as well as to platinum complexes.

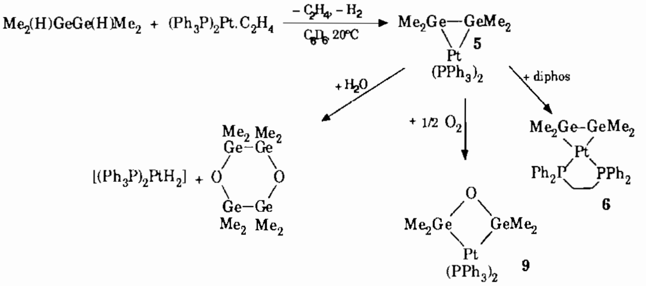
The reactions of **1–8** are for the most part those expected for metals in oxidation level 2 and coordination number 4. Many electrophilic and nucleophilic reagents cleave the Ge–Pt under metal conditions.

Reaction of 7 with pyridine

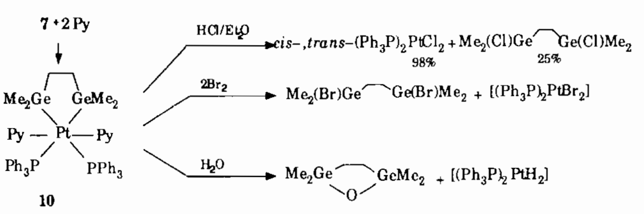
On treatment with pyridine the polymeric complex [Me$_2$Ge(CH$_2$)$_2$Ge(Me$_2$)Pt(PPh$_3$)$_2$]$_m$ picks up two extra ligands on each platinum atom to form the monomeric octahedral platinum complex [Me$_2$GeCH$_2$CH$_2$Ge(Me$_2$)Pt(PPh$_3$)$_2$Py$_2$] (**10**). **10** was identified by ^{1}H, ^{13}C, ^{31}P NMR and chemical reactivity (Scheme 5).

Reaction with hydrogen halides

Anhydrous hydrogen chloride cleaves the Pt–Ge bond of **1** or **2** to give a mixture of germylated chlorides and hydrides, the percentage of which is dependent on the length of the experiment.



Scheme 4.



Scheme 5.

$$\mathbf{1} \text{ or } \mathbf{2} \xrightarrow{2HCl/Et_2O} Me_2(Cl)Ge(CH_2)_2Ge(Cl)Me_2 \quad >70\%$$

$$+ Me_2(H)Ge(CH_2)_2Ge(H)Me_2 \quad \text{(traces } <5\%\text{)}$$

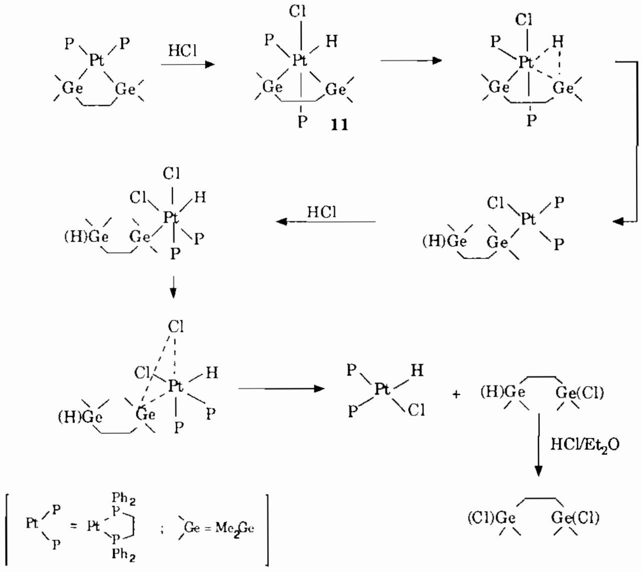
$$+ Me_2(H)Ge(CH_2)_2Ge(Cl)Me_2 \quad 15\%$$

This reaction can be explained by two successive addition elimination reactions (two steps) identical to that which has been shown to account for the hydrogen cleavage of various platinum–carbon σ-bond and the Pt–Ge bond of *cis*[$(Ph_2PCH_2CH_2PPh_2)Pt(GeR_3)_2$] [18, 31]. The reaction leading to the dichloride $Me_2(Cl)Ge(CH_2)_2Ge(Cl)Me_2$ proceeds probably in two steps: (i) *cis*-addition of hydrogen chloride, the hydrogen going in *trans* to the ligand of highest *trans*-effect gives the platinum(II) intermediate **11** which then reverts to platinum(II) complex with Ge–H bond by *cis*-elimination; (ii) in the second step *cis* addition of hydrogen chloride with the hydrogen *trans* to the ligand of highest *trans*-influence occurs then *cis*-elimination leads to the formation of the Ge–Cl bond; the formed chlorogermane $Me_2(Cl)Ge(CH_2)_2Ge(H)Me_2$ reacting immediately with an excess of HCl to form the germylated dichloride (Scheme 6).

Reaction with halogens

Platinum–germanium bonds of the complexes **1** or **2** are easily cleaved in benzene solution at room temperature.

The reaction probably occurs by electrophilic attack of the halogen on the platinum(II) complex to give a six-coordinate platinum(IV) intermediate which then breaks down to give the observed platinum(II) complex (*cis* or *trans* depending on the starting material) and the halogen adduct of the Group 14 metal.



Scheme 6.

$$\mathbf{1} \text{ or } \mathbf{2} + 2Br_2 \longrightarrow trans\text{- or } cis\text{-}(Ph_3P)_2PtBr_2 + Me_2(Br)Ge(CH_2)_2Ge(Br)Me_2$$

Reaction with alkyl halides

Reactions of these platinum-germylated complexes with alkyl halides follow the expected route shown in the following equation.

$$\mathbf{1} \text{ or } \mathbf{2} + 2MeI \longrightarrow trans\text{- or } cis(Ph_3P)_2PtI_2 + Me_3Ge(CH_2)_2GeMe_3$$

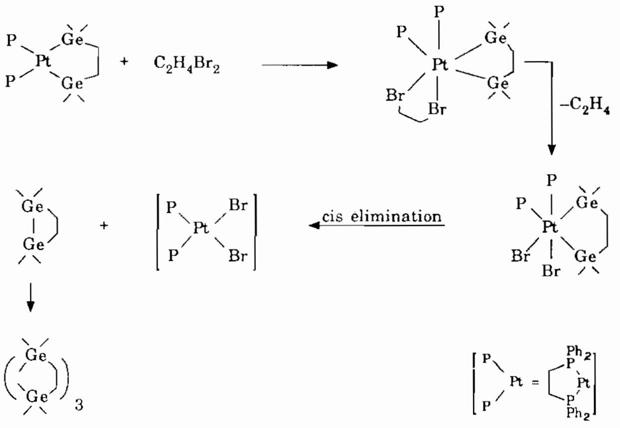
1,2-Dibromoethane also cleaves the platinum–germanium bonds according to the very characteristic Scheme 7.

These two cleavages probably involve octahedral platinum(IV) intermediates as previously postulated.

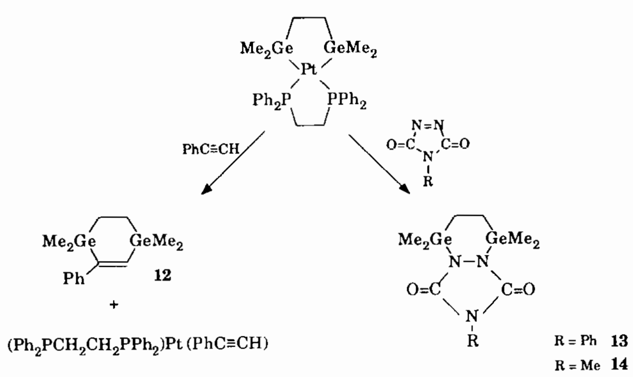
Reactions with phenylacetylene and N-phenyl and N-methyl triazolinediones

Double germylation of these unsaturated systems is observed in nearly quantitative yield.

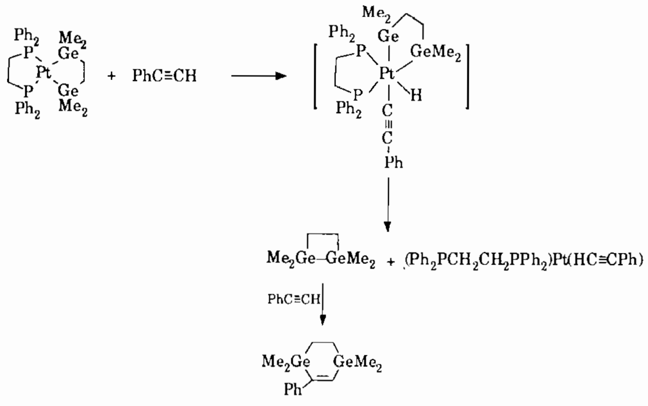
For example compound **2** reacts at room temperature and immediately with *N*-phenyl and *N*-methyltriazolinediones and only at 65 °C with phenylacetylene producing new digermanium heterocycles **12**–**14** in high yields (Scheme 8). Heterocycles **12**–**14** that are formally



Scheme 7.



Scheme 8.

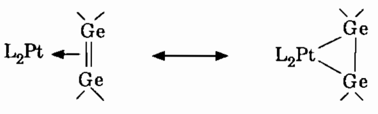


Scheme 9.

the adducts of the 1,1,2,2-tetramethylgermetane $Me_2\overline{GeCH_2CH_2Ge}Me_2$ with phenylacetylene or with triazolinediones were characterized by NMR, MS and element analysis.

The reaction with phenylacetylene could be explained in terms of an initial classical *cis*-addition of $PhC{\equiv}CH$ to platinum(II) to give a labile platinum(IV) intermediate (Scheme 9).

We are now investigating the chemistry of **5** and **6** with a wide variety of both nucleophilic and electrophilic reagents; **5** and **6** appear as the formal complexes of the digermene $[Me_2Ge{=}GeMe_2]$ with platinum.



The preliminary results show analogies with the chemistry of both digermenes and three-membered ring compounds and will be reported in a future publication.

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