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Successive Formation of Hydrido(germyl)platinum, Germaplatinacycle, and Germylene-Bridged Dinuclear Platinum Complexes from the Reaction of a Zerovalent Platinum Complex with α,ω-Dihydrodigermanes

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Summary: The reaction of $Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2$ (**1**) *with* $HPh_2Ge(SiMe_2)_nGePh_2H$ (**2**; $n = 0-3$) *initially forms the hydrido(germyl)platinum complex* *cis*-$Pt(H)[GePh_2(SiMe_2)_nGePh_2H](PPh_3)_2$ (**3**), *followed by the generation of the cyclic bis(germyl)platinum complex* $Pt[GePh_2(SiMe_2)_nGePh_2](PPh_3)_2$ (**4**) *and finally formation of a dinuclear platinum complex with bridging diphenylgermyl ligands containing a Pt−Pt bond,* $[Pt(\mu\text{-}GePh_2)(PPh_3)]_2$ (**5**). *The structures of* **4** ($n = 2$) *and* **5** *were determined by X-ray crystallography.*

Group 14 element compounds have attracted growing interest not only as possible synthetic tools in organic chemistry but also for their potential use as new materials.[1] In particular, considerable effort has been devoted to syntheses of group 14 element compounds binding late transition metals, as these complexes are regarded as intermediates in a number of transition-metal-catalyzed transformations of group 14 element compounds.[2,3] However, there has been little research on germanium compounds having a transition-metal−germanium bond, especially in comparison to the much studied silicon chemistry.[2] We have recently isolated divalent bis(germyl)platinum complexes stabilized by tertiary phosphines from the reaction of $PtCl_2L_2$ with $LiGeR_3$[4a] as an intermediate in the bis-germylation of alkynes catalyzed by zerovalent Pt complexes.[4] Useful syntheses of Pt complexes containing Pt−group 14 element bonds proceed from salt elimination using a Pt halide and MER_3 (M = Li, K, Na, Hg; E = Si, Ge, Sn)[2,5] or oxidative addition of R_3E-ER_3,[6] R_3C-ER_3,[7] $H-ER_3$,[8] or $X-ER_3$[9] to a zerovalent Pt complex. Herein are reported new synthetic methods for germylplatinum complexes from the treatment of zerovalent platinum centers with α,ω-dihydrodigermanes and the unexpected successive formation of a hydrido(germyl)platinum complex, germaplatinacycle complex, and dinuclear platinum complex with bridging germylene ligands.

The reaction of $Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2$ (**1**) with $HPh_2GeGePh_2H$ (**2a**) proceeded to form *cis*-$Pt(H)(GePh_2GePh_2H)(PPh_3)_2$ (**3a**) in 93% yield with liberation of C_2H_4 within 10 min at room temperature in toluene. Complex **3a** was isolated as a white powder and was identified from IR and NMR spectra.[10]

Similar treatment of **1** with $HPh_2Ge(SiMe_2)GePh_2H$ (**2b**) immediately generated *cis*-$Pt(H)[GePh_2(SiMe_2)GePh_2H](PPh_3)_2$ (**3b**) in quantitative yield by NMR in

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(10) **3a**: ^1H NMR (300.4 MHz, toluene-d_8) δ −3.17 (dd, $^2J_{H-P(trans)} = 180.2$ Hz, $^2J_{H-P(cis)} = 36.0$ Hz, $^1J_{H-Pt} = 869.6$ Hz, 1H, Pt*H*), 5.70 (s, $^3J_{H-Pt} = 50.8$ Hz, 1H, Ge*H*), 6.8−7.6 (m, 50H, GeC_6H_5, PC_6H_5); ^{31}P-{^1H} NMR (121.5 MHz, toluene-d_8) δ 30.9 (d, $^2J_{P-P} = 10$ Hz, $^1J_{P-Pt} = 2411$ Hz), 33.3 (d, $^2J_{P-P} = 10$ Hz, $^1J_{P-Pt} = 2276$ Hz); IR (KBr) 2089, 1967 cm^{-1}.

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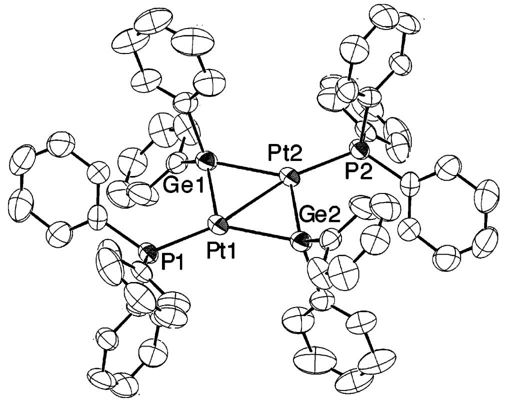

Figure 1. ORTEP view of **5**. Selected bond lengths (Å) and angles (deg): Pt1−Pt2 = 2.7211(6), Pt1−Ge1 = 2.3901(13), Pt1−Ge2 = 2.4974(12), Pt1−P1 = 2.221(3); Ge1−Pt1−Ge2 = 112.38(4), P1−Pt1−Ge1 = 106.12(7), P1−Pt1−Ge2 = 141.34(8), Ge1−Pt1−Pt2 = 58.07(3), Ge2−Pt1−Pt2 = 54.31(3).

toluene-d_8 or dichloromethane-d_2.[11] The NMR signals for the hydride complex **3b** gradually decreased, and the formation of the germaplatinacycle Pt[GePh$_2$(SiMe$_2$)GePh$_2$](PPh$_3$)$_2$ (**4a**) was then revealed with the liberation of H_2 at room temperature over 3 h.[12] Complex **4a** was gradually transformed to the complex **5** in dichloromethane-d_2, which shows one singlet peak at 14.9 ppm with large Pt satellites (3674 Hz) in the $^{31}P\{^1H\}$ NMR spectrum, with an equimolar amount of triphenylphosphine oxide (28.1 ppm).[13] Yellow single crystals of **5** were grown from cold dichloromethane/hexane solution from the resulting mixture of **1** and **2b**, and the structure was confirmed by X-ray crystallography. The final product in this reaction in dichloromethane was found to be a dinuclear platinum complex with bridging germylene ligands, [Pt(μ-GePh$_2$)(PPh$_3$)]$_2$ (**5**), as shown in Figure 1.[14] The distance between two platinum atoms is 2.7211 Å, which suggests a direct Pt−Pt bond. There are two very different Pt−Ge distances (2.3901 and 2.4974 Å), P−Pt−Ge angles (106.12 and 141.34°), and Ge−Pt−Pt angles (58.07 and 54.31°) in complex **5**, respectively. The packing of crystals has an influence on the asymmetric structure of **5**. Dinuclear complexes having Pt−Pt bonds with bridging HSiR$_2$ ligands [(R$_3$P)Pt(μ-η^2-HSiR$_2$)]$_2$ show large Pt satellites of about 3500 Hz in $^{31}P\{^1H\}$ NMR, which is consistent with the result of the $^{31}P\{^1H\}$ NMR study for **5** ($^1J_{P-Pt} = 3674$ Hz).[15a−g] There are no hydride peaks at −50 °C in CD$_2$Cl$_2$ in the ^1H NMR spectrum, and a Pt−H resonance was not observed in the IR spectrum for **5**. The reaction of **1** with **2a**,**b** in dichloromethane finally produced **5**, while **5** was not generated in toluene or benzene. A dinuclear Pt complex containing a direct Ge−Ge bond did not form, while dinuclear silylene complexes are normally stabilized by a direct Si−Si bond or Si−H bridging.[15]

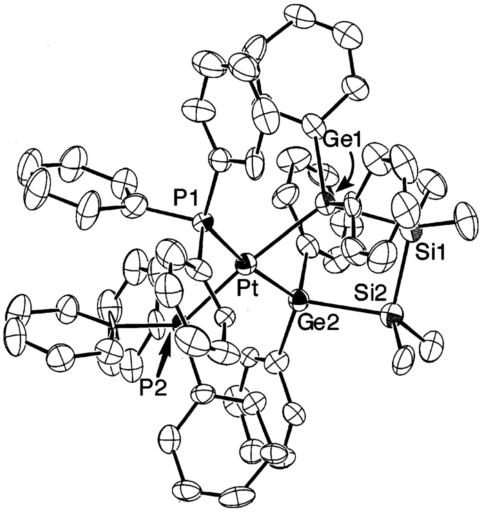

Figure 2. ORTEP drawing of **4b**. Selected bond lengths (Å) and angles (deg): Pt1−Ge1 = 2.4979(13), Pt1−Ge1 = 2.4985(13), Pt1−P1 = 2.290(3), Pt1−Pt2 = 2.336(3); Ge1−Pt1−Ge2 = 83.47(4), Ge1−Pt1−P1 = 88.52(8), Ge1−Pt1−P2 = 174.43(9), Ge2−Pt1−P1 = 171.76(8), Ge2−Pt1−P2 = 91.02(8), P1−Pt1−P2 = 97.01(11).

The reaction of **1** with HPh$_2$Ge(SiMe$_2$)$_2$GePh$_2$H (**2c**) yielded the corresponding germaplatinacycle complex Pt[GePh$_2$(SiMe$_2$)$_2$GePh$_2$](PPh$_3$)$_2$ (**4b**) in 83% yield after 4 h in benzene.[16] Complex **4b** was characterized by NMR, and the structure was determined by X-ray crystallography, as shown in Figure 2.[17,18] The sum of the bond angles around Pt was 360.0°, which suggests

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[11] **3b**: ^1H NMR (300.4 MHz, toluene-d_8) δ −3.09 (dd, $^2J_{H-P(trans)} = 163.0$ Hz, $^2J_{H-P(cis)} = 21.5$ Hz, $^1J_{H-Pt} = 866.6$ Hz, 1H, Pt*H*), 0.56 (s, 6H, SiCH_3), 5.30 (s, 1H, Ge*H*), 6.8−7.6 (m, 50H, GeC$_6H_5$, PC$_6H_5$); $^{31}P\{^1H\}$ NMR (121.5 MHz, toluene-d_8) δ 31.5 (d, $^2J_{P-P} = 10$ Hz, $^1J_{P-Pt} = 2425$ Hz), 32.0 (d, $^2J_{P-P} = 10$ Hz, $^1J_{P-Pt} = 2204$ Hz).

[12] **4a**: ^1H NMR (300.4 MHz, toluene-d_8) δ 0.33 (s, 6H, SiCH$_3$), 6.6−7.2 (m, 50H, GeC$_6$H$_5$, PC$_6$H$_5$); $^{31}P\{^1H\}$ NMR (121.5 MHz, toluene-d_8) δ 24.9 (s, $^1J_{P-Pt} = 2047$ Hz).

[13] **5**: ^1H NMR (300.4 MHz, dichloromethane-d_2) δ 6.8−7.5 (m, GeC$_6$H$_5$, PC$_6$H$_5$); $^{31}P\{^1H\}$ NMR (121.5 MHz, dichloromethane-d_2) δ 14.9 (s, $^1J_{P-Pt} = 3674$ Hz).

[14] Crystallographic data for **5**: C$_{60}$H$_{50}$Ge$_2$P$_2$Pt$_2$, $M_r = 1368.30$, triclinic, $P\bar{1}$, $a = 9.4802(13)$ Å, $b = 11.8928(17)$ Å, $c = 23.244(4)$ Å, $\alpha = 80.341(9)°$, $\beta = 80.978(11)°$, $\gamma = 73.924(10)°$, $V = 2465.6(6)$ Å^3, $Z = 2$, $D_{calcd} = 1.843$ g cm^{-3}, $F(000) = 1320$, $\mu = 6.945$ mm^{-1}, R1 = 0.0736 ($I > 2\sigma(I)$), wR2 = 0.1864 (all data), GOF = 0.943.

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[16] **4b**: ^1H NMR (300.4 MHz, toluene-d_8) δ 0.22 (s, 12H, SiCH_3), 6.7−7.7 (m, 50H, GeC$_6H_5$, PC$_6H_5$); $^{31}P\{^1H\}$ NMR (121.5 MHz, toluene-d_8) δ 27.4 (s, $^1J_{P-Pt} = 2081$ Hz).

[17] Crystallographic data for **4b**: C$_{70}$H$_{67}$Ge$_2$P$_2$PtSi$_2$, $M_r = 1366.63$, monoclinic, *Cc*, $a = 22.344(2)$ Å, $b = 12.8430(14)$ Å, $c = 22.869(2)$ Å, $\beta = 111.360(6)°$, $V = 6111.8(11)$ Å^3, $Z = 4$, $D_{calcd} = 1.485$ g cm^{-3}, $F(000) = 2748$, $\mu = 3.393$ mm^{-1}, R1 = 0.0393 ($I > 2\sigma(I)$), wR2 = 0.1148 (all data), GOF = 1.051.

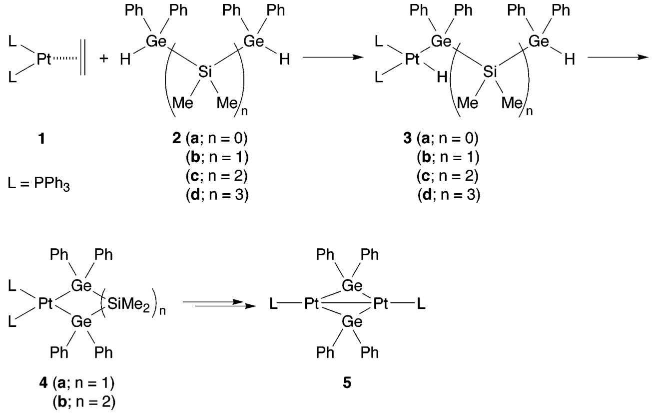
[18] Synthesis of a platinacyclosilane by the oxidative addition of 1,4-dihydrotetrasilane to Pt(η^2-C$_2$H$_4$)L$_2$: (a) Lemanski, M. F.; Schram, E. P. *Inorg. Chem.* **1976**, *15*, 1489−1492. Synthesis of the germaplatinacycle complex Pt[GeMe$_2$(CMe$_2$)$_n$GeMe$_2$]L$_2$ ($n = 0−2$) from the reaction of Pt(η^2-C$_2$H$_4$)L$_2$ with HGeMe$_2$(CH$_2$)$_n$GeMe$_2$H: (b) Barrau, J.; Rima, G.; Cassano, V.; Satgé, J. *Inorg. Chim. Acta* **1992**, *198−200*, 461−467.

that **4b** contains a square-planar structure. The ^{1}H and ^{31}P NMR study for this reaction revealed the formation of *cis*-$Pt(H)[GePh_2(SiMe_2)_2GePh_2](PPh_3)_2$ (**3c**) as an intermediate before the stepwise generation of **4b**.[19] Complex **4b** quantitatively converted to the dinuclear complex **5** in 1 day at ambient temperature in dichloromethane-d_2 in vacuo or under Ar, while the clear yellow toluene-d_8 or benzene-d_6 solution of **4b** changed to a dark red oil with decomposition at room temperature after 3 days, without the generation of **5**. The dinuclear complex **5** easily forms in chlorinated solvents such as CH_2Cl_2, $CHCl_3$, and $(CH_2Cl)_2$, from the reaction of **1** with **2** and from isolated complexes **3a** and **4b**. Broad peaks appeared between −0.5 and 0.6 ppm in the ^{1}H NMR spectrum as the formation of **5** proceeded. Although **5** was generated quantitatively from **4b** in CD_2Cl_2 after 20 h, the addition of an equimolar amount of PPh_3 reduced the formation of **5** to 51% yield.

Moreover, the treatment of **1** with $HPh_2Ge(SiMe_2)_3GePh_2H$ (**2d**) smoothly generated *cis*-$Pt(H)[GePh_2(SiMe_2)_3GePh_2H](PPh_3)_2$ (**3d**) within 10 min at room temperature in dichloromethane-d_2 and then directly converted to complex **5**.[20]

A series of reactions of $Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2$ (**1**) with $HPh_2Ge(SiMe_2)_nGePh_2H$ (**2**; $n = 0{-}3$) successively formed hydrido(germyl)platinum complexes, *cis*-$Pt(H)[GePh_2(SiMe_2)_nGePh_2H](PPh_3)_2$ (**3**), germaplatinacycle complexes, $Pt[GePh_2(SiMe_2)_nGePh_2](PPh_3)_2$ (**4**), and a dinuclear platinum complex with bridging germylene ligands, $[Pt(\mu\text{-}GePh_2)(PPh_3)]_2$ (**5**), as shown in Scheme 1. The corresponding three-membered germaplatinacycle $Pt(GePh_2GePh_2)(PPh_3)_2$ or digermene-coordinated platinum complex $Pt[\eta^2\text{-}(GePh_2{=}GePh_2)](PPh_3)_2$, as an equilibrium complex of the three-membered platinacycle, and six-membered platinacycle $Pt[GePh_2(SiMe_2)_3GePh_2](PPh_3)_2$ in reactions of **1** with **2a**,**d**, respectively, were not detected by ^{1}H and ^{31}P NMR monitoring, though they were generated in the same stepwise course.[18,21] The proposed mechanism for the formation of **5** from **4** involves the initial liberation of 1 equiv of PPh_3 followed by the dissociation of Pt−Ge and Ge−Si bonds for the generation of Ge−Si doubly bonded species or divalent species such as $[Ph_2Ge(SiMe_2)_{n-1}SiMe_2]$, $[:GePh_2]$, and/or $[:SiMe_2]$, which convert to polymers without observation.[1b] This successive reaction is considered to involve these bond cleavages probably via generation of the putative germylene complex $[LPt{=}GePh_2]$, which dimerizes to form complex **5**. Triphenylphosphine oxide is simultaneously generated with the formation of **5** in quantitative yield from reactions of **1** with **2a**−**d** even when using dried solvent in a sealed NMR tube in vacuo. Further investigations of a detailed mechanism for the formation of **5** and reactivities of novel germylplatinum complexes **3**−**5** are underway, including the limitation of this reaction as a synthetic method for group 14 element compounds binding group 10 metals.

Scheme 1. Reaction of $Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2$ with $HPh_2Ge(SiMe_2)_nGePh_2H$



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Supporting Information Available: CIF files giving crystal data for **5** and **4b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[19] **3c**: ^{1}H NMR (300.4 MHz, toluene-d_8) δ −3.16 (dd, $^{2}J_{H-P(trans)} = 165.2$ Hz, $^{2}J_{H-P(cis)} = 24.0$ Hz, $^{1}J_{H-Pt} = 862.1$ Hz, 1H, Pt*H*), 0.22 (s, 6H, $SiCH_3$), 0.34 (s, 6H, $SiCH_3$), 5.29 (s, 1H, Ge*H*), 7.2−7.7 (m, 50H, GeC_6H_5, PC_6H_5); $^{31}P\{^{1}H\}$ NMR (121.5 MHz, toluene-d_8) δ 31.3 (d, $^{2}J_{P-P} = 10$ Hz, $^{1}J_{P-Pt} = 2160$ Hz), 31.6 (d, $^{2}J_{P-P} = 10$ Hz, $^{1}J_{P-Pt} = 2429$ Hz).

[20] **3d**: ^{1}H NMR (300.4 MHz, toluene-d_8) δ −3.12 (dd, $^{2}J_{H-P(trans)} = 164.6$ Hz, $^{2}J_{H-P(cis)} = 22.6$ Hz, $^{1}J_{H-Pt} = 864.3$ Hz, 1H, Pt*H*), 0.08 (s, 6H, $SiCH_3$), 0.13 (s, 6H, $SiCH_3$), 0.19 (s, 6H, $SiCH_3$), 5.18 (s, 1H, Ge*H*), 7.1−7.7 (m, 50H, GeC_6H_5, PC_6H_5); $^{31}P\{^{1}H\}$ NMR (121.5 MHz, toluene-d_8) δ 31.4 (d, $^{2}J_{P-P} = 10$ Hz, $^{1}J_{P-Pt} = 2143$ Hz), 31.8 (d, $^{2}J_{P-P} = 10$ Hz, $^{1}J_{P-Pt} = 2442$ Hz).

[21] Synthesis of a η^2-disilene Pt complex by the reaction of $Pt(\eta^2\text{-}C_2H_4)L_2$ with disilane: (a) Pham, E. K.; West, R. *J. Am. Chem. Soc.* **1989**, *111*, 7667−7668. Oxidative addition of digermirane to a zerovalent palladium complex: (b) Tsumuraya, T.; Ando, W. *Organometallics* **1989**, *8*, 2286−2288. Isolation of a platinum η^2-disilene complex: (c) Hashimoto, H.; Sekiguchi, Y.; Iwamoto, T.; Kabuto, C.; Kira, M. *Organometallics* **2002**, *21*, 454−456.