

Platinum–Germanium Compounds from the Reactions of (COD)PtMe₂ (COD = 1,5-cyclooctadiene) with HGePh₃

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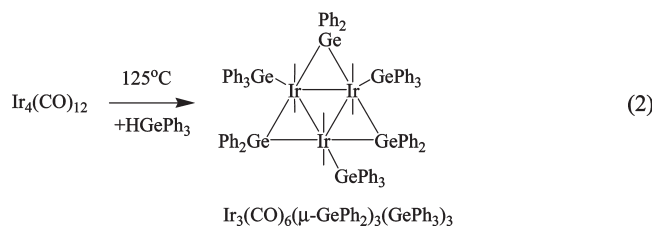
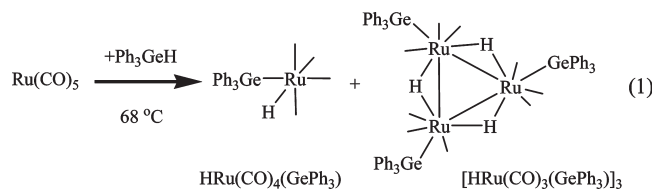
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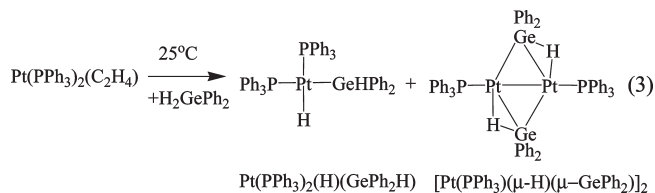
The reaction of Pt(COD)Me₂ with HGePh₃ in hexane solvent at room temperature for 30 h yielded the two new compounds Pt(COD)(Me)(GePh₃), **1** (16%), and Pt(COD)(GePh₃)₂, **2** (9%), by replacement of the methyl groups by GePh₃ ligands. When this reaction was performed under an atmosphere of CO the compound *trans*-Pt(CO)₂(GePh₃)₂, **3** was obtained in 26% yield together with a new compound Pt₂(CO)₂(GePh₃)₂(μ-GePh₂)₂, **4** in 10% yield. Compound **2** was obtained from **1** in 51% yield by reaction with an additional quantity of HGePh₃ and **3** was obtained from **2** in 16% yield by treatment with CO. All four products were characterized by single crystal X-ray diffraction analyses. Compound **4** contains two platinum atoms with two bridging GePh₂ ligands and a Pt–Pt single bond. Fenske–Hall molecular orbital calculations on a model for **4** were performed to understand its bonding.

Introduction

It is well-known that aryl and alkylgermanes react readily with transition metal carbonyls at the GeH bond(s) to yield products containing M–Ge bonds, for example, eqs 1, 2.^{1–5}



Platinum phosphine complexes react similarly to yield phosphine containing products containing Pt–Ge bonds, for example, eq 3.^{6–9}



In recent studies we have shown that transition metal complexes containing tin ligands can serve as precursors to heterogeneous nanocatalysts that exhibit extraordinary activity and selectivity for certain types of catalytic hydrogenation reactions.^{10–13} As a result, we decided to investigate

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the synthesis of some phosphine-free platinum–germanium complexes for potential use as precursors to new types of nanoscale heterogeneous PtGe catalysts.

In this report we describe our studies of the reactions of Pt(COD)Me₂ (COD=1,5-cyclooctadiene) with HGePh₃ which have led to the synthesis and characterization of the new phosphine-free PtGe complexes Pt(COD)(Me)(GePh₃), **1**, and Pt(COD)(GePh₃)₂, **2**. When this reaction was performed under a CO atmosphere, two new compounds, *trans*-Pt(CO)₂(GePh₃)₂, **3**, and Pt₂(CO)₂(GePh₃)₂(μ -GePh₂)₂, **4**, were formed.

Experimental Section

General Data. All the reactions were performed under a nitrogen atmosphere using the standard Schlenk techniques, unless otherwise stated. Reagent grade solvents were dried by the standard procedures and were freshly distilled prior to use. Infrared spectra were recorded on an AVATAR 360 FT-IR spectrophotometer at room temperature. ¹H NMR spectra were recorded on a Varian Mercury 400 spectrometer operating at 399 MHz at room temperature. The resonance for methane was identified based on an independent measurement of authentic material. Mass spectrometric measurements performed by direct exposure probe (DEP) using electron impact ionization (EI) were made on a VG 70S instrument. Triphenylgermane (HGePh₃) was purchased from Aldrich and was used without further purification. Pt(COD)Me₂ was prepared according to a previously published procedure.¹⁴ Product separations were performed by TLC in air on Analtech 0.25 mm silica gel 60 Å F254 glass plates.

Reaction of Pt(COD)Me₂ with HGePh₃. A 24.0 mg amount of Pt(COD)Me₂ (0.072 mmol) was dissolved in 20 mL of hexane in a 100 mL three-neck flask. To this solution a 109.8 mg amount of HGePh₃ (0.36 mmol) was added and stirred at room temperature for 40 h. The solvent was then removed in vacuo, and the products were separated by TLC by using 4:1 hexane-methylene chloride solvent mixture to yield 7.0 mg of colorless Pt(COD)(Me)GePh₃, **1** (16%), and 5.6 mg of colorless Pt(COD)(GePh₃)₂, **2** (9%). The major component is unreacted Pt(COD)Me₂. Unfortunately, heating the reaction does not improve the yields because of decomposition of the products. Spectral data for **1**: ¹H NMR (CDCl₃, in ppm): δ = 7.17–7.55 (m, 15 H, Ph), 5.42 (s, 2H, CH, ²J_{H-H} = 13.1 Hz), 4.65 (s, 2H, CH, ²J_{Pt-H} = 41 Hz), 2.27 (broad, 8H, CH₂), 0.97 (s, 3H, CH₃, ¹J_{Pt-H} = 70 Hz). Mass Spec. DEP/MS *m/z*: 622, M⁺; 607, M⁺–CH₃. Spectral data for **2**: ¹H NMR (CDCl₃, in ppm): δ = 7.00–7.32 (m, 30 H, Ph), 5.25 (s, 4H, CH, ²J_{H-H} = 13.1 Hz), 2.25 (br, 8H, CH₂). Mass Spec. DEP/MS *m/z*: 910, M⁺.

Reaction of Pt(COD)Me₂ with HGePh₃ in an NMR Tube. A 10.0 mg amount of Pt(COD)Me₂ (0.030 mmol) was dissolved in 2 mL of CDCl₃ in an NMR tube. To this solution a 27.5 mg amount of HGePh₃ (0.090 mmol) was added, and the solution was sealed under nitrogen. ¹H NMR spectra were taken at the beginning and after 2 days. A resonance at δ = 0.20 due to the presence of methane was observed. The resonances of **1** and **2** were also observed.

Reaction of **1 with HGePh₃.** A 20.0 mg amount of **1** (0.032 mmol) was dissolved in 20 mL of CH₂Cl₂ in a 100 mL three-neck flask. To this solution a 19.5 mg amount of HGePh₃ (0.064 mmol) was added and stirred at room temperature for 2 days. The solvent was then removed in vacuo, and the products were separated by TLC by using 4:1 hexane-methylene chloride solvent mixture to yield 9.1 mg of colorless **1** (45%) and 15.0 mg of colorless **2** (51%).

Reaction of **1 with HGePh₃ in an NMR Tube.** A 7.0 mg amount of **1** (0.011 mmol) was dissolved in 2 mL of CDCl₃ in an NMR tube. To this solution a 6.9 mg amount of HGePh₃ (0.023 mmol) was added, and the solution was sealed under nitrogen. ¹H NMR spectra were taken after a few minutes and after a few hours. A resonance at δ = 0.20 due to the presence of methane formed and increased with time.

Reaction of Pt(COD)Me₂ with HGePh₃ under CO. A 20.5 mg amount of Pt(COD)Me₂ (0.061 mmol) was dissolved in 20 mL of hexane in a 100 mL three-neck flask. The solution was purged with CO and stirred at room temperature for 10 min. To this solution a 55.0 mg amount of HGePh₃ (0.18 mmol) was added and refluxed for 2 h. The solvent was then removed in vacuo, and the products were separated by TLC by using 4:1 hexane-methylene chloride solvent mixture to yield 13.6 mg of purple Pt(CO)₂(GePh₃)₂, **3** (26%), and 4.7 mg of yellow Pt₂(CO)₂(GePh₃)₂(μ -GePh₂)₂, **4** (10%). Spectral data for **3**: IR ν_{CO} (cm⁻¹ in CH₂Cl₂): 2057 (s). ¹H NMR (CDCl₃, in ppm): δ = 7.23–7.52 (m, 30 H, Ph); Elemental Anal. %Calcd: C, 53.14; H, 3.52, %Found: C, 53.73; H, 3.68. Spectral data for **4**: IR ν_{CO} (cm⁻¹ in CH₂Cl₂): 2040 (s). ¹H NMR (CDCl₃, in ppm): δ = 6.96–7.34 (m, 50 H, Ph). Mass Spec. DEP/MS *m/z*: 1508, M⁺ (weak); 1480, M⁺–CO; 1452, M⁺–2 CO.

Alternative Preparation for **3.** A 15.0 mg amount of **2** (0.016 mmol) was dissolved in 20 mL of CH₂Cl₂ in a 100 mL three-neck flask. This solution was purged with CO and stirred at room temperature for 10 min. During this time the color of the solution turned to purple. The solvent was then removed in vacuo, and the product was separated by TLC by using 4:1 hexane-methylene chloride solvent mixture to yield 5.8 mg of purple **3** (17%).

Reaction of Pt(COD)Me₂ with CO and HGePh₃ in an NMR Tube. An 11.0 mg amount of Pt(COD)Me₂ (0.033 mmol) was dissolved in 1 mL of CDCl₃ in an NMR tube. The tube was sealed, purged, and filled with CO. To this solution a 35.2 mg amount of HGePh₃ (0.115 mmol) dissolved in 1 mL of CDCl₃ was added via syringe. A ¹H NMR spectrum taken after 10 min showed the formation of methane, δ = 0.20.

Crystallographic Analyses. Colorless single crystals of **1** and **2** and yellow crystals of **4** suitable for X-ray diffraction analyses were each obtained by slow evaporation of solvent from a solution in methylene chloride/hexane solvent mixtures at –20 °C. Purple single crystals of **3** suitable for X-ray diffraction analysis were obtained from a solution in a methylene chloride/hexane solvent mixtures under a CO atmosphere in a closed vial by cooling to –20 °C. Each data crystal was glued onto the end of a thin glass fiber. X-ray intensity data were measured by using a Bruker SMART APEX CCD-based diffractometer using Mo K α radiation (λ = 0.71073 Å). The raw data frames were integrated with the SAINT+ program by using a narrow-frame integration algorithm.¹⁵ Corrections for Lorentz and polarization effects were also applied with SAINT+. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied using the program SADABS. All structures were solved by a combination of direct methods and difference Fourier syntheses, and refined by full-matrix least-squares on *F*², using the SHELXTL software package.¹⁶ All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in geometrically idealized positions and included as standard riding atoms during the least-squares refinements. Crystal data, data collection parameters, and results of the refinements are listed in Table 1.

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Table 1. Crystallographic Data for Compounds 1–4

	1	2	3	4
empirical formula	PtGeC ₂₇ H ₃₀	PtGe ₂ C ₄₄ H ₄₂	PtGe ₂ O ₂ C ₃₈ H ₃₀	Pt ₂ Ge ₄ O ₂ C ₆₂ H ₅₀
formula weight	622.19	911.05	858.89	1507.56
crystal system	triclinic	monoclinic	triclinic	monoclinic
lattice parameters				
<i>a</i> (Å)	11.3509(6)	9.8177(4)	8.4587(5)	12.2302(7)
<i>b</i> (Å)	15.0194(7)	16.4878(7)	9.5315(6)	14.2508(9)
<i>c</i> (Å)	15.8322(8)	22.4301(10)	11.7137(7)	15.5895(10)
α (deg)	73.439(1)	90.00	72.609(1)	90.00
β (deg)	70.848(1)	95.235(1)	78.597(1)	93.847(1)
γ (deg)	69.571(1)	90.00	66.601(1)	90.00
<i>V</i> (Å ³)	2344.6(2)	3615.7(3)	823.75(9)	2711.0(3)
space group	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> 2 ₁ / <i>n</i> (No. 14)
<i>Z</i> value	4	4	1	2
ρ_{calc} (g/cm ³)	1.763	1.674	1.731	1.847
μ (Mo K α) (mm ⁻¹)	7.252	5.542	6.080	7.372
temperature (K)	294(2)	294(2)	294(2)	294(2)
2 θ_{max} (deg)	41.54	52.18	53.26	50.86
no. obs. (<i>I</i> > 2 σ (<i>I</i>))	6088	6878	4077	6753
no. parameters	525	424	196	416
goodness of fit (GOF) ^a	0.931	0.979	1.087	0.985
max. shift in cycle	0.003	0.003	0.007	0.004
residuals ^a : R ₁ ; wR ₂	0.0430; 0.0713	0.0279; 0.0579	0.0352; 0.0775	0.0249; 0.0524
absorption correction, max/min	multiscan 1.000/0.730	multiscan 1.000/0.528	multiscan 1.000/0.689	multiscan 1.000/0.564
largest pk in final diff. map (e ⁻ /Å ³)	1.733	1.333	1.331	1.053

$$^a R = \sum_{\text{hkl}} (|F_{\text{obs}}| - |F_{\text{calc}}|) / \sum_{\text{hkl}} |F_{\text{obs}}|; R_w = [\sum_{\text{hkl}} w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2 / \sum_{\text{hkl}} w F_{\text{obs}}^2]^{1/2}, w = 1/\sigma^2(F_{\text{obs}}); \text{GOF} = [\sum_{\text{hkl}} w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2 / (n_{\text{data}} - n_{\text{vari}})]^{1/2}.$$

Compounds **1** and **3** both crystallized in the triclinic crystal system. The space group *P* $\bar{1}$ was assumed and confirmed by the successful refinement and solution of both structures. For **1** with *Z* = 4, there are two symmetry independent molecules present in the asymmetric crystal unit. On the other hand, compound **3** has *Z* = 1, and the complex lies on a crystallographic center of symmetry in the solid state.

Compound **2** and **4** both crystallized in the monoclinic crystal system. The systematic absences in the intensity data identified the unique space group *P*2₁/*n*. The crystal contains one independent formula equivalent of the complex in the asymmetric crystal unit. For **4**, *Z* = 2, and the complex lies on a crystallographic center of symmetry.

Molecular Orbital Calculations. A single point molecular orbital calculation was performed on a model for **4** by using the atomic coordinates derived from the single crystal X-ray diffraction analysis. GeH₃ and GeH₂ were used in place of GePh₃ and GePh₂, respectively, in these calculations. The Ge–H distances were set at 1.52 Å. The molecular orbital calculations reported herein were performed by using the Fenske–Hall method.¹⁷ Contracted double- ζ basis sets were used for the Pt 5d, Ge 4p, and C and O 2p atomic orbitals. The Fenske–Hall molecular orbital method is an approximate self-consistent-field (SCF) nonempirical method that is capable of calculating molecular orbitals for very large transition metal systems and has built-in fragment analysis routines that allow one to assemble transition metal cluster structures from the ligand-containing fragments.

Results and Discussion

The reaction of Pt(COD)Me₂ with HGePh₃ in hexane solvent at room temperature for 30 h yielded the two new compounds **1** (16%) and **2** (9%). Both compounds

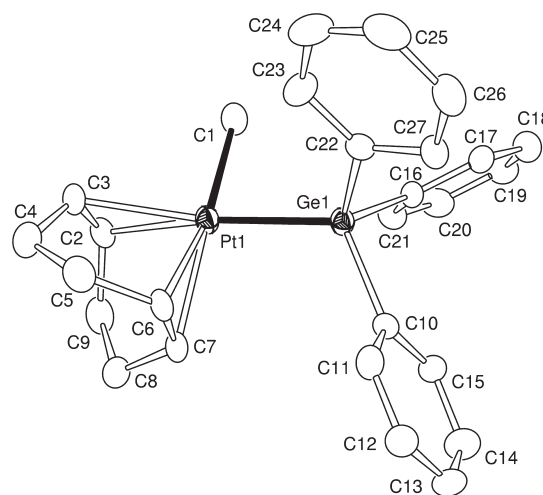


Figure 1. ORTEP diagram of the molecular structure of Pt(COD)(Me)(GePh₃), **1**, showing 30% probability thermal ellipsoids. Selected bond distances (Å) and angles (deg) are as follow: Molecule 1: Pt(1)–Ge(1) = 2.4045(8), Pt(1)–C(1) = 2.068(7), Pt(1)–C(6) = 2.218(7), Pt(1)–C(7) = 2.264(7), Pt(1)–C(2) = 2.274(7), Pt(1)–C(3) = 2.327(7), Pt(1)–Ge(1) = 2.4045(8), C(2)–C(3) = 1.315(10), C(6)–C(7) = 1.359(9), C(1)–Pt(1)–Ge(1) = 86.2(2); Molecule 2: Pt(2)–Ge(2) = 2.4014(8), Pt(2)–C(31) = 2.061(7), Pt(2)–C(32) = 2.226(7), Pt(2)–C(33) = 2.261(7), Pt(2)–C(36) = 2.288(7), Pt(2)–C(37) = 2.316(7), C(32)–C(33) = 1.365(9), C(36)–C(37) = 1.331(10); C(31)–Pt(2)–Ge(2) = 85.4(2).

were characterized by IR, ¹H NMR, mass spectral, and single-crystal X-ray diffraction analyses. Compound **1** crystallizes with two completely independent molecules in the asymmetric crystal unit. Both molecules are structurally similar. An Oak Ridge Thermal Ellipsoid Plot (ORTEP) diagram of the molecular structure of one of the two molecules of **1** is shown in Figure 1. The Pt–Ge distance, Pt(1)–Ge(1) = 2.4045(8) Å, [Molecule 2: Pt(2)–Ge(2) = 2.4014(8) Å] is slightly shorter than the Pt–Ge distances to the GePh₃ ligand found in the complexes cis-Pt(PPhMe₂)₂(Me)(GePh₃),

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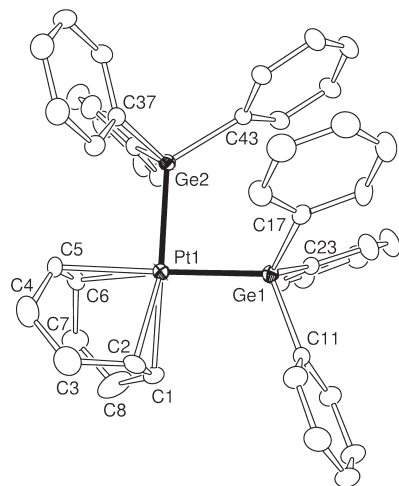


Figure 2. ORTEP diagram of the molecular structure of $\text{Pt}(\text{COD})-(\text{GePh}_3)_2$, **2** showing 30% probability thermal ellipsoids. Selected bond distances (Å) and angles are as follow: $\text{Pt}(1)-\text{Ge}(1)=2.4292(3)$, $\text{Pt}(1)-\text{Ge}(2)=2.4350(4)$, $\text{Pt}(1)-\text{C}(2)=2.287(4)$, $\text{Pt}(1)-\text{C}(1)=2.300(4)$, $\text{Pt}(1)-\text{C}(6)=2.312(3)$, $\text{Pt}(1)-\text{C}(5)=2.322(3)$, $\text{C}(1)-\text{C}(2)=1.364(6)$, $\text{C}(5)-\text{C}(6)=1.338(5)$; $\text{Ge}(1)-\text{Pt}(1)-\text{Ge}(2)=89.483(12)$.

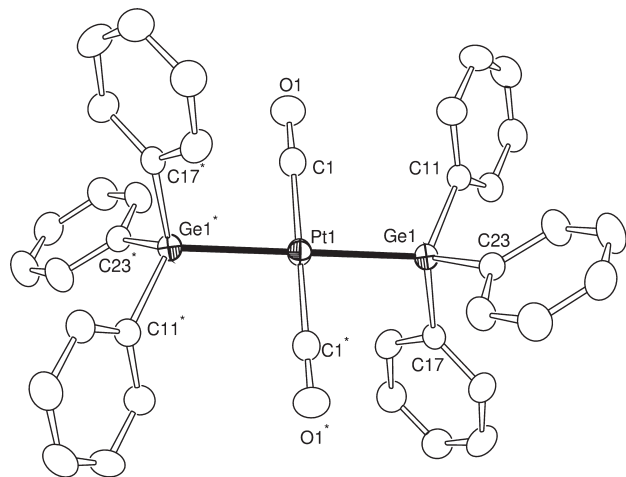


Figure 3. ORTEP diagram of the molecular structure of *trans*- $\text{Pt}(\text{CO})_2-(\text{GePh}_3)_2$, **3**, showing 30% probability thermal ellipsoids. Selected bond distances (Å) and angles are as follow: $\text{Pt}(1)-\text{C}(1)=1.895(5)$, $\text{Pt}(1)-\text{Ge}(1)=2.5095(4)$; $\text{Ge}(1)-\text{Pt}(1)-\text{Ge}(1)=180.0$, $\text{C}(1)-\text{Pt}(1)-\text{C}(1)=180.0$.

5, $\text{Pt}-\text{Ge}=2.4495(5)$ Å¹⁸ and *cis*- $\text{Pt}(\text{PPhMe}_2)_2(\text{Et})(\text{GePh}_3)$, **6**, $\text{Pt}-\text{Ge}=2.437(1)$ Å.¹⁹ The Pt–C distance to the CH₃ ligand, $\text{Pt}(1)-\text{C}(1)$ is 2.068(7) Å [*Molecule 2*: $\text{Pt}(2)-\text{C}(31)=2.061(7)$ Å] is significantly shorter than the Pt–C distance to the methyl group in **5**, 2.127(5) Å and in $\text{Pt}(\text{COD})\text{Me}_2$, 2.134(6) Å [20]. The Ge–Pt–C angle is $\text{C}(1)-\text{Pt}(1)-\text{Ge}(1)=86.2(2)^\circ$ [*Molecule 2*: $\text{C}(31)-\text{Pt}(2)-\text{Ge}(2)=85.4(2)^\circ$]. The C–C distances of the coordinate double bonds on the COD ligand are short, $\text{C}(2)-\text{C}(3)=1.315(10)$ Å, $\text{C}(6)-\text{C}(7)=1.359(9)$ Å [*Molecule 2*: $\text{C}(32)-\text{C}(33)=1.365(9)$ Å, $\text{C}(36)-\text{C}(37)=1.331(10)$ Å, as expected and similar to those observed in $\text{Pt}(\text{COD})\text{Me}_2$, 1.388(12) Å and ;1.374(11) Å.²⁰

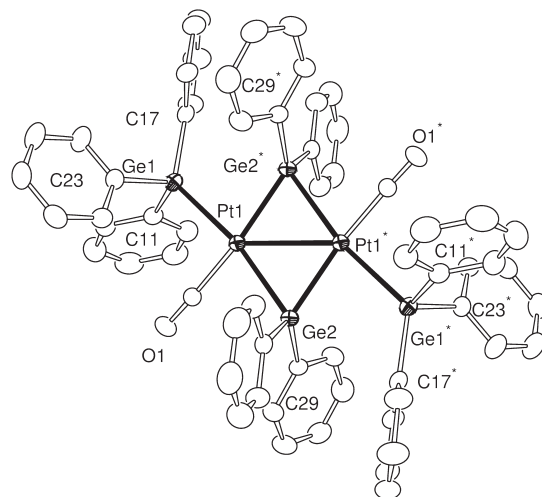


Figure 4. ORTEP diagram of the molecular structure of $\text{Pt}_2(\text{CO})_2-(\text{GePh}_3)_2(\mu\text{-GePh}_3)_2$, **4**, showing 30% probability thermal ellipsoids. Selected bond distances (Å) and angles are as follow: $\text{Pt}(1)-\text{Pt}(1)=2.8394(3)$, $\text{Pt}(1)-\text{Ge}(1)=2.5088(4)$, $\text{Pt}(1)-\text{Ge}(2)=2.5322(4)$, $\text{Pt}(1)-\text{Ge}(2^*)=2.3800(3)$, $\text{Pt}(1)-\text{C}(1)=1.893(3)$; $\text{C}(1)-\text{Pt}(1)-\text{Ge}(1)=90.28(10)$, $\text{Ge}(2)-\text{Pt}(1)-\text{Ge}(1)=81.113(12)$, $\text{Ge}(1)-\text{Pt}(1)-\text{Ge}(2)=169.358(12)$, $\text{Ge}(2)-\text{Pt}(1)-\text{Pt}(1)=57.235(8)$, $\text{Ge}(1)-\text{Pt}(1)-\text{Pt}(1)=138.329(11)$.

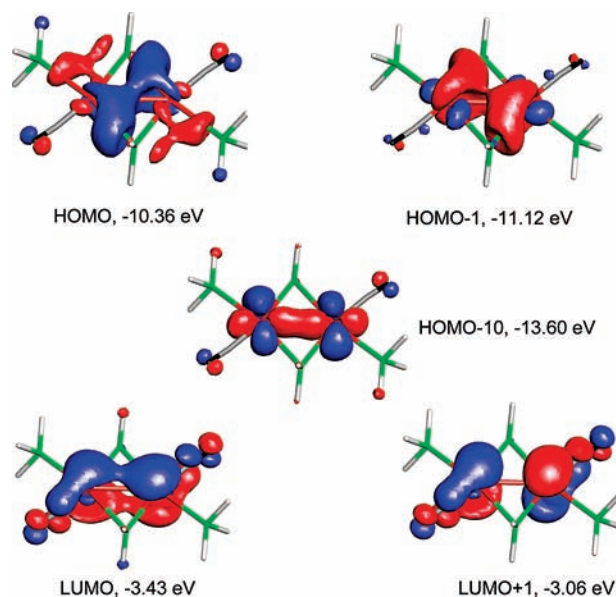


Figure 5. Contour diagrams for some selected Fenske–Hall molecular orbitals for **4**: Upper left, HOMO; upper right HOMO-1, center HOMO-10, lower left, LUMO and lower right LUMO+1.

An ORTEP diagram of the molecular structure of **2** is shown in Figure 2. The Pt–Ge distances, $\text{Pt}(1)-\text{Ge}(1)=2.4292(3)$ Å, $\text{Pt}(1)-\text{Ge}(2)=2.4350(4)$ Å, are slightly longer than that found in **1**, but are similar to those found in **5** and **6**. The Ge–Pt–Ge angle is $89.483(12)^\circ$. The C–C distances of the coordinated double bonds are $\text{C}(1)-\text{C}(2)=1.364(6)$ Å and $\text{C}(5)-\text{C}(6)=1.338(5)$ Å. Not surprisingly, compound **2** was obtained from **1** by reaction with an additional quantity of HGePh_3 . The yield was good, 51%, but the conversion was low; 45% of the **1** was recovered after 2 days of reaction at 25 °C. Heating this reaction did not improve the yield of **2**.

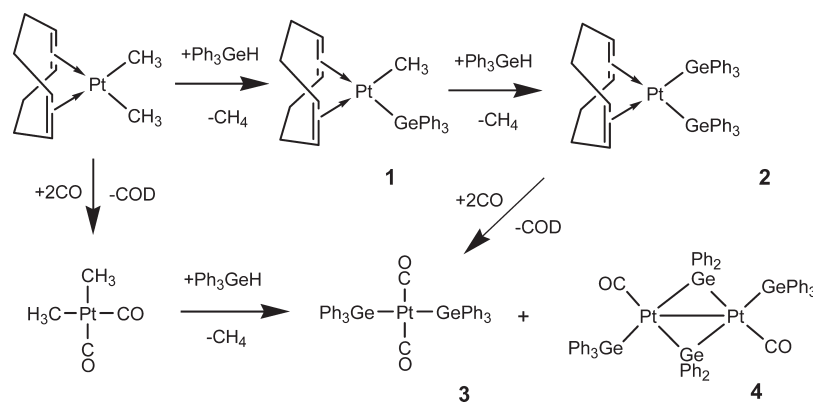
When $\text{Pt}(\text{COD})\text{Me}_2$ was allowed to react with HGePh_3 in hexane solution at reflux under a CO atmosphere, two new

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Scheme 1



compounds were obtained: $\text{Pt}(\text{CO})_2(\text{GePh}_3)_2$, **3** (26% yield) and $\text{Pt}_2(\text{CO})_2(\text{GePh}_3)_2(\mu\text{-GePh}_2)_2$, **4** (10% yield). This reaction appears to proceed through the intermediacy of the compound $\text{Pt}(\text{CO})_2\text{Me}_2$ ²¹ which was observed by infrared spectroscopic analysis at the start of the reaction and then disappeared as the reaction progressed. Compounds **3** and **4** were both characterized by IR, ¹H NMR, and single-crystal X-ray diffraction analyses. An ORTEP diagram of the molecular structure of **3** is shown in Figure 3. In the solid state compound **3** lies on a crystallographic center of symmetry. The molecule has a *trans*-geometry. The one independent Pt–Ge distance, Pt(1)–Ge(1) = 2.5095(4) Å, is significantly longer than those found in **1**, **2**, **5**, and **6**, but is slightly shorter than the Pt–Ge distances found in the complex $\text{Pt}(\text{PPhMe}_2)_2(\text{Et})(\text{GePh}_3)$, **7** which has a *trans*-geometry for the PPhMe_2 ligands, Pt–Ge = 2.5207(1) Å and 2.5239(4) Å.²² The one independent Pt–C distance to the CO ligands is 1.895(5) Å. Also, compound **3** was obtained directly from **2** by reaction with CO, but the yield, 17%, was low.

An ORTEP diagram of the molecular structure of **4** is shown in Figure 4. In the solid state compound **4** also lies on a crystallographic center of symmetry. Compound **4** contains two platinum atoms that are linked by two bridging GePh_2 ligands. There is one GePh_3 ligand and one terminal carbonyl ligand coordinated to each platinum atom, Pt(1)–Ge(1) = 2.5088(4) Å and Pt(1)–C(1) = 1.893(3) Å. The Pt_2Ge_4 core of the molecule is planar. The Pt–Pt distance of 2.8394(3) Å is sufficiently short to imply the existence of a Pt–Pt single bond. The Pt–Pt distance is slightly longer than the Pt–Pt distances observed for the compounds $\text{Pt}_2(\text{PPh}_3)_2(\mu\text{-H})_2(\mu\text{-GePh}_2)_2$,⁶ see eq 3, Pt–Pt = 2.7452(3) Å and $\text{Pt}_2(\text{PPh}_3)_2(\mu\text{-H})_2(\mu\text{-Ge}(\text{C}_6\text{H}_2\text{Me}_3)\text{H})_2$, Pt–Pt = 2.7614(5) Å which have hydride ligands bridging two of the Pt–Ge bonds.⁸ The bridging GePh_2 ligands are unsymmetrically coordinated to the platinum atoms, Pt(1)–Ge(2) = 2.5322(4) Å and Pt(1)–Ge(2*) = 2.3800(3) Å. This asymmetry may be explained by Fenske–Hall molecular orbital calculations that were also performed. Contour diagrams of selected molecular orbitals of **4** are shown in Figure 5. The highest occupied molecular orbital

(HOMO) and HOMO-1 show the σ -bonding between the platinum atoms and the bridging GePh_2 ligands. The HOMO at –10.36 eV shows the bonding involving the two long Pt–Ge interactions to the bridging GePh_2 ligand, while the lower energy HOMO-1 at –11.12 eV shows the bonding at the two short Pt–Ge interactions and is consistent with stronger bonding at these locations. The HOMO-10 at –13.60 eV shows convincing evidence for a strong Pt–Pt σ -bonding interaction formed by using a d-orbital from each platinum atom. The lowest unoccupied molecular orbital (LUMO) at –3.43 eV and LUMO + 1 at –3.06 eV show symmetrical and antisymmetrical combinations, respectively, of two empty p-orbitals, one from each platinum atom, which suggest a potential site for binuclear ligand additions or for the binuclear activation of small molecules.

The bridging GePh_2 ligands in **4** were apparently formed by the cleavage and elimination of a phenyl ring from a GePh_3 ligand. These cleavage transformations have been observed previously.^{2,5,23} Combined the two metal atoms have a total of 30 valence electrons, and each metal atom contains a 16 valence electron count if one assumes the presence of a Pt–Pt single bond.

A summary of the reactions described in this report is shown in Scheme 1. The compound $\text{Pt}(\text{COD})\text{Me}_2$ has been used to create new platinum complexes containing phenylgermyl ligands by reaction with HGePh_3 . The reaction presumably proceeds by a series of oxidative addition reactions of the Ge–H bond of the germane to the platinum atom, for example, eq 3, and the reductive elimination of methane to yield the compounds **1** and **2**. Compound **2** reacts with CO to replace the COD ligand and form the complex **3** which has a *trans*-geometry. Compound **3** can be obtained in a better yield in a one pot reaction by the reaction of $\text{Pt}(\text{COD})\text{Me}_2$ with HGePh_3 under an atmosphere of CO. This reaction appears to proceed through the intermediacy of the compound $\text{Pt}(\text{CO})_2\text{Me}_2$ which was observed in the reaction mixtures. A number of years ago, Urbancic et al. investigated the reaction of $\text{Pt}(\text{COD})\text{Me}_2$ with $\text{HM}(\text{CO})_5$, M = Mn and Re under a CO atmosphere and observed the formation of methane and the new mixed metal complexes *trans*- $\text{Pt}(\text{CO})_2[\text{M}(\text{CO})_5]_2$.²⁴ The diplatinum compound **4** which is stabilized by bridging

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GePh₂ ligands was obtained in a low yield. This product was formed by the cleavage of a phenyl ring from each of two GePh₃ ligands. A molecular orbital analysis of **4** reveals the presence of two low lying orbitals that could be a source for interesting binuclear reactivity toward small molecules.

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Supporting Information Available: CIF files for each of the structural analyses. This material is available free of charge via the Internet at <http://pubs.acs.org>.