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# Activation of Group 14 El−H Bonds at Platinum(0)

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Acyclic hydrogermanes [$Ar_2GeH_2$; Ar = Ph (**1**), Mes (**8**)] and a hydrostannane ($Ph_2SnH_2$, **5**) were reacted with the Pt(0) precursor $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ (**2**). The mononuclear complexes $(Ph_3P)_2Pt(H)(GePh_2H)$ (**3**), $(Ph_3P)_2Pt(H)(SnPh_2H)$ (**6**), and $(Ph_3P)_2Pt(H)(GeMes_2H)$ (**9**) and the dinuclear complexes $[(Ph_3P)Pt(\mu\text{-}\eta\text{-H-}GePh_2)]_2$ (**4**) and $[(Ph_3P)_2(H)Pt(\mu\text{-}SnPh_2)(\mu\text{-}\eta^2\text{-H-}SnPh_2)Pt(PPh_3)]$ (**7**) were formed in these reactions. The cyclic precursor 9,9-dihydrogermafluorene ($Ar_2GeH_2$; $Ar_2 = C_{12}H_8$, **10**) was prepared and also reacted with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$. Mono-, di-, and trinuclear platinum−germanium products, $(Ph_3P)_2Pt(H)[Ge(C_{12}H_8)H]$ (**11**), $(Ph_3P)_2Pt[Ge(C_{12}H_8)H]_2$ (**14**), $[(Ph_3P)_2(H)Pt(C_{12}H_8GeGeC_{12}H_8)Pt(H)(PPh_3)_2]$ (**12**), $[(Ph_3P)_2(H)Pt(\mu\text{-}GeC_{20}H_{24})(\mu\text{-}\eta^2\text{-H-}GeC_{20}H_{24})Pt(PPh_3)]$ (**15**), and $[(Ph_3P)Pt(\mu\text{-}GeC_{12}H_8)]_3$ (**13**), were identified as products from the reaction. Complexes containing Si−Pt, Ge−Pt, and Sn−Pt bonds were also formed via an exchange reaction starting from the dinuclear complex $[(Ph_3P)_2(H)Pt(\mu\text{-}SiC_{20}H_{24})(\mu\text{-}\eta^2\text{-H}{-}SiC_{20}H_{24})Pt(PPh_3)]$ (**16**) and $H_2ElPh_2$ (El = Si, Ge), where the pre-existing bridging silicon groups were replaced with bridging ($\mu\text{-}\eta^2\text{-H-}ElPh_2$) groups.

## Introduction

In recent years, the focus of our research has involved the activation of Si−H bonds by Pt(0) and Pt(II) centers.[1] The oxidative addition of a Si−H bond to a late transition metal center is an important step in catalytic processes such as dehydrocoupling,[2] hydrosilylation,[3] and redistribution reactions at the silicon center.[4] It is also regarded as the most common and versatile synthetic method for the preparation of complexes containing a metal−silicon bond.[5] In comparison to Si−H bonds, the reactivity of Ge−H and Sn−H bonds toward late transition metals is less well studied. The majority of examples involving Pt and Pd, for example, have utilized commercially available tertiary hydrogermanes or hydrostannanes such as $Ph_3GeH$, $Ph_3SnH$, and $Bu_3SnH$.[6−8] Secondary precursors of the type $R_2ElH_2$ (El = Si, Ge, Sn) contain additional El−H bonds and therefore have the potential to react with one or more transition metal centers. The reactions of secondary hydrogermanes and hydrostannanes with late transition metals may provide a facile route to the formation of novel dinuclear or higher nuclearity Pt−Ge and Pt−Sn complexes.[9] Herein, we report the reaction of $Ph_2GeH_2$ with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$[10] and the analogous reaction between $Ph_2SnH_2$ and $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$. We have also investigated the effect of changing the steric hindrance at germanium on the reactivity of secondary germanes toward the Pt(0) precursor by replacing the phenyl groups in $Ph_2GeH_2$ with

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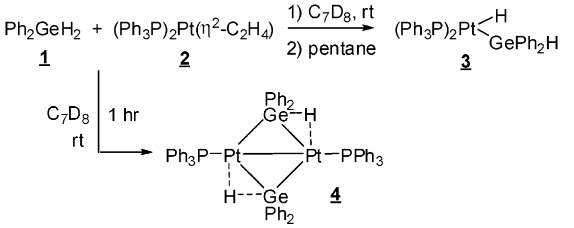
10.1021/om061180+ CCC: \$37.00

**Scheme 1**



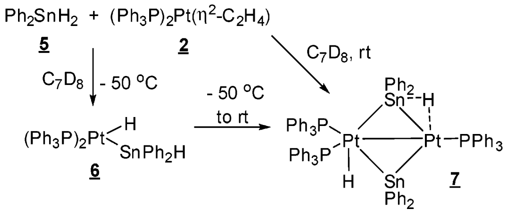
the related secondary germanes $Mes_2GeH_2$ (Mes = 2,4,6-trimethylphenyl) and $(C_{12}H_8)GeH_2$. The bulky mesityl groups are more sterically demanding than a phenyl group, whereas in germafluorene, $(C_{12}H_8)GeH_2$, the two phenyl rings are "tied" together, resulting in a planar tricyclic ring system with reduced steric bulk compared with $Ph_2GeH_2$. We also report novel exchange reactions involving the unsymmetrical dinuclear precursor $[(Ph_3P)_2(H)Pt(\mu\text{-}SiC_{20}H_{24})(\mu\text{-}\eta^2\text{-}H\text{-}SiC_{20}H_{24})Pt(PPh_3)]$ and $Ph_2ElH_2$ (El = Si, Ge, Sn), which produced new dinuclear complexes containing ($\mu$-$ElPh_2$) ligands.

## Results and Discussion

We recently reported the reaction between diphenylgermane, $Ph_2GeH_2$ (**1**), and $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ (**2**) at room temperature in toluene-$d_8$ (Scheme 1).[10] When pentane was added immediately after addition of the two components, the mononuclear complex $(Ph_3P)_2Pt(H)(GePh_2H)$ (**3**) was obtained in 44% yield as a light yellow solid. The analogous silicon complex, $(Ph_3P)_2Pt(H)(SiPh_2H)$, was reported previously from a similar reaction.[1b,11] In contrast, in the absence of added pentane, the major product from the room-temperature reaction in toluene-$d_8$ precipitated as a light yellow solid in 63% yield, whose structure was confirmed by X-ray crystallography to be the symmetrical dinuclear complex $[(Ph_3P)Pt(\mu\text{-}\eta^2\text{-}H\text{-}GePh_2)]_2$ (**4**).[10]

Mononuclear complexes containing Pt−Ge bonds have been reported previously from oxidative addition reactions of Ge−H and Ge−Ge bonds with Pt precursors.[6c] Recently, Mochida et al. reported the formation of a strikingly similar dinuclear complex, $[(Ph_3P)Pt(\mu\text{-}GePh_2)]_2$, from the reaction of $HPh_2Ge(SiMe_2)_nGePh_2H$ ($n$ = 0−3) with **2**.[12] A related dipalladium complex, analogous to **4**, has been synthesized recently by Osakada et al. from the reaction of $Ph_2GeH_2$ with $Pd(PCy_3)_2$.[13] In contrast, the corresponding reaction of $Pt(PCy_3)_2$ with $Ph_2GeH_2$ produced the mononuclear complex *cis*-$(Cy_3P)_2Pt(H)(GeHPh_2)$, which isomerized to the *trans* complex over time but did not produce any of the corresponding diplatinum complexes analogous to **4**.[13] Similar symmetrical diplatinum,[1a,b,f,g,14] dipalladium,[14a,15] and mixed platinum−palladium[14a,16] complexes related to **4** but containing ($\mu$-$\eta^2$-H-$SiR_2$) ligands have been reported previously.

**Scheme 2**



The reaction of diphenylstannane, $Ph_2SnH_2$ (**5**), with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ (**2**) was carried out at low temperature and monitored by NMR spectroscopy. The formation of the mononuclear species $(Ph_3P)_2Pt(H)(SnPh_2H)$ (**6**), analogous to **3**, was observed in the $^1H$ NMR and $^{31}P\{^1H\}$ NMR spectra recorded immediately after addition (Scheme 2). Even at low temperature the signals for this complex disappeared rapidly, and precipitation of **6** by addition of pentane was not attempted due to the rapid decomposition. However, a previously reported triphenylstannyl complex, $(Ph_3P)_2Pt(H)(SnPh_3)$, was stable and the structure was confirmed by X-ray crystallography.[17] The major product from the reaction of **5** was an unsymmetrical dinuclear complex, $[(Ph_3P)_2(H)Pt(\mu\text{-}SnPh_2)(\mu\text{-}\eta^2\text{-}H\text{-}SnPh_2)Pt(PPh_3)]$ (**7**).

The $^{31}P\{^1H\}$ NMR spectrum of the solution at 223 K revealed the presence of a doublet at 17 ppm and a triplet at 28 ppm, each with Pt satellites, characteristic of the formation of an unsymmetrical dinuclear species. These signals broadened as the temperature was gradually increased, a feature of the VT-NMR that was also commonly observed for the unsymmetrical dinuclear complexes containing bridging silicon groups.[1a,b] This behavior has been attributed to a fluxional process involving the dissociation and recoordination of a phosphine ligand.[1b] In the low-temperature (223 K) $^1H$ NMR spectrum, the terminal hydride resonance appeared as a triplet at −7.5 ppm and the bridging hydride as a doublet at 0 ppm. Both signals exhibited Pt satellites. These resonances are similar to those for related silicon systems[1a,b] and were confirmed in the Sn reaction by a 2D $^1H$−$^{31}P$ COSY experiment. When the reaction of $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ (**2**) with $Ph_2SnH_2$ (**5**) was carried out at room temperature, the solution immediately turned dark red and bubbling was observed, likely caused by the release of $H_2$ and $C_2H_4$ gases. The $^{31}P\{^1H\}$ NMR spectrum of the solution recorded at −50 °C revealed that $[(Ph_3P)_2(H)Pt(\mu\text{-}SnPh_2)(\mu\text{-}\eta^2\text{-}H\text{-}SnPh_2)Pt(PPh_3)]$ (**7**) had formed as the major product. Complex **7** was isolated as a dark red powder in 58% yield. Unfortunately, attempts to obtain X-ray-quality crystals of **7** via recrystallization from common hydrocarbon solvents were unsuccessful. To the best of our knowledge, complex **7** is the first example of an unsymmetrical diplatinum complex containing a bridging ($\mu$−$\eta^2$-H-$SnR_2$) ligand. Unsymmetrical diplatinum,[1a−d] dipalladium,[15a] and heterodinuclear palladium−platinum[16] complexes containing ($\mu$-$\eta^2$-H-$SiR_2$) ligands have been prepared previously. In contrast to the clean reactions observed with $Ph_2ElH_2$ (El = Ge, Sn) and $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$, complex reaction mixtures were obtained from reactions utilizing the Pt(0) complex $Pt(PEt_3)_3$.

We were interested in the effect of the R group in $R_2GeH_2$ on products produced in reaction with Pt(0) precursors. When dimesitylgermane, $Mes_2GeH_2$ (**8**),[18] was added to $(Ph_3P)_2Pt$-

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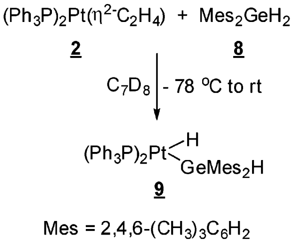
(18) Dimesitylgermane was generously donated by Professor Kim Baines at Western Ontario University.

($\eta^2$-$C_2H_4$) (**2**) in toluene-$d_8$ at −50 °C, the starting materials did not appear to react initially. As the temperature was increased to −40 °C, the NMR spectra began to show small signals that indicated that the reaction had commenced. As the temperature was raised further, the formation of a mononuclear species, $(Ph_3P)_2Pt(H)(GeMes_2H)$ (**9**), analogous to **3**, was observed (eq 1).



(1)

The key features observed in the $^1H$ NMR spectrum for **9** recorded at 223 K were a doublet of doublets at −2.77 ppm that were assigned to the platinum hydride and a multiplet at 4.76 ppm that was assigned to the germanium hydride and that were similar to the NMR data observed for **3**. In the $^{31}P\{^1H\}$ NMR spectrum there was a doublet at 29 ppm ($^1J_{PtP} = 2350$ Hz) that was assigned to the phosphorus *trans* to the hydride and a doublet at 33 ppm ($^1J_{PtP} = 2137$ Hz) that was assigned to the phosphorus *trans* to the germanium center. The smaller coupling between Pt−P was observed for the phosphorus center *trans* to the Ge, but the magnitude of the difference in the coupling was not as pronounced as was generally observed for silyl groups *trans* to a phosphorus due to the stronger *trans* influence of silyl compared to germyl ligands.[19] The $^{31}P$ NMR data for the related complex, *cis*-$(Ph_3P)_2Pt(H)$-$GePh_3$, exhibited peaks at 32.2 and 33.7 ppm for the two inequivalent phosphorus centers.[20] Complex **9** was stable in toluene-$d_8$ solution at room temperature and was isolated as a light yellow solid in 42% yield. The mononuclear complex was the sole product of the room-temperature addition reaction. X-ray-quality crystals of **9** were obtained from the reaction solution after being stored at −40 °C for several weeks. The molecular structure of **9** is shown in Figure 1 along with selected bond distances and angles.

There are few examples of mononuclear platinum complexes containing Pt−Ge bonds reported in the Cambridge Structural Database.[21] The platinum atom in complex **9** has a slightly distorted square planar environment with a Pt−Ge bond distance of 2.43(5) Å, which is comparable to the Pt−Ge bond distances previously reported in such mononuclear complexes (average Pt−Ge distance is about 2.44 Å);[21] for example, in *cis*-$(Ph_3P)_2$-$Pt(H)GePh_3$, the Pt−Ge bond distance is 2.4400(4) Å.[20] The only mononuclear complex with the general structural formula *cis*-$(R_3P)_2Pt(H)(GeR_2H)$ found in the CSD search was for the complex *cis*-$(Et_3P)_2Pt(H)\{Ge(H)[N(SiMe_3)_2]_2\}$, which exhibited a similar Pt−Ge distance (2.422(2) Å) compared to complex **9**.[22] The two Pt−P distances in **9** are essentially identical, also consistent with the lower *trans* influence of Ge compared to Si. For example, the complex *cis*-$(Ph_2MeP)_2Pt(Me)(SiPh_3)$ showed a 0.268 Å difference between the two Pt−P distances, with the longer distance being associated with the P center *trans* to Si.[23] The hydrides in complex **9** were located but not refined. The Ge(1)−Pt(1)−H(1) angle is less than 90° (83.5°), whereas the P(2)−Pt(1)−P(1) angle is about 20° larger (102.5°), and this deviation from ideal square planar angles is probably due to the steric influence of the bulky *cis*-coordinated triphenylphosphine ligands. The germanium center is surrounded by the bulky mesityl groups, which also sterically shield the mononuclear complex and thus inhibit the formation of a dinuclear species, in contrast to the reaction involving the less hindered precursor, $Ph_2GeH_2$, as shown in Scheme 1.

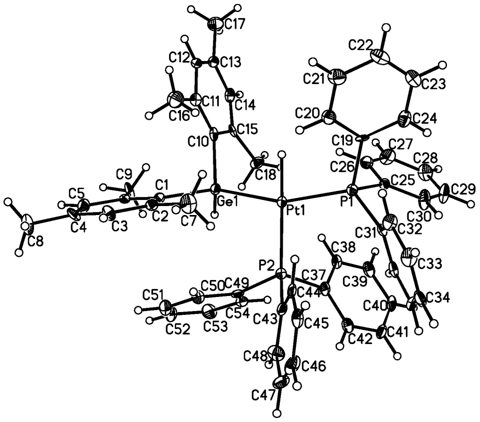


**Figure 1.** Molecular structure of $(Ph_3P)_2Pt(H)(GeMes_2H)$ (**9**). Selected bond distances (Å) and angles (deg): Pt(1)−Ge(1) = 2.4285(5), Pt(1)−P(1) = 2.3202(15), Pt(1)−P(2) = 2.3191(16), Pt-(1)−H(1) = 1.51(5), Ge(1)−H(2) = 1.50(6), Ge(1)−C(1) = 1.991-(5), Ge(1)−C(10) = 1.993(6); P(1)−Pt(1)−Ge(1) = 159.47(5), P(2)−Pt(1)−Ge(1) = 95.39(5), Ge(1)−Pt(1)−H(1) = 83.5(18), P(2)−Pt(1)−P(1) = 102.49(5), P(2)−Pt(1)−H(1) = 178.9(19), P(1)−Pt(1)−H(1) = 78.5(18).

We previously reported that silafluorene reacts with $(Ph_3P)_2$-$Pt(\eta^2$-$C_2H_4)$ (**2**) to yield mono-, di-, and trinuclear Pt−Si species.[1b] The synthesis of germafluorene had not been reported, but West et al. had prepared the potential precursor dichlorogermafluorene from the reaction of *o,o′*-dilithiobiphenyl[24] with germanium tetrachloride.[25] The dichlorogermafluorene was prepared according to the method reported by West et al. and isolated, then subsequently reduced, with $LiAlH_4$ at room temperature to provide germafluorene **10** in 49% yield.

Germafluorene, $C_{12}H_8GeH_2$ (**10**), was added to $(Ph_3P)_2Pt$-$(\eta^2$-$C_2H_4)$ (**2**) in toluene-$d_8$ at 223 K, and the reaction was monitored by $^1H$ and $^{31}P\{^1H\}$ NMR spectroscopy (eq 2). The $^1H$ and $^{31}P\{^1H\}$ NMR data for **11** and **14** are closely related to the corresponding silicon complexes.[1b] Immediately after addition, the Pt−H and Ge−H signals for the mononuclear complex $[(Ph_3P)_2Pt(H)[Ge(C_{12}H_8)H]$ (**11**) were observed in the $^1H$ NMR spectrum at −2.58 and 6.58 ppm, respectively. An additional Ge−H multiplet resonance was observed at 4.89 ppm, which was assigned to the bis(germyl) complex $(Ph_3P)_2$-$Pt[GeH(C_{12}H_8)]_2$ (**14**). Signals for free $C_2H_4$ and $H_2$ were also present in the low-temperature $^1H$ NMR spectrum. As the solution was warmed, the resonances for **11** and **14** broadened slightly and disappeared and a new doublet of doublets

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[21] Data obtained from a search of the Cambridge Structural Database covering the period through mid-December 2006, search topic Pt−Ge bonds, gave 41 hits, of which 33 were for complexes containing only one Pt or other transition metal center.

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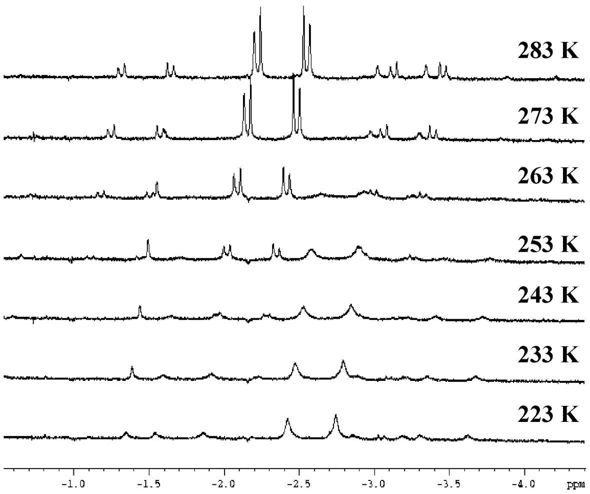
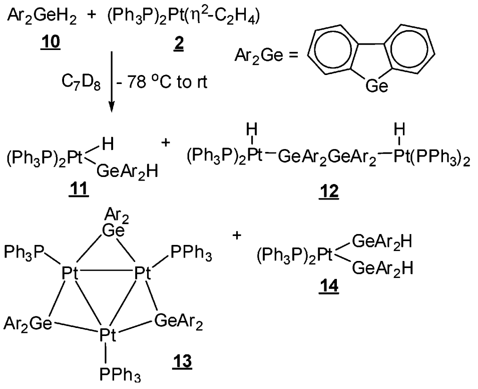


**Figure 2.** Stack plot of selected $^1H$ NMR data showing the Pt−H region from the low-temperature addition of $C_{12}H_8GeH_2$ (**10**) to $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ (**2**).

grew in around −2.20 ppm. A stack plot of selected $^1H$ NMR data recorded after the low-temperature addition is shown in Figure 2.



(2)

The complex responsible for the new doublet of doublets in the $^1H$ NMR spectrum was later determined to be the novel germafluorene complex $[(Ph_3P)_2(H)Pt(C_{12}H_8GeGeC_{12}H_8)Pt(H)(PPh_3)_2]$ (**12**), which may be viewed as a digermane with platinum substituents at both germanium centers. The $^{31}P$ NMR spectrum recorded immediately after addition contained a sharp singlet at 34 ppm assigned to the bis(germyl) complex **14**, a small broad peak at 32 ppm that is unassigned, and two overlapping slightly broadened peaks at 30 ppm assigned to complex **11**. As the solution was warmed above 223 K, the peak at 34 ppm remained, but the signal at 32 ppm disappeared. Three resonances were now observed as two doublets at 30.7 and 30.4 ppm and a singlet at 30.0 ppm, all three with platinum satellites. Finally, at room temperature the only Pt−Ge containing complex observed by $^{31}P\{^1H\}$ NMR spectroscopy was **12**. A doublet was observed in the $^{31}P\{^1H\}$ NMR spectrum at 30.9 and a multiplet at 30.5, both with Pt satellites ($^1J_{PtP}$ = 2390 and 2366 Hz, respectively). The pattern of the peaks for complex **12** was similar to that of the mononuclear species **11**, indicating a phosphorus lying *trans* to a hydride and a phosphorus lying *trans* to a germanium center. The structure of **12** was confirmed by X-ray crystallography (Figure 3); however the hydrides were not located.

The Pt−Ge distances in complex **12** are similar to those observed in the mononuclear complex **3**. The Pt−P distances in **12** are all similar and only slightly shorter than those in **3**. Distortion from square planar geometry at the platinum center is again observed, consistent with the steric requirements of the triphenylphosphine ligands. The two halves of the molecule are close in structure to the mononuclear species **11**, accounting for the similarity in the chemical shifts of the Pt−H and P center resonances for **11** and **12**. The Pt(0) centers are linked by two germafluorenyl units that form a Ge−Ge bond. The Ge−Ge distance of 2.4203(8) Å found in complex **12** is similar to other organodigermanes such as $Ph_3Ge{-}GePh_3$, which exhibited a Ge−Ge distance of 2.437−2.446 Å.[26]

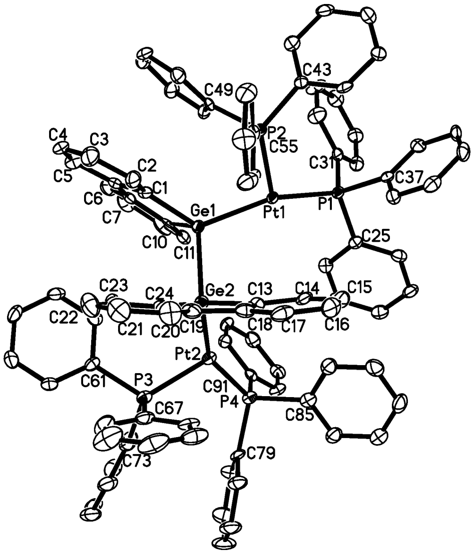


**Figure 3.** Molecular structure of $[(Ph_3P)_2(H)Pt(C_{12}H_8GeGeC_{12}H_8)Pt(PPh_3)_2(H)]$ (**12**). Selected bond distances (Å) and angles (deg): Pt(1)−P(1) = 2.2822(13), Pt(1)−P(2) = 2.2963(14), Pt(1)−Ge(1) = 2.4261(6), Pt(2)−Ge(2) = 2.4364(6), Ge(1)−Ge(2) = 2.4203(8), Ge(1)−C(12) = 1.959(5), Ge(1)−C(1) = 1.966(5), Ge(2)−C(13) = 1.970(5), Ge(2)−C(24) = 1.988(5); P(1)−Pt(1)−P(2) = 108.22(5), P(1)−Pt(1)−Ge(1) = 158.81(4), P(2)−Pt(1)−Ge(1) = 92.11(4), P(4)−Pt(2)−P(3) = 109.23(5), P(4)−Pt(2)−Ge(2) = 152.20(4), P(3)−Pt(2)−Ge(2) = 95.41(4), Ge(2)−Ge(1)−Pt(1) = 111.85(2), Ge(1)−Ge(2)−Pt(2) = 112.63(2). Two molecules of $C_7D_8$ were present in the crystal lattice (not shown).

The Pt−Ge−Ge−Pt motif is rare, although it has been observed in a polymetallic chain attached to carborane cages $[m\text{-}C_2H_2B_{10}H_9HgPt(PPh_3)_2Ge(C_6F_5)_2Ge(C_6F_5)_2Pt(PPh_3)_2HgB_{10}H_9C_2H_2\text{-}m]$, but no X-ray crystal structure was reported.[27] The structure of **12** is reminiscent of a product formed in a catalytic dehydrocoupling reaction.[28] Indeed, there is only one reported example of a structure similar to **12**, and it was isolated as an intermediate in the catalytic dehydrocoupling of arylgermanes.[29] Banaszak-Holl et al. reacted a secondary hydrogermane with electron-withdrawing aryl substituents, $[3,5\text{-}(CF_3)_2C_6H_3]_2GeH_2$, with $(Et_3P)_2PtGe[N(SiMe_3)_2]_2$, and the digermane complex $[(Et_3P)_2(H)PtGe(Ar)_2Ge(Ar)_2Pt(H)(PEt_3)_2]$ was isolated. The reaction proceeded from the initially formed bis(germyl) complex *trans*-$(Et_3P)_2Pt(GeAr_2H)_2$ to the digermyl complex *cis*-$(Et_3P)_2(H)Pt(GeAr_2GeAr_2H)$, which then reacted with the starting Pt precursor to give the Pt−Ge−Ge−Pt-containing product

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(26) (a) Dräger, V. M.; Ross, L. *Z. Anorg. Allg. Chem.* **1980**, *460*, 207. (b) Dräger, V. M.; Ross, L. *Z. Anorg. Allg. Chem.* **1980**, *469*, 115.

(27) Bocharev, M. N.; Fedorova, E. A.; Razuvaev, G. A.; Bregadze, V. I.; Kampel, V. T. *J. Organomet. Chem.* **1984**, *265*, 117.

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with a *cis*-geometry at each Pt center.[29] The Pt−P, Pt−Ge, and Ge−Ge distances are similar to those found for complex **12**.

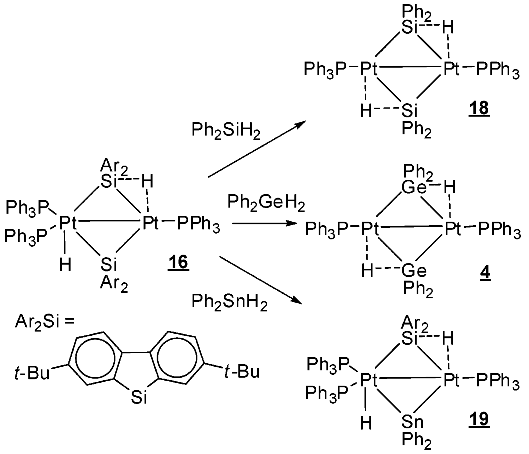
These results are consistent with our observation of the reactive bis(germyl) complex **14** observed in the low-temperature addition of **10** to **2** as the probable precursor of digermane complex **12**. The silicon complex analogous to **12** has not been observed in the silafluorene reactions. The reaction solution was stored at room temperature, and NMR data were recorded periodically to check for the formation of the trinuclear species $[(Ph_3P)Pt(\mu\text{-}GeC_{12}H_8)]_3$ (**13**). After 24 h a signal at 70 ppm exhibiting a complex Pt satellite pattern[30] analogous to the trinuclear silicon complex $[(Ph_3P)Pt(\mu\text{-}SiC_{12}H_8)]_3$ previously reported[1c,d] was observed, supporting the formation of complex **13**.

The results of the low-temperature addition reaction of $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ (**2**) with germafluorene **10** are shown in eq 2. The initial products were the mononuclear complexes $[(Ph_3P)_2Pt(H)[Ge(C_{12}H_8)H]$ (**11**) and $[(Ph_3P)_2Pt[Ge(C_{12}H_8)H]_2$ (**14**), but it is proposed that the former complex rapidly converts to the digermane $[(Ph_3P)_2(H)Pt(C_{12}H_8GeGeC_{12}H_8)Pt(H)(PPh_3)_2]$ (**12**). The trinuclear complex $[(Ph_3P)Pt(\mu\text{-}GeC_{12}H_8)]_3$ (**13**) formed slowly and precipitates from the solution as a red solid. The bis(germyl)[31] complex **14** appeared to be unstable and was only observed in the early stages of the reaction. When the temperature was raised to 253−263 K, the $^{31}P$ NMR signal was only just visible.

When the reaction was carried out at room temperature, $[(Ph_3P)Pt(\mu\text{-}GeC_{12}H_8)]_3$ (**13**) was formed more rapidly. The $^1H$ and $^{31}P\{^1H\}$ NMR spectra recorded immediately after addition exhibited signals for the mononuclear complex **11** and the unsymmetrical dinuclear complex $[(Ph_3P)_2(H)Pt(\mu\text{-}GeC_{12}H_8)(\mu\text{-}\eta^2\text{-}H\text{-}GeC_{12}H_8)Pt(PPh_3)]$ (**15**), analogous to the tin derivative **7** given in Scheme 2. These signals were soon replaced by signals for the digermane complex **12**, and within 2 h after mixing, signals for the trinuclear complex **13** were observed and **13** was eventually isolated as a red crystalline solid in 73% yield. Unfortunately, the crystalline needles did not diffract adequately for the complete structure to be resolved by X-ray crystallography; however, the $Pt_3$ triangle in **13** could be discerned.

The low-temperature reaction of germafluorene **10** with **2** exhibited similarities and differences compared to the analogous reaction involving silafluorene. For example, the silicon-containing mononuclear complexes analogous to **11** and **14** were produced, but when the solution was warmed to room temperature, the major product observed was the unsymmetrical dinuclear silicon complex analogous to complex **15**. In the low-temperature reaction involving germafluorene, the digermane product **12** and not the unsymmetrical dinuclear complex **15** was formed as the major product. The room-temperature reaction involving silafluorene and **2** produced the same products as the low-temperature reaction but also generated the trinuclear complex $[(Ph_3P)Pt(\mu\text{-}SiC_{12}H_8)]_3$, analogous to **13**, in 27% yield.[1c,d] In both reactions involving germafluorene and silafluorene with **2**, the formation of the trinuclear complex was inhibited at low temperature. Attempts to prepare stannafluorene, $H_2SnC_{12}H_8$, by the route described for the preparation of germafluorene were unsuccessful. The reaction of the *o,o′*-dilithiobiphenyl with $SnCl_4$ did not provide dichlorostannafluorene, and thus a comparison of the reaction products generated from $Ph_2SnH_2$ and stannafluorene could not be obtained.

**Scheme 3**



**Exchange Reactions.** Part of our current objective is the development of additional routes to Ge−TM and Sn−TM complexes (TM = transition metal). One possible route involves the exchange of silyl, germyl, or stannyl ligands in a preformed multinuclear complex. When the unsymmetrical dinuclear complex containing silicon bridging groups, $[(Ph_3P)_2(H)Pt(\mu\text{-}SiC_{20}H_{24})(\mu\text{-}\eta^2\text{-}H\text{-}SiC_{20}H_{24})Pt(PPh_3)]$ (**16**),[1c] was reacted with 1 equiv of $Ph_2SiH_2$ (**17**) or $Ph_2GeH_2$ in $C_7D_8$, symmetrical dinuclear complexes containing $(\mu\text{-}\eta^2\text{-}H\text{-}ElPh_2)$ ligands were isolated in 26−28% yield. The preparation of $[(Ph_3P)Pt(\mu\text{-}\eta^2\text{-}H{-}SiPh_2)]_2$ (**18**) was previously reported by Stone et al. from the reaction of $Ph_2SiH_2$ with $[(Ph_3P)Pt(C_2H_4)_2]$.[32] The structure of **18** in this study was confirmed by X-ray crystallography (see Supporting Information).

Recently, Osakada et al. reported the displacement of the $(HSiEt_2)$ units in $[(Cy_3P)Pt(\mu\text{-}\eta^2\text{-}H\text{-}SiEt_2)]_2$ with $(HSiPh_2)$ from the reaction of the dinuclear complex with excess diphenylsilane. A mixture of two intermediate complexes was observed in the stoichiometric reaction indicating a stepwise process, $[\{Pt(PCy_3)\}_2(\mu\text{-}\eta^2\text{-}HSiPh_2)(\mu\text{-}\eta^2\text{-}HSiEt_2)]$ and $[\{Pt(PCy_3\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}H_2SiEt_2)(\mu\text{-}SiPh_2)]$.[33]

The exchange reaction between **16** and $Ph_2SnH_2$ produced a new complex just after mixing at low temperature. The new complex has been tentatively assigned to the mixed silyl−stannyl platinum complex, **19**. After several weeks, the $^{31}P$ NMR signals for **19** were still visible, but the intensity had decreased significantly. A small, new doublet signal was observed at 17 ppm, which is possibly due to the formation of the unsymmetrical dinuclear Sn−Pt complex **7**. However, due to the presence of several components in the reaction solution, isolation of **7** or **19** although attempted was unsuccessful. Exchange reactions involving mononuclear Pt−silyl groups with hydrogermanes or hydrostannanes were reported over 30 years ago,[7i,m] but the reactions shown in Scheme 3 were the first examples involving a dinuclear precursor such as **16**.

## Conclusions

The oxidative addition of secondary hydrogermanes and hydrostannanes to Pt(0) precursors is a facile route to the

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(30) Moor, A.; Pregosin, P. S.; Venanzi, L. M. *Inorg. Chim. Acta* **1981**, *48*, 153.

(31) (a) For a recent report on the preparation of a series of bis(tritolylgermyl)bis(dimethylphenylphosphine)platinum complexes see: Usui, Y.; Fukushima, T.; Nanjo, M.; Mochida, K.; Akasaka, K.; Kudo, T.; Komiya, S. *Chem. Lett.* **2006**, *35*, 810. See also: (b) Mochida, K.; Suzuki, K.; Hatanaka, W.; Nishiyama, Y.; Nanjo, M.; Sekine, A.; Ohashi, Y.; Sakamoto, M.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 124.

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formation of novel Pt−Ge and Pt−Sn complexes. The nature of the group 14 element in the same type of hydride precursor results in differences with respect to the types of products that are produced. The reactions involving $Ph_2GeH_2$ and $Ph_2SnH_2$ produced mononuclear and dinuclear complexes that were identified by VT-NMR spectroscopy. The bulkier R group in $Mes_2GeH_2$ slowed the initial oxidative addition reaction and eventually provided only the mononuclear complex **9**. Germafluorene **10** was synthesized by the reduction of dichlorogermafluorene and then reacted with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ (**2**). Signals for the mononuclear **11**, unsymmetrical dinuclear **15**, and trinuclear **13** complexes analogous to those observed in the reaction with silafluorene were observed in the NMR spectra. The most fascinating aspect of this reaction was the unexpected formation of the digermyl-bridged platinum species $[(Ph_3P)_2(H)Pt(C_{12}H_8GeGeC_{12}H_8)Pt(H)(PPh_3)_2]$ (**12**). The dinuclear germanium complex **4** and the dinuclear tin complex **7** were alternatively prepared via exchange reactions. When diphenylgermane or diphenylstannane was reacted with a dinuclear silicon complex, the bridging silyl groups were replaced with the corresponding germyl or stannyl groups. Further studies are in progress involving other cyclic group 14 hydride precursors with additional late transition metal complexes.

## Experimental Section

**General Comments.** All reactions were performed in flame-dried glassware under dry nitrogen or argon on a dual-manifold Schlenk line. Diethyl ether and THF were distilled from Na/benzophenone or Na/9-fluorenone prior to use. Methylene chloride was distilled from $CaH_2$. (Ethylene)bis(triphenylphosphine)platinum(0) was purchased from Aldrich Chemical Co. and used as received. Diphenylgermane and $GeCl_4$ were purchased from Gelest and used as received. $SnCl_4$ was purchased from Aldrich and used as received. Dimesitylgermane was generously donated by Dr. Kim Baines from Western Ontario University. Dichlorogermafluorene was prepared from a literature procedure.[25] Toluene-$d_8$, acetone-$d_6$, and methylene chloride-$d_2$ were purchased from Cambridge Isotopes, Inc., and degassed by freeze/thaw/pump cycles and dried over activated molecular sieves. Diphenylstannane was prepared from a literature procedure.[34] Melting point determinations were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected. $^1H$ and $^{31}P\{^1H\}$ NMR spectra were recorded at room temperature unless otherwise specified on a Bruker ARX-500 MHz equipped with a broadband probe. Proton and carbon chemical shifts ($\delta$) are reported relative to residual protonated solvents $C_7D_8$ (2.09 ppm), $C_6D_6$ (7.16 ppm), and $CD_2Cl_2$ (5.32 ppm, 54.0 ppm for $^{13}C$). Phosphorus chemical shifts ($\delta$) are reported relative to external $H_3PO_4$ (0 ppm). Chemical shifts are given in ppm and coupling constants in Hz. Elemental analysis determinations were obtained from Atlantic Microlabs, Inc., Norcross, GA. Infrared spectra were recorded on a Thermo-Nicolet Avatar 360 ESP FT-IR spectrometer. High-resolution mass spectra were obtained in FAB mode on a JEOL M Station-JMS700 using nitrobenyl alcohol (NBA) as the solvent. The X-ray crystal structure determinations were performed on a Bruker SMART 1K diffractometer equipped with a CCD area detector.

**Reaction of $Ph_2GeH_2$ with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ at Room Temperature. Formation of $(Ph_3P)_2Pt(H)(GePh_2H)$ (3) and $[(Ph_3P)Pt(\mu\text{-}\eta^2\text{-}H{-}GePh_2)]_2$ (4).[10]** In a drybox, $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ (**2**) (33 mg, 0.044 mmol) was placed in a vial and dissolved in 0.5 mL of toluene. Diphenylgermane (**1**) (10 mg, 0.044 mmol) was weighed into a separate vial and dissolved in 0.5 mL of toluene. The $Ph_2GeH_2$ (**1**) solution was added to the $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ (**2**) solution, and then 1 mL of pentane was added. The vial was placed in a freezer at −50 °C, and after 24 h a crystalline solid had formed. The solvent was decanted from the vial, and the yellow crystalline product, $(Ph_3P)_2Pt(H)GePh_2H$ (**3**) (as $C_7H_8$ solvate), was dried under reduced pressure (20 mg, 44% yield, mp = 90−92 °C). The isolated sample was dissolved in $CD_2Cl_2$, and NMR spectroscopic data were obtained. $^1H$ NMR (500 MHz, $CD_2Cl_2$, 223 K): $\delta$ 7.48−7.05 (ArH), 3.88 (m, GeH), −2.97 (ddd, $^1J_{PtH} = 930$, $^2J_{PH(trans)} = 161$, $^2J_{PH(cis)} = 18$, $^3J_{HH} = 3.2$, PtH). $^{31}P\{^1H\}$ NMR (202 MHz, $CD_2Cl_2$, 223 K): $\delta$ 32.5 (d, $^1J_{PtP} = 2306$, $^2J_{pp}$=12, P *trans* to Ge), 31.7 (br s, $^1J_{PtP} = 2317$, P *trans* to H). IR (solid, $\nu$ $cm^{-1}$): 1931 (PtH), 2069 (GeH). Anal. Calcd for $C_{55}H_{50}GeP_2Pt$: C, 63.48; H, 4.84. Found: C, 63.78; H, 4.85.

In a similar experiment, the reaction was repeated without the addition of pentane, and the solution was stored at room temperature in the drybox. After 1 h a yellow crystalline solid had formed. The solvent was decanted and the product was dried under reduced pressure to give $[(Ph_3P)Pt(\mu\text{-}\eta^2\text{-}H{-}GePh_2)]_2$ (**4**) (38 mg, 63%, as $C_7H_8$ solvate). The NMR data were identical to those observed for the product obtained from the low-temperature addition reaction described below.

**General Procedure for Low-Temperature Addition Reactions.** The reactions were typically run on a 1:1 ratio between the platinum and the hydrogermane or hydrostannane precursors. A solution of the platinum precursor, $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$, was prepared in approximately 0.5 mL of $C_7D_8$ and transferred to a NMR tube capped with a rubber septum. In a separate shortened NMR tube capped with a septum was placed the hydrogermane or hydrostannane precursor in 0.25−0.5 mL of $C_7D_8$. The solutions were cooled in a dry ice/acetone bath (−78 °C unless otherwise noted) and the hydrogermane or hydrostannane solution was added by syringe to the NMR tube containing the platinum precursor. After sitting for a few minutes at low temperature, the tube was removed, shaken vigorously for a few seconds, and then returned to the cold bath. The sample was then placed in the precooled NMR magnet at the desired temperature, and NMR data were then collected at various reaction times after addition.

**Reaction of $Ph_2GeH_2$ with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ at Low Temperature. Formation of $[(Ph_3P)Pt(\mu\text{-}\eta^2\text{-}H\text{-}GePh_2)]_2$ (4).[10]** A toluene-$d_8$ solution containing diphenylgermane, $Ph_2GeH_2$ (**1**) (10 mg, 0.044 mmol), was added by syringe to a toluene-$d_8$ solution containing $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ (**2**) (33 mg, 0.044 mmol). The resulting reaction mixture was immediately placed in a precooled NMR magnet at 223 K. Proton and phosphorus NMR spectra were then recorded. Formation of the mononuclear complex **3** was observed immediately after addition as the major Pt−Ge-containing product along with some unreacted complex **2** and a small amount of $Ph_3PO$.

**Data Collected at 223 K, 5 min after Addition.** $^1H$ NMR (500 MHz, $C_7D_8$, 223 K): $\delta$ 8.1−6.8 (ArH), 5.29 (s, $C_2H_4$), 4.74 (m, GeH, **3**), 2.69 (s, $^2J_{PtH} = 30$, $C_2H_4$ for **2**), −1.98 (ddd, $^1J_{PtH} = 935$, $^2J_{PH(trans)} = 161$, $^2J_{PH(cis)} = 20$, PtH, **3**). $^{31}P\{^1H\}$ NMR (202 MHz, $C_7D_8$, 223 K): $\delta$ 34.0 (s, $^1J_{PtP} = 3714$, **2**), 33.4 (d, $^1J_{PtP} = 2367$, $^2J_{pp} = 11$, P *trans* to Ge, **3**), 32.7 (d, $^1J_{PtP} = 2276$, P *trans* to H, **3**).

The temperature was raised slowly from 223 to 300 K over a period of 1 h; data were recorded at 10 min intervals after each 20 deg temperature increase. The spectra remained essentially unchanged until 283 K, when the signals for **2** and **3** became significantly broadened. At 300 K, the resonances for **2** and **3** were negligible.

Upon removal from the NMR probe a yellow crystalline solid was observed in the NMR tube. The solvent was decanted from the NMR tube, and the product was dried under reduced pressure to give crystals of $[(Ph_3P)Pt(\mu\text{-}\eta^2\text{-}H{-}GePh_2)]_2$ (**4**) as the $C_7D_8$ solvate (20 mg, 62% yield, mp 218−220 °C (dec)). The isolated sample was dissolved in $CD_2Cl_2$, and spectroscopic data were obtained. $^1H$ NMR (500 MHz, $CD_2Cl_2$, 300 K): $\delta$ 7.8−6.9 (ArH), 0.43 (s, $^1J_{PtH} = 785$, $^2J_{PtH} = 96$, Pt⋯H⋯Ge). $^{31}P\{^1H\}$ NMR (202

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(34) Kuivila, H. G. *J. Org. Chem.* **1961**, *26*, 1426.

MHz, $CD_2Cl_2$, 300 K): $\delta$ 33.5 (s, ${}^1J_{PtP} = 4383$, ${}^2J_{PtP} = 162$, ${}^3J_{PP} = 58$). IR (solid, $\nu$ cm$^{-1}$): 1736 (Pt···H···Ge). Anal. Calcd for $C_{60}H_{50}Ge_2P_2Pt_2 \cdot C_7D_8$: C, 54.72; H, 4.65. Found: C, 53.52; H, 3.84.

**Reaction of $Ph_2SnH_2$ with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ at Low Temperature. Formation of $(Ph_3P)_2Pt(H)(SnPh_2H)$ and $[(Ph_3P)_2(H)Pt(\mu\text{-}SnPh_2)(\mu\text{-}\eta^2\text{-}H{-}SnPh_2)Pt(PPh_3)]$.** A toluene-$d_8$ solution of $Ph_2SnH_2$ (**5**) (5 mg, 0.0017 mmol) was added by syringe to a toluene-$d_8$ solution containing $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ (**2**) (13 mg, 0.0017 mmol). The resulting reaction mixture was immediately placed in a precooled NMR magnet at 223 K. Proton and phosphorus NMR spectra were recorded 5 min after addition.

**Data Recorded at 223 K, 5 min after Addition**. Selected $^1$H NMR (500 MHz, $C_7D_8$, 223 K): $\delta$ 6.21 (d, $J = 36$, SnH, unassigned), 5.90 (s, ${}^2J_{PtH} = 41$, SnH, unassigned), 5.43 (br s, unassigned), 5.33 (s, $C_2H_4$), 4.59 (s, $H_2$), 0.01 (br d, Pt···H···Sn, **7**), −2.38 (br m, ${}^2J_{PtH} = 824$, PtH, **6**), −7.85 (br m, PtH, **7**), −10.41 (br m, PtH, unassigned), −10.69 (br m, PtH, unassigned). $^{31}$P{$^1$H} NMR (202 MHz, $C_7D_8$, 223 K): $\delta$ 36.7 (s, unassigned), 32.9 (s, P *trans* to Sn, **6**, tentative assignment), 32.0 (s, P *trans* to H, **6**, tentative assignment), 28.4 (t, ${}^3J_{PP} = 38$, $PtPPh_3$, **7**), 25.4 (s, $Ph_3PO$), 17.1 (d, ${}^3J_{PP} = 38$, $Pt(PPh_3)_2$, **7**), 4.4 (m, unassigned), 1.1 (m, unassigned), −2.0 (m, unassigned), −6.8 (br s, $PPh_3$), several minor resonances were observed between −5 and 45 ppm.

The temperature was raised slowly from 223 to 300 K over a period of 3 h; data were recorded after each 10 deg temperature increase. When the temperature was increased to 233 K (30 min after addition) the major signals observed were for **7** and $PPh_3$. As the temperature was raised further, the signals for **7** broadened until at room temperature (3 h after addition) they were no longer discernible. A stack plot showing the selected chemical shift region for the $^{31}$P NMR signals for **7** and the disappearance of the signals with increasing temperature is available in the Supporting Information.

**Reaction of $Ph_2SnH_2$ with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ at Room Temperature. Formation of $[(Ph_3P)_2(H)Pt(\mu\text{-}SnPh_2)(\mu\text{-}\eta^2\text{-}H{-}SnPh_2)Pt(PPh_3)]$.** A toluene-$d_8$ solution of $Ph_2SnH_2$ (**5**) (5 mg, 0.0017 mmol) was added to a toluene-$d_8$ solution containing $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ (**2**) (13 mg, 0.0017 mmol). The resulting solution immediately turned dark red and bubbling was observed.

**Selected Data Recorded at 223 K, 2 h after Addition**. $^{31}$P{$^1$H} NMR (202 MHz, $C_7D_8$, 223 K): $\delta$ 34.8 (s, unreacted **2**), 32.9 (s, P *trans* to Sn, **6**, tentative assignment), 32.0 (s, P *trans* to H, **6**, tentative assignment), 28.4 (t, ${}^1J_{PtP} = 4446$, ${}^3J_{PP} = 38$, $PtPPh_3$, **7**), 25.4 (s, $Ph_3PO$), 17.1 (d, ${}^1J_{PtP} = 3915$, ${}^3J_{PP} = 38$, $Pt(PPh_3)_2$, **7**), −5.6 (br, $PPh_3$).

**Selected Data Recorded at 183 K, 3 h after Addition**. $^{31}$P{$^1$H} NMR (202 MHz, $C_7D_8$, 183 K): $\delta$ 29.2 (br, **7**), 25.5 (s, $Ph_3PO$), 16.7 (br, **7**), 10.2 (s, ${}^1J_{PtH} = 3836$, $(Pt(PPh_3)_4)$,[35] −7.8 (s, $PPh_3$).

The solvent was removed under vacuum on the Schlenk line, and a dark red solid was obtained. The dark red-brown solid **7** was washed with 10 1-mL portions of pentane, then dried under vacuum (18 mg, 58% yield, mp = 114−116 °C (dec)). A sample of **7** was dissolved in toluene-$d_8$, and $^1$H and $^{31}$P{$^1$H} NMR spectra were recorded. $^1$H NMR (500 MHz, $C_7D_8$, 223 K): $\delta$ 7.9−6.7 (ArH), 0.01 (d, ${}^1J_{PtH} = 904$, ${}^2J_{PtH} = 396$, ${}^2J_{PH} = 9$, Pt···H···Sn), −7.45 (t, ${}^1J_{PtH} = 786$, ${}^2J_{PtH} = 355$, ${}^2J_{PH} = 12$, PtH). $^{31}$P{$^1$H} NMR (202 MHz, $C_7D_8$, 223 K): $\delta$ 28.4 (t, ${}^1J_{PtP} = 4458$, ${}^3J_{PP} = 38$, $PtPPh_3$), 25.6 (s, $Ph_3PO$), 17.1 (d, ${}^1J_{PtP} = 3918$, ${}^2J_{PP} = 38$). $^1$H−$^{31}$P COSY (500 MHz, $C_7D_8$, 223 K): correlations observed between ($^1$H, $^{31}$P) resonances at [0.01 (Pt···H···Sn), 28.4 ($PtPPh_3$)], [−7.45 (PtH), 17.1 ($Pt(PPh_3)_2$)], [−7.45 (PtH), 28.4 ($PtPPh_3$)]. IR (solid, $\nu$ cm$^{-1}$): 1571 (Pt···H···Sn). Anal. Calcd for $C_{78}H_{67}Sn_2P_3Pt_2$: C, 54.31; H, 3.92. Found: C, 53.66; H, 4.09.

**Reaction of $Mes_2GeH_2$ with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ at Room Temperature.** A $C_7D_8$ solution of $Mes_2GeH_2$ (**8**) (10 mg, 0.032 mmol) was added to a $C_7D_8$ solution of $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ (**2**) (24 mg, 0.032 mmol). After 28 days at −40 °C, a yellow crystalline solid was collected from the reaction solution (24 mg, 42% yield, mp = 108−110 °C (dec)). The molecular structure was confirmed by X-ray crystallography (see X-ray section below). NMR spectra were recorded for the isolated complex **9** at 223 and 300 K. $^1$H NMR (500 MHz, $C_7D_8$, 223 K): $\delta$ 7.5−6.7 (ArH), 4.76 (m, GeH), 2.67 (s, ArMe), 2.22 (s, ArMe), −2.65 (ddd, ${}^1J_{PtH} = 933$, ${}^2J_{PH(trans)} = 146$, ${}^2J_{PH(cis)} = 21$, ${}^3J_{HH} = 4$, PtH). $^{31}$P{$^1$H} NMR (202 MHz, $C_7D_8$, 223 K): $\delta$ 33.3 (d, ${}^1J_{PtP} = 2350$, ${}^2J_{pp} = 10$, P *trans* to Ge), 29.5 (d, ${}^1J_{PtP} = 2137$, ${}^2J_{pp} = 10$, P *trans* to H). The spectra were unchanged at 300 K. IR (solid, $\nu$ cm$^{-1}$): 2069 (GeH), 1976 (PtH). Anal. Calcd for $C_{54}H_{54}GeP_2Pt$: C, 62.80; H, 5.28. Found: C, 62.82; H, 5.32.

In a similar reaction between **8** and **2** performed at 223 K, no resonances were observed for complex **9** immediately after addition and the major resonances observed by $^1$H and $^{31}$P{$^1$H} NMR spectroscopy at 223 K were for unreacted **2** and **8**. As the temperature was raised to 233 K, small signals for **9** were observable and continued to increase in intensity (as the signals for **2** and **8** decreased in intensity) as the temperature was gradually increased to 300 K over a period of 3 h. The NMR data for complex **9** obtained from the low-temperature experiment were essentially identical to the data obtained from the isolated sample.

**Reduction of 9,9-Dichloro-9-germafluorene: Formation of 9,9-Dihydrogermafluorene (10).** 9,9-Dichloro-9-germafluorene[25] (278 mg, 0.094 mmol) was added to 100 mL of ether in a three-neck round-bottom flask equipped with a condenser. Lithium aluminum hydride (24 mg, 0.062 mmol) was placed in a bent tube, and the tube was attached to the round-bottomed flask. The $LiAlH_4$ was added slowly at room temperature by tapping the end of the bent tube, and the reaction was left to stir overnight. Saturated ammonium chloride (5 mL), bulk diethyl ether (50 mL), and water (50 mL) were added slowly to the flask, and the solution was then transferred to a 500 mL Erlenmeyer flask. The organic layer was separated and dried over anhydrous magnesium sulfate for 1 h. The solvent was removed using a rotary evaporator, and a yellow oily material was observed. Residual solvent was removed from the sample in vacuo. Germafluorene was obtained in 49% yield (105 mg). $^1$H NMR (500 MHz, $C_6D_6$, 300 K): $\delta$ 7.67 (d, $J = 7.95$, ArH), 7.48 (d, $J = 6.99$, ArH), 7.21 (dt, $J = 7.95$, 1.0, ArH), 7.09 (dt, $J = 6.99$, 1.0, ArH), 4.98 (s, GeH). $^{13}$C{$^1$H} NMR (125 MHz, $CD_2Cl_2$, 300 K): $\delta$ 147.9, 134.8, 134.7, 130.4, 128.3, 122.3 (ArC). IR (solid, $\nu$ cm$^{-1}$): 2059 (Ge−H). Anal. Calcd for $C_{12}H_{10}Ge$: C, 63.55; H, 4.44. Found: C, 63.26; H, 4.31.

**Reaction of Germafluorene with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ at Low Temperature.** A solution of germafluorene **10** (10 mg, 0.044 mmol) in $C_7D_8$ was syringed into a $C_7D_8$ solution of $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ (**2**) (33 mg, 0.044 mmol) at −78 °C. The resulting reaction mixture was immediately placed in a precooled NMR magnet at 223 K. Proton and phosphorus NMR spectra were recorded 5 min after addition.

The temperature was raised slowly from 223 to 300 K over a period of 160 min; data were recorded after each 10 deg temperature increase. The signals for **11** in the $^1$H NMR began to broaden and disappear as the temperature was raised. When the temperature had been raised to 253 K (1 h after addition), the signals for **12** were observed. When the temperature had been raised to 300 K (160 min after addition), only the signals for **12** remained. After warming to room temperature, the solution was cooled to 223 K and NMR data were recorded. Representative data recorded at 223 K (5 min after addition), 253 K (1 h after addition), 300 K (2 h 40 min after addition), 223 K (3 h after addition), and 300 K (7 days after addition) are listed below. A stack plot showing the changes in the Pt−H region in the $^1$H NMR spectrum is shown in Figure 2. A stack plot showing the changes in the $^{31}$P{$^1$H} NMR spectrum with temperature is provided in the Supporting Information.

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[35] Sen, A.; Halpern, J. *Inorg. Chem.* **1980**, *19*, 1073.

**Data Recorded at 223 K, 5 min after Addition**. Selected $^1$H NMR (500 MHz, $C_7D_8$, 223 K): $\delta$ 6.58 (m, GeH, **11**, tentative assignment), 5.29 (s, $C_2H_4$), 4.89 (m, GeH, **14**, tentative assignment), 4.80, (s, unreacted **10**, minor amount), 4.55 (s, $H_2$), −2.58 (br d, $^1J_{PtH} = 883$, $^2J_{PH(trans)} = 160$, PtH, **11**). $^{31}P\{^1H\}$ NMR (202 MHz, $C_7D_8$, 223 K): $\delta$ 34.2 (s, $^1J_{PtP} = 2415$, **14**), 32.6 (br, $^1J_{PtP} = 2368$, unassigned), 30.2 (br s, $^1J_{PtP} = 2356$, P *trans* to Ge for **11**), 30.0 (br s, $^1J_{PtP} = 2489$, P *trans* to H for **11**), 25.6 (s, $OPh_3$).

**Data Recorded at 253 K, 1 h after Addition.** Selected $^1$H NMR (500 MHz, $C_7D_8$, 253 K): $\delta$ 6.63 (m, GeH, **11**, tentative assignment), 5.28 (s, $C_2H_4$), 4.82 (m, GeH, **14**, tentative assignment), 4.53 (s, $H_2$), −1.5 (s, unassigned), −2.18 (dd, $^2J_{PH(trans)} = 165$, $^2J_{PH(cis)} = 20$, $^1J_{PtH}$ not resolved, PtH, **12**), −2.75 (br d, $^1J_{PtH} = 874$, $^2J_{PH(trans)} = 161$, PtH, **11**). $^{31}P\{^1H\}$ NMR (202 MHz, $C_7D_8$, 253 K): $\delta$ 34.4 (s, $^1J_{PtP} = 2413$, **14**), 30.7 (d, $^1J_{PtP} = 2372$, $^2J_{PP} = 8$, **12**), 30.4 (d, $^1J_{PtP} = 2380$, $^2J_{PP} = 8$, **12**), 30.0 (br s, $^1J_{PtP} = 2473$, **11**), 25.9 (s, $OPPh_3$).

**Data Recorded at 300 K, 2 h 40 min after Addition.** Selected $^1$H NMR (500 MHz, $C_7D_8$, 300 K): $\delta$ 5.25 (s, $C_2H_4$), 4.50 (s, $H_2$), −2.50 (dd, $^1J_{PtH} = 909$, $^2J_{PH(trans)} = 164$, $^2J_{PH(cis)} = 19$, PtH, **12**). $^{31}P\{^1H\}$ NMR (202 MHz, $C_7D_8$, 300 K): $\delta$ 30.9 (d, $^1J_{PtP} = 2390$, $^2J_{PP} = 8$, P *trans* to H, **12**), 30.5 (dd, $^1J_{PtP} = 2366$, $^4J_{PtP} = 40$, $^2J_{PP} = 6$, $^5J_{PP} = 2$, P *trans* to Ge, **12**), 24.9 (s, $OPPh_3$).

**Data Recorded at 223 K, 3 h after Addition**. Selected $^1$H NMR (500 MHz, $C_7D_8$, 223 K): $\delta$ 5.29 (s, $C_2H_4$), 4.54 (s, $H_2$), −1.99 (br d, $^1J_{PtH} = 923$, $^2J_{PH} = 165$, **12**). $^{31}P\{^1H\}$ NMR (202 MHz, $C_7D_8$, 223 K): $\delta$ 30.5 (br s, $^1J_{PtP} = 2371$, **12**), 30.3 (br s, $^1J_{PtP} = 2389$, **12**), 26.7 (s, $OPPh_3$).

**Data Recorded at 300 K, 7 days after Addition**. Selected $^1$H NMR (500 MHz, $C_7D_8$, 300 K): $\delta$ 5.26 (s, $C_2H_4$), −2.48 (br dd, $^1J_{PtH} = 910$, $^2J_{PH} = 164$, $^2J_{PH} = 20$, **12**). $^{31}P\{^1H\}$ NMR (202 MHz, $C_7D_8$, 300 K): $\delta$ 70.9 (s, $^2J_{PtP} = 428$, $^3J_{PP} = 91$, $^1J_{PtP}$ not resolved, **13**), 30.9 (br s, $^1J_{PtP} = 2380$, **12**), 30.5 (br d, $^1J_{PtP} = 2375$, $^2J_{PP} = 7$, **12**), 24.6 (s, $OPPh_3$). After 14 days at room temperature the proton and phosphorus spectra were unchanged.

**Reaction of Germafluorene with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ at Room Temperature.** A $C_7D_8$ solution of germafluorene **10** (10 mg, 0.044 mmol) was added to a $C_7D_8$ solution of $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ (**2**) (33 mg, 0.044 mmol), and the reaction mixture was transferred to an NMR tube. NMR spectra were recorded at 300 K (10 min to 2 h after addition) and then at 223 K (2−5 h after addition). The solution was then stored at room temperature for 24 h, and proton and phosphorus spectra were again recorded at 300 K.

**Data Recorded at 300 K, 10 min to 2 h after Addition (300 K)**. Selected $^1$H NMR (500 MHz, $C_7D_8$): $\delta$ 5.26 (s, $C_2H_4$), 4.50 (s, $H_2$), −2.44 (dd, $^1J_{PtH} = 910$, $^2J_{PH(trans)} = 164$, $^2J_{PH(cis)} = 19$, PtH, **12**). $^{31}P\{^1H\}$ NMR (202 MHz, $C_7D_8$): $\delta$ 30.9 (d, $^1J_{PtP} = 2393$, $^2J_{PP} = 7$, P *trans* to Ge, **12**), 30.5 (d, $^1J_{PtP} = 2367$, $^2J_{PP} = 7$, $^4J_{PtP} = 40$, P *trans* to H, **12**), 24.4 (s, $OPPh_3$).

**Data Recorded at 223 K, 2−5 h after Addition (223 K).** Selected $^1$H NMR (500 MHz, $C_7D_8$): $\delta$ 5.29 (s, $C_2H_4$), 4.55 (s, $H_2$), −2.04 (br d, $^1J_{PtH} = 928$, $^2J_{PH(trans)} = 163$, **12**), −6.03 (m, $J_{PtH}$ not resolved, PtH, **15**), bridging (Pt···H···Ge) for **15** not located. $^{31}P\{^1H\}$ NMR (202 MHz, $C_7D_8$): $\delta$ 70.4 (s, **13**, minor component), 30.5 (br s, $^1J_{PtP} = 2370$, P *trans* to Ge, **12**), 30.4 (br s, $^1J_{PtP} = 2391$, P *trans* to H, **12**), 26.4 (t, $^1J_{PtP}$ not resolved, $^3J_{PP} = 27$, Pt($PPh_3$), **15**), 25.8 (s, $Ph_3PO$), 17.9 (d, $^1J_{PtP} = 3869$, $^3J_{PP} = 26$, **15**).

**Data Recorded at 300 K, 24 h after Addition (300 K)**. Selected $^1$H NMR (500 MHz, $C_7D_8$): $\delta$ 5.25 (s, $C_2H_4$), 4.51 (s, $H_2$, minor component), −2.51 (dd, $^1J_{PtH} = 910$, $^3J_{PP(trans)} = 165$, $^3J_{PP(cis)} = 19$, **12**). $^{31}P\{^1H\}$ NMR (202 MHz, $C_7D_8$): $\delta$ 70.9 (s, $^1J_{PtP}$ not resolved, $^2J_{PtP} = 425$, $^3J_{PP} = 88$, **13**), 30.9 (d, $^1J_{PtP} = 2389$, $^2J_{PP} = 7$, P *trans* to Ge, **12**), 30.5 (d, $^1J_{PtP} = 2369$, $^2J_{PP} = 6$, P *trans* to H, **12**), 24.6 (s, $OPPh_3$), −6 (s, $PPh_3$). The $^{31}P\{^1H\}$ NMR spectrum recorded at 223 K after 24 h was similar to the data collected after 5 h at 223 K except that the signals for **13** were more intense and the signals for **15** were less intense.

The solution was checked by NMR after 8 days and then again after 14 days. The spectra were unchanged apart from a slight reduction in intensity of the signals for complex **13** as it slowly precipitated from solution. Complex **13** was isolated as a red, crystalline solid in 73% yield (22 mg, mp = 190−200 °C (dec)). A sample of **13** was dissolved in $CD_2Cl_2$, and NMR spectra were recorded. $^1$H NMR (500 MHz, $CD_2Cl_2$, 223 K): $\delta$ 7.26 (d, $J = 7$, ArH), 7.05 (m, ArH), 6.92 (t, $J = 7$, ArH), 6.86 (m, ArH), 6.66 (t, $J = 7$, ArH). $^{31}P\{^1H\}$ NMR (202 MHz, $CD_2Cl_2$, 223 K): $\delta$ 70.8 (s, $^1J_{PtP} = 3280$, $^2J_{PtP} = 422$, $^3J_{PP} = 88$). Anal. Calcd for $C_{90}H_{69}Ge_3P_3Pt_3$: C, 52.82; H, 3.40. Found: C, 52.23; H, 3.63.

Attempts to obtain a significant amount of complex **12** for elemental analysis were unsuccessful. A small amount of X-ray-quality crystals of **12** were obtained from a toluene solution (see X-ray section below) and were manually separated from the reaction mixture. IR (solid, $\nu$ cm$^{-1}$): 2041 (Pt−H). FAB(+) MS (NBA matrix): 945 *m/z*. The cluster pattern from 941 to 950 amu is similar to the calculated isotopic distribution for $GePtP_2C_{48}H_{39}$ (half of the molecule).

**Reaction of $[(Ph_3P)_2(H)Pt(\mu\text{-}SiC_{20}H_{24})(\mu\text{-}\eta^2\text{-}H\text{-}SiC_{20}H_{24})Pt(PPh_3)]$ with $Ph_2SiH_2$ at Low Temperature. Formation of $[(Ph_3P)Pt(\mu\text{-}\eta^2\text{-}H{-}SiPh_2)]_2$ (18).[1b,32]** A $C_7D_8$ solution (0.3 mL) containing $Ph_2SiH_2$ (**17**) (1 mg, 0.005 mmol) was syringed into a $C_7D_8$ solution (0.5 mL) of $[(Ph_3P)_2(H)Pt(\mu\text{-}SiC_{20}H_{24})(\mu\text{-}\eta^2\text{-}SiC_{20}H_{24})Pt(PPh_3)]$ (**16**) (10 mg, 0.005 mmol) at 195 K. The temperature was raised slowly to 300 K over a period of several hours, then the solution was stored at room temperature. After two weeks a pale yellow, crystalline solid was isolated in a 28% yield (2 mg). The molecular structure of $[(Ph_3P)Pt(\mu\text{-}\eta^2\text{-}H\text{-}SiPh_2)]_2$ was confirmed by X-ray crystallography (see Supporting Information). $^1$H NMR (500 MHz, $CD_2Cl_2$, 223 K): $\delta$ 7.71−6.75 (ArH), 2.80 (s, $^1J_{PtH} = 620$, $^2J_{PtH} = 115$, Pt···H···Si). $^{31}P\{^1H\}$ NMR (202 MHz, $CD_2Cl_2$, 223 K): $\delta$ 34.6 (s, $^1J_{PtP} = 4242$ Hz, $^2J_{PtP} = 282$ Hz, $^3J_{PP} = 52$ Hz). IR (solid, $\nu$ cm$^{-1}$): 1685 (Pt···H···Si).

**Reaction of $[(Ph_3P)_2(H)Pt(\mu\text{-}SiC_{20}H_{24})(\mu\text{-}\eta^2\text{-}H\text{-}SiC_{20}H_{24})Pt(PPh_3)]$ with $Ph_2GeH_2$ at Low Temperature. Formation of $[(Ph_3P)Pt(\mu\text{-}\eta^2\text{-}H\text{-}GePh_2)]_2$ (4).** A $C_7D_8$ solution (0.3 mL) containing $Ph_2GeH_2$ (**1**) (1 mg, 0.005 mmol) was syringed into a $C_7D_8$ solution (0.5 mL) of $[(Ph_3P)_2(H)Pt(\mu\text{-}SiC_{20}H_{24})(\mu\text{-}\eta^2\text{-}SiC_{20}H_{24})Pt(PPh_3)]$ (**16**) (10 mg, 0.005 mmol) at 195 K. The temperature was raised slowly to 300 K over a period of several hours, and the solution was then stored at room temperature. After two weeks a pale yellow, crystalline solid was isolated in 26% yield (2 mg). The $^1$H and $^{31}P\{^1H\}$ NMR data for the isolated solid were essentially identical to the data obtained for isolated **4** prepared from the reaction of $Ph_2GeH_2$ with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ described above.

**Reaction of $[(Ph_3P)_2(H)Pt(\mu\text{-}SiC_{20}H_{24})(\mu\text{-}\eta^2\text{-}H\text{-}SiC_{20}H_{24})Pt(PPh_3)]$ with $Ph_2SnH_2$ at Low Temperature. Formation of $[(Ph_3P)_2(H)Pt(\mu\text{-}SnPh_2)(\mu\text{-}\eta^2\text{-}H\text{-}SiC_{20}H_{24})Pt(PPh_3)]$ (19).** A $C_7D_8$ solution (0.3 mL) of $Ph_2SnH_2$ (**5**) (3 mg, 0.006 mmol) was syringed into a $C_7D_8$ solution (0.5 mL) containing $[(Ph_3P)_2(H)Pt(\mu\text{-}SiC_{20}H_{24})(\mu\text{-}\eta^2\text{-}SiC_{20}H_{24})Pt(PPh_3)]$ (**16**) (11 mg, 0.006 mmol) at 195 K. NMR spectroscopic data were recorded immediately after addition at 223 K. The temperature was then raised to 300 K over a period of several hours. Attempts to isolate a pure sample of **19** were unsuccessful. Selected $^1$H NMR (500 MHz, $C_7D_8$, 223 K, just after addition): 4.94 (s, $^1J_{SiH} = 205$, SiH, $H_2SiC_{20}H_{24}$),[36] 4.55 (s, $H_2$), 1.93 (d, $^2J_{PH} = 13$, $^1J_{PtH}$ and $^1J_{SiH}$ not resolved, (Pt···H···Si), **16**), 1.75 (d, $^2J_{PH} = 13$, $^1J_{PtH}$ and $^1J_{SiH}$ not resolved, (Pt···H···El), unassigned), −0.18 (d, $^2J_{PH} = 9$, $^1J_{PtH}$ and $^1J_{SiH}$ not resolved, (Pt···H···Sn), **19**, tentative assignment), −5.20 (t, $^1J_{PtH} = 578$, $^2J_{PH} = 8$, PtH, **16**), −6.24 (t, $^1J_{PtH} = 756$, $^3J_{PP} = 8$, PtH, **19**), −6.43 (d, $^2J_{PH} = 10$, $^1J_{PtH}$ not resolved, unassigned). $^{31}P\{^1H\}$ NMR (202 MHz, $C_7D_8$, 223 K, just after addition): $\delta$ 31.7 (t, $^1J_{PtP} = 4660$, $^3J_{PP} = 30$, Pt($PPh_3$), **19**), 30.3 (t, $^1J_{PtP} = 4169$, $^3J_{PP} = 25$, Pt($PPh_3$), **16**),[1b]

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24.6 (s, $OPPh_3$), 21.5 (br, $^1J_{PtP} = 3500$, $Pt(PPh_3)_2$, **16**),[1b] 14.9 (d, $^1J_{PtP} = 3530$, $^3J_{PP} = 30$, $Pt(PPh_3)_2$, **19**), −6.8 (s, $PPh_3$).

**X-ray Structure Determination for $(Ph_3P)_2Pt(H)[GeMes_2H)$ (9) and $[(Ph_3P)_2(H)Pt(C_{12}H_8GeGeC_{12}H_8)Pt(H)(PPh_3)_2]$ (12).** Crystals of appropriate dimensions were obtained by slow evaporation of $C_7D_8$ and were mounted on glass fibers in random orientations. Preliminary examination and data collection were performed using a Bruker Kappa Apex II charge coupled device (CCD) detector system single-crystal X-ray diffractometer equipped with an Oxford Cryostream LT device. All data were collected using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) from fine focus sealed tube X-ray source. Preliminary unit cell constants were determined with a set of 36 narrow frame scans. Typical data sets consist of combinations of $\omega$ and $\phi$ scan frames with a typical scan width of 0.5° and counting time of 10 s/frame at a crystal to detector distance of 4.0 cm. The collected frames were integrated using an orientation matrix determined from the narrow frame scans. Apex II and SAINT software packages (Bruker Analytical X-Ray, Madison, WI, 2005) were used for data collection and data integration. Analysis of the integrated data did not show any decay. Final cell constants were determined by global refinement of *xyz* centroids of thresholded reflections from the complete data set. Collected data were corrected for systematic errors using SADABS[37] based on the Laue symmetry using equivalent reflections.

Structure solution and refinement were carried out using the SHELXTL-PLUS software package (Sheldrick, G. M., Bruker Analytical X-Ray Division, Madison, WI, 2005). The structures were solved by direct methods and refined successfully in the space groups $Pna2_1$ and $P\bar{1}$, respectively. Full matrix least-squares refinement was carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$. The non-hydrogen atoms were refined anisotropically to convergence. The hydrogen atoms were treated using an appropriate riding model (AFIX m3). The hydride H atoms were located but not refined in the structure of $(Ph_3P)_2Pt(H)(GeMes_2H)$ (**9**). Of the two molecules of toluene solvate, one was disorderd in $[(Ph_3P)_2(H)Pt(C_{12}H_8GeGeC_{12}H_8)Pt(H)(PPh_3)_2]$ (**12**).

Crystal data and intensity data collection parameters, final residual values, and structure refinement parameters, complete listings of positional and isotropic displacement coefficients for hydrogen atoms, and anisotropic displacement coefficients for the non-hydrogen atoms are deposited as Supporting Information. Tables of calculated and observed structure factors are available in electronic format from the authors. The X-ray structural data can be obtained from the Cambridge Crystallographic Data Center (CCCD numbers 636302, 636301, and 636300 for complexes, **9**, **12**, and **18**, respectively).

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**Supporting Information Available:** Selected NMR spectroscopic data, X-ray crystallographic analysis for complex **18**, and CIF files containing X-ray crystallographic data for complexes **9**, **12**, and **18** are available free of charge via the Internet at http://pubs.acs.org.

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