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Reaction of Diphenylgermane with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$: Generation of Mono- and Dinuclear Complexes Containing Pt−Ge Bonds. X-ray Crystal Structure Determination of $[(Ph_3P)Pt(\mu\text{-}\eta^2\text{-}H\text{-}GePh_2)]_2$

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Summary: The reaction of diphenylgermane (Ph_2GeH_2) with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ provided both mononuclear $(Ph_3P)_2Pt(H)(GePh_2H)$ and dinuclear $[(Ph_3P)Pt(\mu\text{-}\eta^2\text{-}H\text{-}GePh_2)]_2$ complexes. The structure of the dinuclear complex was determined by X-ray crystallography. The dinuclear complex could also be obtained from an unusual exchange reaction involving the unsymmetrical dinuclear complex $[(Ph_3P)_2(H)Pt(\mu\text{-}SiR_2)(\mu\text{-}\eta^2\text{-}H\text{-}SiR_2)\text{-}Pt(PPh_3)]$ ($SiR_2 = SiC_{20}H_{24}$) with Ph_2GeH_2.

The activation of group 14 element−hydrogen bonds by a transition metal has received considerable attention in the last two decades.[1] However, most of the focus has been on reactions of Si−H bonds[2] and to a much lesser extent with the heavier El−H bonds (El = Ge, Sn, Pb). Of special interest are the interactions of El−H bonds with late transition metals such as Pt and Pd due to their involvement in catalytic processes such as addition of El−H to multiple bonds,[1d,i,3] dehydrocoupling,[1f−h,j] and redistribution reactions at the group 14 element center.[4] Future development of the chemistry of El−TM (TM = transition metal) containing complexes and materials requires a better understanding of how complexes are formed and their reactivity patterns.

Our current efforts are focused on the activation of El−H bonds (El = Si, Ge, Sn) with Pt(0) and Pt(II) phosphine complexes. There are a limited number of published examples of Ge−H bond activation reactions with group 10 transition metal complexes compared to those of the analogous Si−H bonds, and the majority of these have focused on tertiary systems, R_3GeH, where R = Ph or Me.[5−7] To the best of our knowledge, there are no known reports of Ge−H bond activations utilizing secondary hydrogermanes with Pt(0) or Pt(II) complexes. A number of complexes containing Pt−Ge bonds have been prepared by either salt-elimination reactions[8,9c] or activation of other Ge−X bonds[9−11] by the metal center, but the Ge−H bond activation route should provide a more versatile method for the formation of Pt−Ge bonds due to the availability of suitable precursors to the requisite hydrogermanes. Herein, we report the preparation and characterization of both mononuclear and dinuclear platinum complexes containing Ge−Pt bonds. The dinuclear complex exhibits a nonclassical Pt···H···Ge interaction that was confirmed by NMR spectroscopy and X-ray crystallography.

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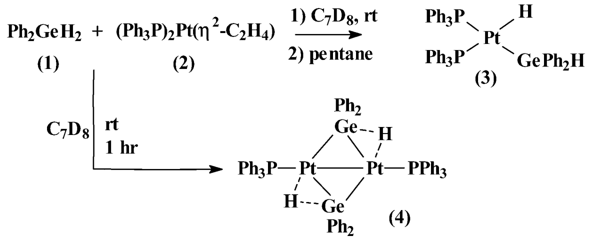
Scheme 1



Reaction of diphenylgermane, Ph_2GeH_2 (**1**), with the Pt(0) complex $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ (**2**) at room temperature in toluene-d_8 followed by immediate addition of pentane provided the mononuclear complex $(Ph_3P)_2Pt(H)(GePh_2H)$ (**3**) in 48% yield as a light yellow solid (Scheme 1).[12] Complex **3** was characterized by multinuclear NMR, IR, and elemental analysis.[13] The analogous silicon complex, $(Ph_3P)_2Pt(H)(SiPh_2H)$, was reported previously, but limited spectroscopic data were provided.[14]

The ^1H NMR spectrum of **3** exhibited two key hydride resonances for the Ge−H and Pt−H sites. The high-frequency multiplet observed at 3.9 ppm was assigned to the Ge−H resonance and the low-frequency signal at −2.9 ppm to the terminal Pt−H unit, both resonances showing coupling to Pt and P.[12] The $^{31}P\{^1H\}$ NMR spectrum for **3** revealed two different peaks for the inequivalent phosphine sites at 31 and 32 ppm, both with one set of Pt satellites.[12] There are a limited number of Pt-germyl complexes with a general structure analogous to **3**.[15] The related triphenylgermyl-platinum complex $(Ph_3P)_2Pt(H)(GePh_3)$ was reported from an unexpected reaction of $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ with 2-triphenylgermyl-(4-*tert*-butylcatecholato)borane (^{31}P NMR data were comparable to those for complex **3**[9d]).

After approximately 1 h when the reaction of **1** and **2** was performed at room temperature in toluene solution without the subsequent addition of pentane, the formation of a light yellow crystalline solid was observed (63% yield). The ^1H and $^{31}P\{^1H\}$ NMR spectra obtained for the crystalline solid in CD_2Cl_2 indicated that the product was the symmetrical dinuclear complex $[(Ph_3P)Pt(\mu\text{-}\eta^2\text{-}H\text{-}GePh_2)]_2$ (**4**) (Scheme 1).[16]

Immediately after mixing **1** and **2** at low temperature, the reaction was monitored by ^1H and $^{31}P\{^1H\}$ NMR at −50 °C.[17] The ^1H and $^{31}P\{^1H\}$ NMR spectra showed the formation of the mononuclear complex **3**, and the resonances match those of **3** described previously. Upon warming the solution to room temperature over a period of 2 h, precipitation of the dinuclear complex **4** occurred.[18]

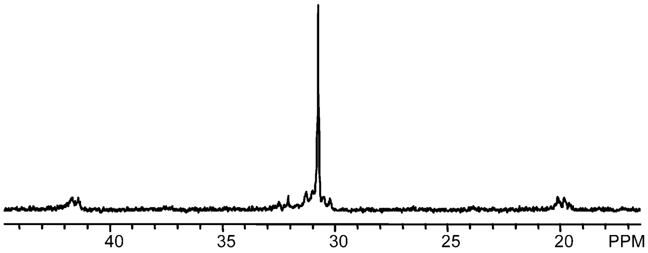


Figure 1. $^{31}P\{^1H\}$ NMR spectrum (202 MHz, CD_2Cl_2, 223 K) of $[(Ph_3P)Pt(\mu\text{-}\eta^2\text{-}H\text{-}GePh_2)]_2$ (**4**).

The ^1H NMR spectrum for **4** obtained at room temperature in CD_2Cl_2 displayed a resonance at 0.5 ppm with two sets of Pt satellites assigned to the Pt···*H*···Ge hydride. The $^{31}P\{^1H\}$ NMR spectrum for **4** exhibited a symmetrical resonance pattern centered at 33.5 ppm with two sets of Pt satellites, indicative of an AA′XX′ spin system (Figure 1). The ^{31}P resonance pattern and coupling constants for **4** are similar to those found in related dinuclear complexes $[(Ph_3P)Pt(\mu\text{-}\eta^2\text{-}H\text{-}SiArH)]_2$ previously prepared by our group.[19]

There are several reports of the preparation and characterization of symmetrical dinuclear platinum complexes containing $(\mu\text{-}\eta^2\text{-}H\text{-}SiR_2)$ ligands. The silicon complex $[(Ph_3P)Pt(\mu\text{-}\eta^2\text{-}H\text{-}SiPh_2)]_2$ analogous to **4** was reported in 1980 by Stone et al. from the reaction of $(Ph_3P)Pt(\eta^2\text{-}C_2H_4)_2$ with Ph_2SiH_2, but the complex was reported to be unstable and insoluble; thus only partial characterization data were provided. However, several other complexes with different phosphine ligands and either $(\mu\text{-}\eta^2\text{-}H\text{-}SiMe_2)$ or $(\mu\text{-}\eta^2\text{-}H\text{-}SiPh_2)$ groups were prepared by the same synthetic method, and the X-ray crystal structure of $[(Cy_3P)Pt(\mu\text{-}\eta^2\text{-}H\text{-}SiMe_2)]_2$ was reported.[20] More recently, we prepared a number of related symmetrical dinuclear complexes, $[(Ph_3P)Pt(\mu\text{-}\eta^2\text{-}H\text{-}SiArH)]_2$, from reaction of $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ with sterically hindered primary arylsilanes ($ArSiH_3$), and the structures of three of the complexes were confirmed by X-ray crystallography.[19] Osakada et al. have prepared similar complexes with Pd as well as mixed Pt−Pd dinuclear complexes containing (μ-η^2-silane) ligands.[21] The bonding features of these dinuclear bis(μ-η^2-silane)

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[12] Data for **3**. ^1H NMR (500 MHz, CD_2Cl_2, 223 K): δ 7.48−7.05 (aromatic CH resonances), 3.88 (m, Ge−H), −2.97 (ddd w/Pt satellites, $^1J_{PtH} = 930$, $^2J_{PH} = 161$ (trans), 18 (cis) Hz). Selected $^1H\{^{31}P\}$ NMR (500 MHz, CD_2Cl_2, 223 K): δ 3.88 (d w/Pt satellites, Ge−H, $^2J_{PtH} = 50$, $^3J_{HH} = 4.5$ Hz). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 223 K): δ 32.5 (d w/Pt satellites, $^1J_{PtP} = 2306$, $^2J_{PP} = 12$ Hz, P trans to Ge), 31.7 (br s, $^1J_{PtP} = 2317$, P trans to H). IR (neat, cm^{-1}): ν 2069 (Ge−H) 1931 (Pt−H) (tentative assignments). Mp: 90−92 °C. Anal. Calcd for $C_{48}H_{42}GeP_2Pt\cdot C_7H_8$: C, 63.48; H, 4.84. Found: C, 63.78; H, 4.85.

[13] Several attempts have been made to obtain X-ray quality crystals of **3** but have been unsuccessful.

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[16] Data for **4**. ^1H NMR (300 MHz, CD_2Cl_2, 300 K): δ 6.9−7.8 (aromatic CH resonances), 0.43 (s w/Pt satellites, Pt···H···Ge, $^1J_{PtH} = 785$, $^2J_{PtH} = 96$ Hz). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 223 K): δ 30.7 (s w/Pt satellites, $^1J_{PtP} = 4383$, $^2J_{PtP} = 162$, $^3J_{PP} = 58$ Hz), IR (neat, cm^{-1}): ν 1736 (Pt···H···Ge). Mp: 218 °C (dec). Anal. Calcd for $C_{67}H_{60}Ge_2P_2Pt_2\cdot C_7D_8$: C, 54.72; H, 4.65. Found: C, 53.52; H, 3.84.

[17] The addition was performed at −78 °C and the solution immediately transferred to a precooled NMR magnet at −50 °C.

[18] Careful examination of the low-temperature NMR data for the initial reaction mixture and data obtained after subsequent warming of the reaction solution to room temperature over a 2−3 h period did not show any signals for *trans*-$(Ph_3P)_2Pt(H)(GePh_2H)$ or other Pt−Ge phosphine-containing products. Complex **4** is insoluble in C_7D_8 and thus not observed.

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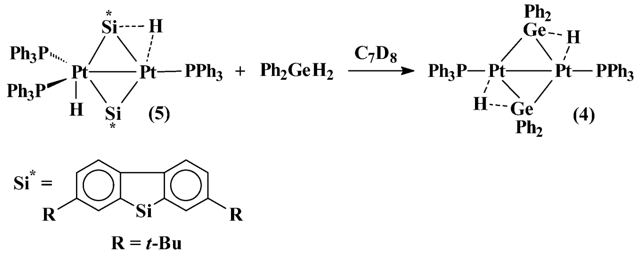
complexes have also been studied using density functional theory and molecular orbital calculations.[22] It is expected that the symmetrical dinuclear germanium complexes similar to **4** will have structural properties similar to the related silicon systems. The properties and reactivity of bimetallic complexes containing bridging group 14 centers are of significant interest.[23]

Part of our current objective is the development of additional routes to Ge−TM and Sn−TM complexes. One possible pathway involves the exchange of Si for Ge in a preformed multinuclear complex. When the unsymmetrical dinuclear complex containing silicon bridging groups, $[(Ph_3P)_2(H)Pt(\mu\text{-}SiC_{20}H_{24})(\mu\text{-}\eta^2\text{-}H\text{-}SiC_{20}H_{24})Pt(PPh_3)]$ (**5**),[24] was reacted with 1 equiv of Ph_2GeH_2 in C_7D_8, formation of the symmetrical dinuclear complex **4** containing (μ-η^2-H-$GePh_2$) ligands that replaced the silicon units was obtained in 26% yield (eq 1).[25] Exchange reactions involving mononuclear Pt-silyl groups with hydrogermanes or hydrostannanes were reported over thirty years ago,[26] but the reaction shown in eq 1 is the first example involving a dinuclear precursor.



X-ray quality, light yellow crystals of **4** (as a C_7D_8 solvate) were obtained from the room-temperature NMR reaction between **5** and 1 equiv of Ph_2GeH_2.[27] To the best of our knowledge, no other dinuclear platinum phosphine complexes containing germanium ligands have been structurally characterized by X-ray crystallography, as determined from a search of the Cambridge Structural Database. The molecular structure of **4** is shown in Figure 2 along with selected bond distances and angles.[28]

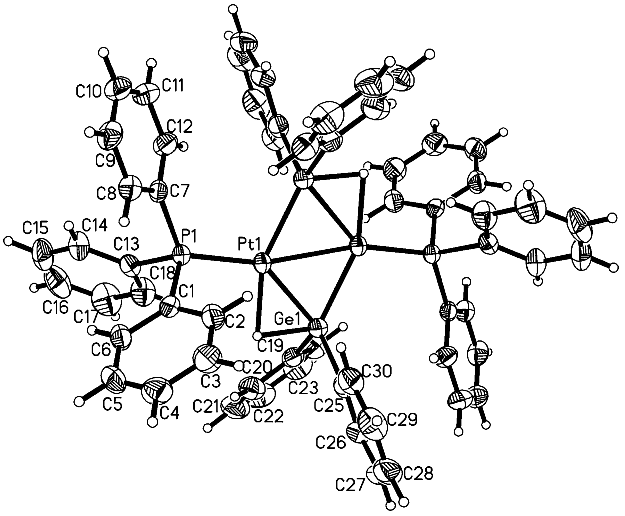


Figure 2. Molecular structure of $[(Ph_3P)Pt(\mu\text{-}\eta^2\text{-}H\text{-}GePh_2)]_2$ (**4**). Selected bond distances (Å) and angle (deg): Pt(1)−Pt(#1) 2.7452(3), Pt(1)−P(1) 2.2380(9), Pt(1)−Ge(1) 2.4785(4), Pt(1)−Ge(#1) 2.3821(4), Pt(1)−H(11A) 1.90(7), Ge(1)−H(11A) 1.76(7). P(1)−Pt(1)−Pt(#1) 165.07(3), Ge(#1)−Pt(1)−Ge(1) 111.256(12), Pt(#1)−Ge(1)−Pt(1) 68.743(12).

A prominent feature observed in the X-ray crystal structure of **4** is the presence of two significantly different Pt−Ge bonds (2.38 vs 2.47 Å). The longer Pt−Ge distance is associated with the nonclassical Pt···H···Ge interaction, whereas the shorter distance is on the smaller end of the range for typical single Pt−Ge bond lengths.[9d,29] The PPh_3 ligands bend away from the region of the Pt···H···Ge 3c-2e interaction, resulting in a nonlinear P−Pt−Pt angle (~165°), as is also observed in related $P_2Pt_2Si_2$ systems.[19−21] The central core containing the Pt, Ge, P, and H atoms is planar. The two symmetry-related hydride ligands were located and refined, and their presence was confirmed by ^1H NMR spectroscopy. The bond distance to the bridging nonclassical hydride was found to be 1.90 and 1.76 Å for Pt−H and Ge−H, respectively, indicating that the hydride is located closer to the Ge center than the Pt center.

The reactivity of other secondary germanes and stannanes with Pt(0) and Pt(II) phosphine complexes is being investigated. The potential catalytic activity of dinuclear complexes containing the heavier group 14 containing ligands is also under investigation.

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Supporting Information Available: Experimental description for the preparation of complexes **3** and **4**, selected NMR spectroscopic data, and tables of crystallographic data (CIF file) for **4** including data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters, and torsion angles are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) Ogino, H.; Tobita, H. *Adv. Organomet. Chem.* **1998**, *42*, 223.

(24) Braddock-Wilking, J.; Corey, J. Y.; Trankler, K. A.; Dill, K. M.; French, L. M.; Rath, N. P. *Organometallics* **2004**, *23*, 4575.

(25) NMR spectroscopic data for **4** obtained from the exchange reaction were identical to the data for **4** collected from the reaction of Ph_2GeH_2 with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$. The reaction solution after precipitation of **4** showed unreacted **5** and PPh_3 as the major components by ^{31}P NMR spectroscopy along with an additional product that is tentatively assigned to a mixed dinuclear complex containing bridging Si and Ge centers.

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(27) X-ray quality crystals of **4** were also obtained from the reaction of Ph_2GeH_2 with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$, but the structure was of insufficient quality to refine the bridging hydrides.

(28) Crystallographic data for **4**: $C_{60}H_{52}Ge_2P_2Pt_2\cdot C_7D_8$, fw = 1462.45, triclinic space group $P\bar{1}$, a = 10.0439(2) Å, b = 12.5191(3) Å, c = 12.9326(3) Å, α = 112.203(1)°, β = 97.705(1)°, γ = 102.863(1)°, V = 1424.26(6) Å^3, Z = 1, T = 170(2) K, μ(Mo Kα) = 6.037 mm^{-1}, 7307 independent reflections, $R(F)$ = 0.030 for 348 parameters, $wR(F^2)$ = 0.072, GOF = 1.03. Molecule contains a crystallographic center of symmetry at the midpoint of the Pt−Pt bond. The bridging H was located from the difference Fourier map and refined freely. All other H atoms were treated using appropriate riding models. The asymmetric unit contains 0.5 molecule of disordered toluene-d_8 solvate.

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