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Preparation and Structure of a New Dipalladium Complex with Bridging Diphenylgermyl Ligands. Diverse Reactivities of $Pd(PCy_3)_2$ and $Pt(PCy_3)_2$ toward Ph_2GeH_2

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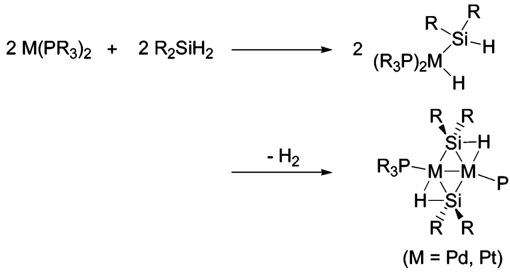
*Summary: A dinuclear palladium complex having bridging diphenylgermyl ligands, $[\{Pd(PCy_3)\}_2(\mu\text{-}HGePh_2)_2]$ (**1**), was obtained from the reaction of Ph_2GeH_2 with $[Pd(PCy_3)_2]$. X-ray crystallographic results and NMR spectra of **1** revealed coordination of the Ge ligands to two Pd centers via a Ge−H−Pd three-center−two-electron bond and a Ge−Pd σ bond. The reaction of Ph_2GeH_2 with $[Pt(PCy_3)_2]$ produces the (germyl)hydridoplatinum complexes cis-$[Pt(H)(GeHPh_2)(PCy_3)_2]$ (**cis-3**) and trans-$[Pt(H)(GeHPh_2)(PCy_3)_2]$ (**trans-3**) as the kinetic and thermodynamic products, respectively.*

Introduction

Reactions of primary (SiH_3R) and secondary (SiH_2R_2) organosilanes with low-valent late-transition-metal complexes provide a convenient method for preparation of the dinuclear complexes with bridging silyl ligands.[1] The dinuclear Pd(I) and Pt(I) complexes formed by this procedure contain a single bond between the two d^9 metal centers, which are bridged by two organosilyl ligands by three-center−two-electron (M−H−Si) bonds and M−Si σ bonds.[2−5] Scheme 1 depicts a possible pathway for the formation of these dinuclear complexes. Initial oxidative addition of a Si−H bond to Pd(0)− and Pt(0)−phosphine complexes forms mononuclear intermediates with hydride and silyl ligands, and subsequent dimerization of these intermediates leads to the dinuclear complexes of Pd(I) and Pt(I).

Despite the large number of the Pd and Pt complexes having bridging organosilyl ligands that have been reported so far, there have been only a few reports of similar dinuclear complexes with bridging organogermyl ligands. Recently, Braddock-Wilking prepared a diplatinum complex having bridging $GeHPh_2$ ligands, $[\{Pt(PPh_3)\}_2(\mu\text{-}HGePh_2)_2]$, from the reaction of H_2GePh_2 with $[Pt(PPh_3)_2(CH_2{=}CH_2)]$.[6] The intermediate mononuclear complex *cis*-$[Pt(H)(GeHPh_2)(PPh_3)_2]$ was isolated at an early stage of the reaction. Mochida reported that the reaction of $HPh_2Ge(SiMe_2)_nGePh_2H$ ($n = 0-3$) with a Pt(0) complex produced mononuclear Pt(II) complexes with hydride and germyl ligands as the oxidative addition products, which were further converted into $[\{Pt(PPh_3)\}_2(\mu\text{-}GePh_2)_2]$ via intermediate digermaplatinacycles.[7] An analogous dipalladium complex with bridging organogermyl ligands has no precedent, although mononuclear complexes with Pd−Ge and Pd═Ge bonds have been prepared by using R_3GeLi, digermylenes, and germylenes as the source of the Ge ligands.[8−13] Herein, we report the reaction of H_2GePh_2 with Pd(0) and Pt(0) complexes having PCy_3 ligands and the structure of a new dipalladium complex bridged by diphenylgermyl ligands.

Scheme 1



Results and Discussion

Treatment of H_2GePh_2 with $[Pd(PCy_3)_2]$ at room temperature for 18 h yields a dinuclear palladium complex with bridging

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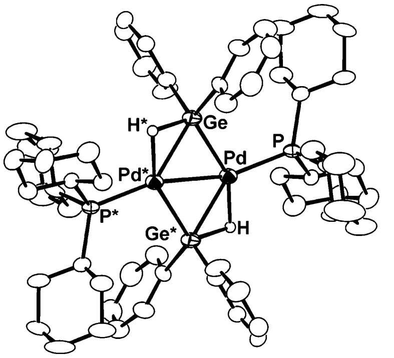
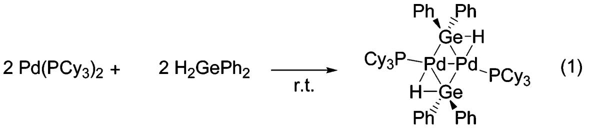


Figure 1. ORTEP drawing of **1** with ellipsoids drawn at the 30% probability level. The molecule has a C_2 symmetry center at the midpoint of two Pd centers. Atoms with asterisks are crystallographically equivalent to those having the same number without asterisks. Selected distances (Å) and angles (deg): Pd−Pd* = 2.752(1), Pd−P = 2.308(2), Pd−Ge = 2.440(1), Pd−Ge* = 2.415(1), Pd−H = 1.84(7), Ge−H* = 1.90(7); P−Pd−Ge = 104.89(6), P−Pd−Ge* = 142.65(7), Pd−Ge−Pd* = 69.05(3), Ge−Pd−Ge* = 110.95(4), P−Pd−Pd* = 158.50(6).

diphenylgermyl ligands, $[\{Pd(PCy_3)\}_2(\mu\text{-}HGePh_2)_2]$ (**1**), as a light yellow solid in 85% yield, as shown in eq 1. Figure 1 displays the molecular structure of **1** determined by X-ray crystallography. The molecule has crystallographic C_2 symmetry around the midpoint of the two Pd centers. The distance between the two Pd centers (2.752(1) Å) suggests the presence of a Pd−Pd bond, although it is significantly longer than that of $[\{Pd(PCy_3)\}_2(\mu\text{-}HSiPh_2)_2]$ (**2**) (2.691(1) Å).[4a] The Pd_2Ge_2 four-membered cyclic core is composed of two Pd−H−Ge three-center−two-electron bonds and two Pd−Ge σ bonds. The final *D* map shows the bridging hydrogens involved in the Pd−H−Ge bond. The Pd−Ge distance involved in the former bonding (2.440(1) Å) is longer than that in the latter (2.415(1) Å). The Si analogue **2** contains shorter Pd−Si distances of the Pd−H−Si three-center−two-electron bond (2.384(2) Å) and of the Pd−Si σ bond (2.326(2) Å) as compared to the corresponding Pd−Ge distances of **1**, due to the covalent radius of Ge (1.22 Å) being greater than that of Si (1.17 Å). Ge−H (1.90(7) Å) and Pd−H (1.84(7) Å) bond distances of **1** are longer compared with the Si−H (1.63 Å) and Pd−H (1.61 Å) bonds of **2**, respectively.

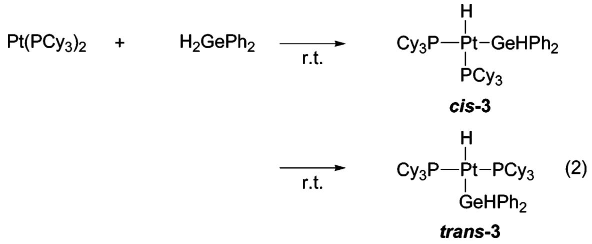


(1)

1

The ${}^1H$ NMR spectrum of **1** exhibits an apparent triplet at δ 0.42. This signal is assigned to the hydrogen involved in Pd−H−Ge bonding and shows splitting due to virtual coupling with two phosphorus nuclei. The peak position is almost the same as that for the diplatinum complex with bridging diphenylgermyl and PPh_3 ligands, $[\{Pt(PPh_3)\}_2(\mu\text{-}HGePh_2)_2]$ (δ 0.43),[6] while it appears at a much higher field position than the Pd−H−Si hydrogen of **2** (δ 2.07). The ${}^{31}P\{{}^1H\}$ NMR spectrum of **1** contains a single signal at δ 52.8, while the PCy_3 ligand of the dipalladium complex **2** with $SiHPh_2$ ligands shows the signal at δ 45.1.

The reaction of H_2GePh_2 with $[Pt(PCy_3)_2]$ at room temperature for 72 h forms a mononuclear (germyl)hydridoplatinum complex, *trans*-$[Pt(H)(GeHPh_2)(PCy_3)_2]$ (***trans*-3**), as shown in eq 2. ***trans*-3** was isolated in 87% yield and characterized by NMR (${}^1H$, ${}^{13}C\{{}^1H\}$, and ${}^{31}P\{{}^1H\}$) spectroscopy and elemental analysis. The ${}^{31}P\{{}^1H\}$ NMR spectrum of ***trans*-3** displays a singlet with a coupling to ${}^{195}Pt$ nuclei (J_{PPt} = 2650 Hz), indicating that PCy_3 ligands occupy trans positions. The ${}^1H$ NMR spectrum of ***trans*-3** exhibits the signal for the hydride ligand at δ −4.71 and that for the H bonded to the Ge center at δ 5.77. The J_{HPt} value of the hydride signal (798 Hz) is much larger than that of *trans*-$[Pt(H)(SiHPh_2)(PCy_3)_2]$ (δ −1.3, J_{HPt} = 666 Hz).[14]



(2)

The ${}^1H$ NMR spectrum of the reaction mixture after 1.5 h exhibits signals indicating the formation of ***trans*-3** and *cis*-$[Pt(H)(GeHPh_2)(PCy_3)_2]$ (***cis*-3**) in a 9:91 ratio. The ratio gradually changes to 96:4 in 48 h, indicating that ***cis*-3** is initially formed by oxidative addition of H_2GePh_2 to Pt(0) and is isomerized into thermodynamically more stable ***trans*-3** during the reaction 2. ***cis*-3** has been characterized by ${}^1H$ and ${}^{31}P\{{}^1H\}$ NMR spectra of the reaction mixture in C_6D_6. The ${}^{31}P\{{}^1H\}$ NMR spectrum shows two doublets at δ 35.8 and 43.4 with similar coupling constants (J_{PPt} = 2505, 2219 Hz). The former signal is assigned as the PCy_3 ligand at the position trans to the H atom on the basis of comparison with the data for *cis*-$[Pt(H)(SiHPh_2)(PCy_3)_2]$ (***cis*-4**) (δ 38.5, J_{PPt} = 2632 Hz).[14] The P−Pt coupling constant of the latter signal, which is assigned to PCy_3 trans to the Ge atom, is much larger than that of the phosphorus trans to the Si atom of ***cis*-4** (δ 46.2, J_{PPt} = 1675 Hz). The ${}^1H$ NMR spectrum of ***cis*-3** shows characteristic Ge−H and Pt−H signals at δ 5.45 and −4.48, which are split by ${}^{31}P-{}^1H$ and ${}^1H-{}^1H$ coupling.

Reaction 2 is contrasted with the reaction of H_2GePh_2 with $[Pt(PPh_3)_2(CH_2{=}CH_2)]$, which affords a dinuclear Pt complex with bridging $GeHPh_2$ ligands via the intermediate mononuclear complex *cis*-$[Pt(H)(GeHPh_2)(PPh_3)_2]$.[6] Dissociation of a PPh_3 ligand from the mononuclear intermediate or its cis geometry may induce its dimerization accompanied by intermolecular reductive elimination of the two hydride ligands. ***cis*-3** is isomerized into the thermodynamically more stable isomer with a trans structure but does not dimerize, due to dissociation of the PCy_3 ligand being more difficult than that of PPh_3.

We have reported the preparation of the germyl-bridged dinuclear palladium complex **1** and the mononuclear (germyl)hydridoplatinum complex **3** from the oxidative addition reaction of Ge−H bonds to the zerovalent complexes $[M(PCy_3)_2]$ (M = Pd, Pt). The former reaction probably involves a mononuclear Pd(II) complex formulated as $[Pd(H)(GePh_2H)(PCy_3)_2]$, although the intermediate was neither isolated nor characterized because of its facile conversion into the dinuclear Pd(I) complex.

Experimental Section

General Procedures. All manipulations of the complexes were carried out using standard Schlenk techniques under an argon or a nitrogen atmosphere. Hexane and toluene were distilled from sodium benzophenone ketyl and stored under nitrogen. ${}^1H$, ${}^{13}C\{{}^1H\}$, and ${}^{31}P\{{}^1H\}$ NMR spectra were recorded on a Varian Mercury 300 spectrometer. The peak position of the ${}^{31}P\{{}^1H\}$ NMR

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spectrum was referenced to external 85% H_3PO_4. Diphenylgermane was obtained from Gelest and used as received. IR absorption spectra were recorded with a Shimadzu FT/IR-8100 spectrometer. Elemental analyses were carried out with a Yanaco MT-5 CHN autocorder.

Preparation of $[Pd(PCy_3)_2]$. The reported preparation method[15] was modified. To a toluene solution (7 mL) of $[Pd(Me)_2(tmeda)]$ (tmeda = *N,N,N′,N′*-tetramethylethylenediamine) (0.748 g, 2.96 mmol) was added twice the molar amount of PCy_3 (1.66 g, 5.92 mmol). The reaction mixture was stirred for 1 h at room temperature. The solvent was removed under reduced pressure to yield a white solid. The solid was washed twice with 4 mL portions of hexane and dried in vacuo to give $[Pd(PCy_3)_2]$ (1.50 g, 76%). ^{1}H NMR (300 MHz, C_6D_6, room temperature): δ 2.20 (d, 12H, $J_{HP} = 12$ Hz), 1.81−1.65 (m, 36H), 1.29 (m, 18H). $^{13}C\{^{1}H\}$ NMR (75 MHz, C_6D_6, room temperature): δ 34.6 (P*C*H), 32.3 (PCH*C*H$_2$), 27.9 (PCHCH$_2$*C*H$_2$), 27.0 (PCHCH$_2$CH$_2$*C*H$_2$). $^{31}P\{^{1}H\}$ NMR (121 MHz, C_6D_6, room temperature): δ 39.7.

Preparation of $[Pt(Ph)_2(PCy_3)_2]$. To a toluene solution (7 mL) of $[Pt(Ph)_2(cod)]$[16] (1.01 mg, 2.20 mmol) was added PCy_3 (1.50 g, 5.35 mmol) at room temperature. Stirring the solution for 1 h at that temperature caused separation of a white solid, which was collected through filtration, washed three times with 4 mL portions of hexane, and dried in vacuo to yield $[Pt(Ph)_2(PCy_3)_2]$ (1.79 g, 90%). ^{1}H NMR (300 MHz, C_6D_6, room temperature): δ 7.69 (m, 4H, C$_6$*H*$_5$ ortho, $J_{HPt} = 58$ Hz), 7.06 (t, 4H, C$_6$*H*$_5$ meta, $J_{HH} = 7$ Hz), 6.81 (t, 2H, C$_6$*H*$_5$ para, $J_{HH} = 7$ Hz), 2.21 (m, 18H, P*Cy*$_3$), 1.50−1.80 (m, 30H, P*Cy*$_3$), 1.18 (br, 18H, P*Cy*$_3$).

Preparation of $[\{Pd(PCy_3)\}_2(\mu\text{-}HGePh_2)_2]$ (1). To a toluene (5 mL) solution of $[Pd(PCy_3)_2]$ (90.1 mg, 0.14 mmol) was added an equimolar amount of Ph_2GeH_2 (30 μL, 0.16 mmol), and the mixture was stirred at room temperature for 18 h. The solvent was removed under reduced pressure to yield a light yellow solid, which was washed five times with 2 mL portions of hexane and dried in vacuo to give **1** as a yellow solid (71 mg, 85%). Anal. Calcd for $C_{60}H_{88}Ge_2P_2Pd_2$: C, 58.62; H, 7.22. Found: C, 58.39; H, 7.10. ^{1}H NMR (300 MHz, C_6D_6, room temperature): δ 8.07 (d, 8H, C$_6$*H*$_5$ ortho, $J_{HH} = 7$ Hz), 7.33 (t, 8H, C$_6$*H*$_5$ meta, $J_{HH} = 7$ Hz), 7.18 (t, 4H, C$_6$*H*$_5$ para, $J_{HH} = 7$ Hz), 1.90−1.70 (m, 18H, C$_6$*H*$_{11}$), 1.58−1.50 (m, 18H, C$_6$*H*$_{11}$), 1.38−1.25 (m, 12H, C$_6$*H*$_{11}$), 1.05−0.81 (m, 18H, C$_6$*H*$_{11}$), 0.42 (apparent triplet, 2H, Ge*H*, $J_{HP} = 5.3$ Hz). $^{13}C\{^{1}H\}$ NMR (75 MHz, CD_2Cl_2, room temperature): δ 150.1 (s, *C*$_6$H$_5$ ipso), 135.6 (s, *C*$_6$H$_5$ ortho), 127.8 (s, *C*$_6$H$_5$ para), 127.5 (s, *C*$_6$H$_5$ meta), 36.9 (apparent triplet, P*C*H, $J_{CP} = 7.8$ Hz), 30.8 (s, PCH*C*H$_2$), 27.7 (apparent triplet, PCHCH$_2$*C*H$_2$, $J_{CP} = 5.5$ Hz), 26.5 (s, PCHCH$_2$CH$_2$*C*H$_2$). $^{31}P\{^{1}H\}$ NMR (121 MHz, C_6D_6, room temperature): δ 52.8.

Preparation of *trans*-$[Pt(H)(GeHPh_2)(PCy_3)_2]$ (*trans*-3). Ph_2GeH_2 (62 μL, 0.33 mmol) was added to the toluene (7 mL) solution of $[Pt(PCy_3)_2]$, which was prepared via reductive elimination of *cis*-$[Pt(Ph)_2(PCy_3)_2]$ (302 mg, 0.33 mmol) at 60 °C for 1 h. The reaction mixture was stirred at room temperature for 72 h. The solution was filtered to remove a small mount of an impurity. The solvent was removed under reduced pressure. The residual material was washed twice with 3 mL portions of hexane and dried in vacuo to give *trans*-**3** as a white solid (283 mg, 87%). Anal. Calcd for $C_{48}H_{78}GeP_2Pt$: C, 58.54; H, 7.98. Found: C, 58.84; H, 8.09. ^{1}H NMR (300 MHz, C_6D_6, room temperature): δ 8.07 (d, 4H, C$_6$*H*$_5$ ortho, $J_{HH} = 7$ Hz), 7.31 (t, 4H, C$_6$*H*$_5$ meta, $J_{HH} = 7$ Hz), 7.19 (t, 2H, C$_6$*H*$_5$ para, $J_{HH} = 7$ Hz, overlapped with solvent), 5.77 (br, 1H, Ge*H*, $^{2}J_{HPt} = 60$ Hz), 2.28 (br, 6H, PC*H*), 2.05 (d, 12H, PCHC*H*$_2$, $J_{HP} = 12$ Hz), 1.69 (br, 12H, PCHCH$_2$C*H*$_2$) 1.61 (br, 18H, PCHC*H*$_2$ and PCHCH$_2$CH$_2$C*H*$_2$), 1.16 (br, 18H, PCHCH$_2$C*H*$_2$ and PCHCH$_2$CH$_2$C*H*$_2$), −4.71 (t, 1H, Pt*H*, $^{2}J_{HP} = 13$ Hz, $J_{HPt} = 798$ Hz). $^{13}C\{^{1}H\}$ NMR (75 MHz, C_6D_6, room temperature): δ 150.9 (s, *C*$_6$H$_5$ ipso, $^{2}J_{CPt} = 43$ Hz), 137.8 (s, *C*$_6$H$_5$ ortho, $^{3}J_{CPt} = 11$ Hz), 127.3 (s, *C*$_6$H$_5$ meta), 126.4 (s, *C*$_6$H$_5$ para), 37.6 (apparent triplet, P*C*H, $J_{CP} = 14$ Hz, $J_{CPt} = 28$ Hz), 30.8 (apparent triplet, PCH*C*H$_2$, $J_{CP} = 14$ Hz), 27.6 (apparent triplet, PCHCH$_2$*C*H$_2$, $J_{CP} = 5.5$ Hz), 26.9 (s, PCHCH$_2$CH$_2$*C*H$_2$). $^{31}P\{^{1}H\}$ NMR (121 MHz, C_6D_6, room temperature): δ 39.2 ($J_{PPt} = 2650$ Hz). IR (KBr, cm^{-1}): ν 1970, 1918.

Table 1. Crystallographic Data and Details of Refinement of 1

formula	$C_{60}H_{88}P_2Pd_2Ge_2$
formula wt	1229.28
color	yellow
cryst size/mm	0.20 × 0.38 × 0.42
cryst syst	monoclinic
space group	$P2_1/c$ (No. 14)
a/Å	10.272(10)
b/Å	14.025(14)
c/Å	20.255(19)
β/deg	93.092(12)
V/Å^3	2914(5)
Z	2
D_{calcd}/g cm^{-3}	1.401
F(000)	1268.00
μ/cm^{-1}	17.189
no. of unique rflns	6075 ($R_{int} = 0.040$)
no. of obsd rflns ($I > 2.00\sigma(I)$)	2843
no. of variables	345
R1 ($I > 2.00\sigma(I)$)	0.0762
wR2 (all data)	0.2150
GOF	0.991

Characterization of *cis*-$[Pt(H)(GeHPh_2)(PCy_3)_2]$ (*cis*-3). An NMR tube containing a C_6D_6 (600 μL) solution of *cis*-$[Pt(Ph)_2(PCy_3)_2]$ (17 mg, 0.018 mmol) was heated to produce $[Pt(PCy_3)_2]$ as described above. Addition of Ph_2GeH_2 (3.4 μL, 0.018 mmol) to the solution afforded a *cis*-(germyl)hydridoplatinum complex (***cis*-3**), which isomerized into ***trans*-3** over time. ***cis*-3** was characterized from the ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra of the reaction mixture collected a few minutes after addition. The cis/trans ratio for complex **3** was determined from the integration of the ortho position of $GePh_2H$ in ^{1}H NMR spectra. ^{1}H NMR (300 MHz, C_6D_6, room temperature): δ 8.15 (d, C$_6$*H*$_5$ ortho, $J_{HH} = 7$ Hz), 7.5−7.1 (C$_6$*H*$_5$ meta and para of GePh$_2$H, overlapped with biphenyl’s proton), 5.45 (ddd, Ge*H*, $^{3}J_{HH} = 5.4$ Hz, $^{3}J_{HP} = 8.4$ Hz (cis), 24.3 Hz (trans)), 1.9−0.3 (P*Cy*$_3$ region), −4.48 (ddd, Pt*H*, $^{3}J_{HH} = 5.4$ Hz, $^{2}J_{HP} = 22$ Hz (cis), 149 Hz (trans), $J_{HPt} = 762$ Hz). $^{31}P\{^{1}H\}$ NMR (121 MHz, C_6D_6, room temperature): δ 35.8 (*P* trans to H, $^{2}J_{PP} = 11$ Hz, $J_{PPt} = 2505$ Hz), 43.4 (*P* trans to Ge, $^{2}J_{PP} = 11$ Hz, $J_{PPt} = 2219$ Hz).

X-ray Crystallography. A crystal of **1** suitable for X-ray diffraction study was mounted on a glass capillary. Data for **1** were collected at −160 °C on a Rigaku Saturn CCD diffractometer equipped with monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). Calculations were carried out by using the program package Crystal Structure version 3.7 for Windows. A full-matrix least-squares refinement was used for the non-hydrogen atoms with anisotropic thermal parameters. Hydrogen atoms, except for the GeH hydrogens of **1**, were located by assuming ideal geometry and were included in the structure calculations without further refinement of the parameters. Crystallographic data and details of refinement are summarized in Table 1.

Acknowledgment. This work was supported by Grants-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

Supporting Information Available: Crystallographic data for **1** as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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