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Spectroscopic and Reactivity Studies of Platinum−Silicon Monomers and Dimers

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Mononuclear Pt−Si-containing complexes with the general formulas $(Ph_3P)_2Pt(H)(SiAr_2H)$ and $(Ph_3P)_2Pt(SiAr_2H)_2$ were produced at low temperature from the reaction of the secondary arylhydrosilanes Ph_2SiH_2, $C_{12}H_8SiH_2$ (silafluorene), and $C_{20}H_{24}SiH_2$ (3,7-di-*tert*-butylsilafluorene) with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$. When solutions of the mononuclear complexes were run at low temperature and then warmed to room temperature, or when the reactions were run at room temperature or above, dinuclear Pt−Si-containing complexes were produced, $[(Ph_3P)Pt(\mu\text{-}\eta^2\text{-}HSiAr_2)]_2$ (Ar = Ph (**4**)) and $[(Ph_3P)_2Pt(H)(\mu\text{-}SiAr_2)(\mu\text{-}\eta^2\text{-}HSiAr_2)Pt(PPh_3)]$ (Ar_2 = $C_{12}H_8$ (**8**), $C_{20}H_{24}$ (**15**); both fluxional). A mechanism is proposed for the formation of the unsymmetrical dinuclear complexes (**8** and **15**) that involves a bimolecular reaction between two mononuclear species, $(Ph_3P)_2Pt(H)(SiAr_2H)$ and $(Ph_3P)Pt(H)(SiAr_2H)$. VT-NMR studies of complexes **8** and **15** illustrate that a fluxional process occurs which can be explained by elimination and recoordination of a PPh_3 ligand. Complex **15** reacted with added $P(p\text{-Tol})_3$ to produce a mixture of dinuclear products consistent with the presence of both types of phosphines in the dinuclear complexes. Reaction of the dinuclear complex **8** with the mononuclear complex **16** as well as the elevated-temperature reaction between **8** and **15** will be described.

Introduction

The field of transition-metal silicon chemistry continues to attract substantial interest. Complexes containing transition-metal−silicon bonds are readily prepared by formal insertion of a transition-metal center into a Si−H bond.[1,2] Hydrosilanes containing varying numbers of Si−H bonds, from SiH_4 to $HSiR_3$, are known to react with a range of transition-metal precursors, but by far, the majority of examples reported involve tertiary hydrosilanes ($HSiR_3$).[1] Secondary (R_2SiH_2) and primary ($RSiH_3$) systems are interesting precursors, due to the presence of additional potential sites of reactivity at the silicon center. The expected initial product from Si−H activation of a tertiary hydrosilane at a metal center is a complex with the general formula $L_nM(H)(SiR_3)$. The formation of a σ-complex, $L_nM(\eta^2\text{-}HSiR_3)$, resulting from an arrested addition of the Si−H bond at the metal center could also be produced. A common product observed with Si−H bond activation of secondary hydrosilanes has been a dinuclear complex containing either a bridging μ-SiR_2 unit or a μ-η^2-$HSiR_2$ group.[3−6] Activation of Si−H bonds by late-transition-metal centers such as Pt and Pd are of considerable interest, due to the involvement of these metals in catalytic processes such as hydrosilylation.[2e]

Recently, we reported the room-temperature reactions of 9,9-dihydrosilafluorene (abbreviated silafluorene) and the related substituted system 3,7-di-*tert*-butylsilafluorene with the Pt(0) complex $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$.[6] The formation of mono-, di-, and trinuclear Pt−Si complexes was described, and the formation of the last type can be attributed to activation of both Si−H bonds in the silafluorene precursors.[6] An intriguing question arose from these studies: "How are these complexes formed, and what intermediate species are involved in the reaction pathway?" To address this question, several variable-temperature experiments were performed to try to observe potential intermediates in the reaction and to gain insight into the mechanistic

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[1] Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175.

[2] (a) Tilley, T. D. Transition-Metal Silyl Derivatives. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; p 1416. (b) Tilley, T. D. Transition-Metal Silyl Derivatives. In *The Silicon Heteroatom Bond*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1991; p 245. (c) Eisen, M. Transition-Metal Silyl Complexes. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1998; 2 (Pt. 3), p 2037. (d) Ojima, I.; Li, Z.; Zhu, J. Recent Advances in Hydrosilylation and Related Reactions. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1998; Vol. 2 (pt. 2), p 1687. (e). Lewis, L. N.; Stein, J.; Gao, Y.; Colborn, R. E.; Hutchins, G. *Platinum Met. Rev.* **1997**, *41*, 66. (f) Corey, J. Y. Dehydrogenative Coupling Reactions of Hydrosilanes. *Adv. Silicon Chem.* **1991**, *1*, 327. (g) Corey, J. Y. Dehydrocoupling of Hydrosilanes to Polysilanes and Silicon Oligomers: A 30 Year Overview. *Adv. Organomet. Chem.* **2004**, *51*, 1. (h) Gauvin, F.; Harrod, J. F.; Woo, H. G. Catalytic Dehydrocoupling: A General Strategy for the Formation of Element-Element Bonds. *Adv. Organomet. Chem.* **1998**, *42*, 363−405. (i) Schubert, U. *Transition Met. Chem.* **1991**, *16*, 126. (j) Aylett, B. J. *Adv. Inorg. Chem. Radiochem.* **1982**, *25*, 1.

[3] (a) Osakada, K.; Tanabe, M. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 1887. (b) Yamada, T.; Tanabe, M.; Osakada, K.; Kim, Y.-J. *Organometallics* **2004**, *23*, 4771. (c) Tanabe, M.; Yamada, T.; Osakada, K. *Organometallics* **2003**, *22*, 2190. (d) Braunstein, P.: Boag, N. M. *Angew. Chem., Int. Ed.* **2001**, *40*, 2427. (e) Braddock-Wilking, J.; Levchinsky, Y.; Rath, N. P. *Organometallics* **2000**, *19*, 5500. (f) Sanow, L. M.; Chai, M.; McConnville, D. B.; Galat, K. J.; Simons, R. S.; Rinaldi, P. L.; Youngs, W. J.; Tessier, C. A. *Organometallics* **2000**, *19*, 192. (g) Levchinsky, Y.; Rath, N. P.; Braddock-Wilking, J. *Organometallics* **1999**, *18*, 2583. (h) Kim, Y.-J.; Lee, S.-C.; Park, J −I.; Osakada, K.; Choi, J.-C.; Yamamoto, T. *Dalton Trans.* **2000**, 417. (i) Kim, Y.-J.; Lee, S.-C.; Park, J −I.; Osakada, K.; Choi, J.-C.; Yamamoto, T. *Organometallics* **1998**, *17*, 4929.

[4] For a recent review on bridged silylene and germylene complexes see: Ogino, H.; Tobita, H. *Adv. Organomet. Chem.* **1998**, *42*, 223.

[5] For recent theoretical calculations see: (a) Lin, Z. *Chem. Soc. Rev.* **2002**, 239. (b) Choi, S.-H.; Lin, Z. *J. Organomet. Chem.* **2000**, *608*, 42.

[6] (a) Braddock-Wilking, J.; Corey, J. Y.; Trankler, K. A.; Dill, K. M.; French, L. M.; Rath, N. P. *Organometallics* **2004**, *23*, 4576. (b) Braddock-Wilking, J.; Corey, J. Y.; Dill, K. M.; Rath, N. P. *Organometallics* **2002**, *21*, 5467.

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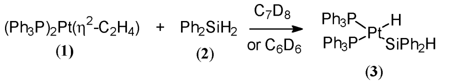
aspects of this and related reactions. Herein, we report these variable-temperature reaction studies of $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ with Ph_2SiH_2, silafluorene, and 3,7-di-*tert*-butylsilafluorene as well as the reactions of silafluorene-d_2. In addition, several reactions were performed to probe the reactivity of the fluxional unsymmetrical dinuclear complexes, including their variable-temperature dynamic NMR behavior.

Results

Reactions with Ph_2SiH_2. The reaction of $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ (**1**) with diphenylsilane, Ph_2SiH_2 (**2**), and a number of tertiary hydrosilanes was reported by Eaborn et al. in the early 1970s.[7] The reaction produced the expected Si−H oxidative-addition product, *cis*-$(Ph_3P)_2Pt(H)(SiPh_2H)$ (**3**; eq 1). However, NMR spectroscopic characterization data for **3** were not reported. Complex **3** was described as an air-stable solid, but other related complexes were reported to undergo slow decomposition in benzene solution.[7]



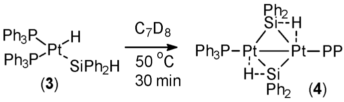
(eq 1)

With our interest in Si−H bond activation reactions of primary and secondary hydrosilanes by Pt(0), we reexamined the reaction of **1** with **2** by multinuclear NMR spectroscopy to obtain spectroscopic data for **3** and to determine if the remaining Si−H bond in **2** could be activated by Pt to form a dinuclear product. Selected spectroscopic data for the major products observed and isolated from the reactions with Ph_2SiH_2 and other substrates described in this study are given in Table 1 (data are presented in the sequence of mononuclear, dinuclear, and trinuclear products).

When the reaction of **1** with **2** was performed at low temperature in C_7D_8 and monitored by NMR spectroscopy (223 K), well-resolved signals for **3** were observed immediately after addition. The expected doublet of doublets pattern for the terminal Pt−H resonance was observed in the ^1H NMR spectrum, as was a signal for the remaining hydride at silicon. The inequivalent phosphorus sites in **3** gave rise to two expected signals in the $^{31}P\{^1H\}$ spectrum. The low-temperature $^{29}Si\{^1H\}$ spectrum exhibited a signal for the silicon center consistent with coupling to two different phosphorus nuclei as well as platinum. The proton and phosphorus spectra remained unchanged for several hours at 223 K. When the temperature was increased slowly over several hours, the resonances began to broaden significantly as the temperature was raised. At room temperature, the ^1H and $^{31}P\{^1H\}$ spectra showed very broad signals and after 5 days broad resonances for **3** were still present, even at low temperature. Free PPh_3 was also observed in the reaction mixture at low temperature as a broad resonance, suggesting that fluxional exchange may be occurring with complex **3**.

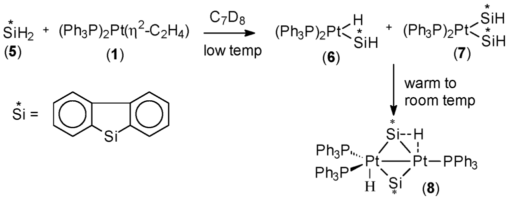
If the reaction of **1** and **2** was conducted at room temperature, the NMR data collected shortly after mixing exhibited substantially broadened resonances assigned to **3**, but after several hours only a broad baseline was observed in the $^{31}P\{^1H\}$ NMR spectrum in the region characteristic of **3**.

Heating a C_7D_8 solution containing the mononuclear complex **3** for 30 min at 323 K resulted in the formation of the symmetrical dinuclear complex $[(Ph_3P)Pt(\mu\text{-}\eta^2\text{-}HSiPh_2)]_2$ (**4**; eq 2). Complex **4** was reported by Stone et al. but limited spectroscopic data were provided.[8] Stone suggested that **4** was unstable in benzene-d_6 solution, but the observation may likely be due to fluxional behavior on the NMR time scale.[8] The low-temperature ^1H NMR spectrum for **4** exhibited a slightly broadened resonance for the two nonclassical Pt⋯H⋯Si hydrides, and the $^{31}P\{^1H\}$ NMR spectrum exhibited a broadened resonance with the expected Pt satellite pattern for a symmetrical diplatinum complex with a phosphine group at each metal center.[8]



(eq 2)

Reactions with $H_2SiC_{12}H_8$ and $D_2SiC_{12}H_8$. We recently found that modifying the spatial requirements of secondary arylhydrosilanes by tying the aryl rings together can greatly enhance the reactivity of the silane.[6] For example, the simplest constrained secondary arylhydrosilane, silafluorene ($H_2SiC_{12}H_8$, **5**), exhibited pronounced reactivity compared to diphenylsilane **2**. When the reaction between **1** and **5** was carried out at low temperature (195 K) and monitored by NMR spectroscopy at 223 K, broadened signals indicating the formation of the mononuclear complex[9] $(Ph_3P)_2Pt(H)[Si(C_{12}H_8)H]$ (**6**), analogous to those of complex **3**, were observed immediately after mixing. In addition, sharp signals consistent with the formation of the bis(silyl) complex[10] *cis*-$(Ph_3P)_2Pt[Si(C_{12}H_8)H]_2$ (**7**) as well as H_2 and C_2H_4 were observed (eq 3). Also identified was the minor byproduct from hydrosilylation, $HSi(C_{12}H_8)(CH_2CH_3)$.[11]



(eq 3)

After the temperature was raised slowly from 223 K to room temperature, the NMR signals broadened significantly. At 283 K, the $^{31}P\{^1H\}$ spectrum exhibited essentially two broad absorbances centered at 37 and 15 ppm, but at room temperature, the major component was only one broad peak centered at 12 ppm. In addition, the ^1H NMR spectrum exhibited a new broad Pt−H signal at −1.3 ppm. After 1 day these signals remained

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[7] (a) Eaborn, C.; Ratcliff, B.; Pidcock, A. *J. Organomet. Chem.* **1974**, *65*, 181. (b) Eaborn, C.; Pidcock, A.; Ratcliff, B. *J. Organomet. Chem.* **1972**, *43*, C5.

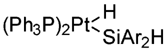
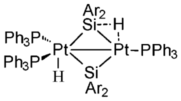
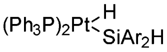
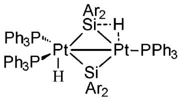
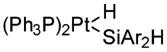
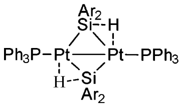
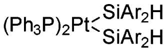
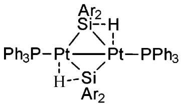
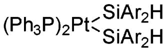
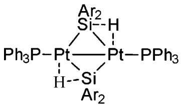
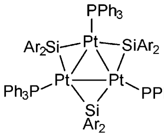
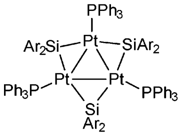
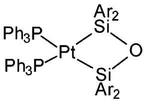
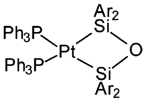
[8] Auburn, M.; Ciriano, M.; Howard, J. A. K.; Murray, M.; Pugh, N. J.; Spencer, J. L.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1980**, 659.

[9] For some recent examples of *cis*- and *trans*-$P_2Pt(H)SiR_3$ complexes see: (a) Chan, D.; Duckett, S. B.; Heath, S. L.; Khazal, I. G.; Perutz, R. N.; Sabo-Etienne, S.; Timmins, P. L. *Organometallics* **2004**, *23*, 5744. (b) Ebsworth, E. A.; Marganian, V. M.; Reed, F. J. S.; Gould, R. O. *J. Chem. Soc. Dalton Trans.* **1978**, 1167. (c) Mullica, D. F.; Sappenfield, E. L.; Hampden-Smith, M. *Polyhedron* **1991**, *10*, 867. (d) Simons, R. S.; Sanow, L. M.; Galat, K. J.; Tessier, C. A.; Youngs, W. J. *Organometallics* **2000**, *19*, 3994. (e) Kang, Y.; Kang, S. O.; Ko, J. *Organometallics* **2000**, *19*, 1216. (f) Feldman, J. D.; Mitchell, G. P.; Nolte, J.-O.; Tilley, T. D. *Can. J. Chem.* **2003**, *81*, 1127. (g) Paonessa, R. S.; Prignano, A. L.; Trogler, W. C. *Organometallics* **1985**, *4*, 647. (h) Abdol Latif, L.; Eaborn, C.; Pidcock, A. P.; Ng, S. W. *J. Organomet. Chem.* **1994**, *414*, 217. (i) Mitchell, G. P.; Tilley, T. D. *J. Am. Chem. Soc.* **1998**, *120*, 7635. (j) Packett, D. L.; Syed, A.; Trogler, W. C. *Organometallics* **1988**, *7*, 159. (k) Koizumi, T.; Osakada, K.; Yamamoto, T. *Organometallics* **1997**, *16*, 6014.

[10] For a related bis(silyl)platinum phosphine complex see: Kim, Y.-J.; Park, J.-I.; Lee, S.-C. *Organometallics* **1999**, *18*, 1349.

[11] The minor product $H(CH_3CH_2)SiC_{12}H_8$) was not isolated and was characterized in solution only: Braddock-Wilking, J.; French, L. A.; Corey, J. Y. Unpublished results.

Table 1. Comparison of Selected NMR Spectroscopic Data for Complexes in This Report[a]

Mononuclear complexes		Dinuclear and trinuclear complexes	
 $(Ph_3P)_2Pt{<}\begin{matrix}H\\SiAr_2H\end{matrix}$ Ar = C_6H_5 (**3**)	^1H NMR data (223 K) 4.82 (m, SiH) -0.96 (dd, $^1J_{PtH}$ = 1008, $^2J_{PH}$ = 155, 21, PtH) $^{31}P\{^1H\}$ NMR data (223 K) 35.5 (d, $^1J_{PtP}$ = 2506, $^2J_{PP}$ = 10) 35.2 (d, trans to Si, $^1J_{PtP}$ = 1785) $^{29}Si\{^1H\}$ NMR data (223 K) 9.6 (dd, $^1J_{PtSi}$ = 1113, $^2J_{PSi}$ = 136, 15)	 $Ar_2 = C_{12}H_8$ (**8**)	^1H NMR data (223 K) 2.0 (d, $^2J_{PH}$ = 12, Pt···H···Si)[b] -4.9 (t, $^1J_{PtH}$ = 577, $^2J_{PtH}$ ~80, $^2J_{PH}$ = 10, PtH) $^{31}P\{^1H\}$ NMR data (223 K) 31.1 (t, $^1J_{PtP}$ = 4260, $^2J_{PtP}$ = 265, $^3J_{PP}$ = 25) 17.3 (d, $^1J_{PtP}$ = 3438, $^2J_{PtP}$ = 135) $^{29}Si\{^1H\}$ NMR data (223 K) 160 (d, $^2J_{PSi}$ = 96)[b] 151 (prob t)[b]
 $(Ph_3P)_2Pt{<}\begin{matrix}H\\SiAr_2H\end{matrix}$ $Ar_2 = C_{12}H_8$ (**6**)	^1H NMR data (223 K) 6.56 (br s, $^2J_{PtH}$ = 56, SiH)[c] -1.61 (br d, $^1J_{PtH}$ = 945, $^2J_{PH}$ = 140, PtH) $^{31}P\{^1H\}$ NMR data (223 K) 35.3 (br s, P trans to Si, $^1J_{PtP}$ = 1885) 33.9 (br s, $^1J_{PtP}$ = 2500) $^{29}Si\{^1H\}$ NMR data (223 K) -20.7 (br)[b]	 $Ar_2 = C_{20}H_{24}$ (**15**)	^1H NMR data (223 K) 1.93 (d, $^2J_{PH}$ = 12, Pt···H···Si)[b] -5.2 (t, $^1J_{PtH}$ = 572, $^2J_{PtH}$ ~90, $^2J_{PH}$ = 9, PtH) $^{31}P\{^1H\}$ NMR data (223 K) 30.3 (t, $^1J_{PtP}$ = 4171, $^2J_{PtP}$ = 278, $^3J_{PP}$ = 26) 21.5 (d, $^1J_{PtP}$ = 3504)[d] $^{29}Si\{^1H\}$ NMR data (223 K) 164 (d, $^2J_{PSi}$ = 94)[b] 154 (m)[b]
 $(Ph_3P)_2Pt{<}\begin{matrix}H\\SiAr_2H\end{matrix}$ $Ar_2 = C_{20}H_{24}$ (**16**)	^1H NMR data (223 K) 7.07 (SiH)[b, c] -1.26 (dd, $^1J_{PtH}$ = 944, $^2J_{PH}$ = 152, 19, PtH) $^{31}P\{^1H\}$ NMR data (223 K) 35.1 (d, $^1J_{PtP}$ = 1876, $^2J_{PP}$ = 10) 33.6 (d, $^1J_{PtP}$ = 2558) $^{29}Si\{^1H\}$ NMR data (223 K) -18.5 (dd, $^1J_{PtSi}$ = 1105 , $^2J_{PSi}$ = 154, 11)[b]	 Ar = C_6H_5 (**4**)	^1H NMR data (223 K) (CD_2Cl_2) 2.84 (s, $^1J_{PtH}$ = 624 , $^2J_{PtH}$ = 111, Pt···H···Si) $^{31}P\{^1H\}$ NMR data (223 K) (CD_2Cl_2) 34.6 (br s, $^1J_{PtP}$ = 4242, $^2J_{PtP}$ = 282, $^3J_{PP}$ = 52)
 $(Ph_3P)_2Pt{<}\begin{matrix}SiAr_2H\\SiAr_2H\end{matrix}$ $Ar_2 = C_{12}H_8$ (**7**)	^1H NMR data (223 K) 5.02 (m, SiH)[b] $^{31}P\{^1H\}$ NMR data (223 K) 37.7 (s, $^1J_{PtP}$ = 1952) $^{29}Si\{^1H\}$ NMR data (223 K) -17.2 (dd, $^2J_{PP}$ = 144, 20)[b]	 $Ar_2 = C_{12}H_8$ (**21**)	^1H NMR data (223 K) (CD_2Cl_2) 2.83 (s, $^1J_{PtH}$ = 696 , $^2J_{PtH}$ = 123, Pt···H···Si) $^{31}P\{^1H\}$ NMR data (223 K) (CD_2Cl_2) 35.7 (s, $^1J_{PtP}$ = 4302, $^2J_{PtP}$ =303, $^3J_{PP}$ = 56)
 $(Ph_3P)_2Pt{<}\begin{matrix}SiAr_2H\\SiAr_2H\end{matrix}$ $Ar_2 = C_{20}H_{24}$ (**17**)	^1H NMR data (223 K) ca. 5.1 (overlapping with C_2H_4 resonance, SiH)[b] $^{31}P\{^1H\}$ NMR data (223 K) 38.4 (s, $^1J_{PtP}$ = 1973) $^{29}Si\{^1H\}$ NMR data (223 K) -17.2 (dd, $^2J_{PP}$ = 141, 19)[b]	 $Ar_2 = C_{20}H_{24}$ (**22**)	^1H NMR data (360 K) 3.27 (s, $^1J_{PtH}$ = 684, $^2J_{PtH}$ = 119, Pt···H···Si) $^{31}P\{^1H\}$ NMR data (300 K) 36.6 (s, $^1J_{PtP}$ = 4290, $^2J_{PtP}$ = 252, $^3J_{PP}$ = 60)
$(Ph_3P)_2Pt(H)_2(SiAr_2H)_2$ $Ar_2 = C_{12}H_8$ (**11**)	^1H NMR data (223 K) 5.59 (m, SiH)[b] -7.52 (t, $^1J_{PtH}$ = 672, $^2J_{PH}$ = 11, PtH) $^{31}P\{^1H\}$ NMR data (223 K) 10.1 (s, $^1J_{PtP}$ = 1330)	 $Ar_2 = C_{12}H_8$ (**9**)	no hydrides $^{31}P\{^1H\}$ NMR data (300 K) 70.5 (s, $^1J_{PtP}$ = 3338, $^2J_{PtP}$ = 421, $^3J_{PP}$ = 80) $^{29}Si\{^1H\}$ NMR data (300 K) 269 (s, $^1J_{PtSi}$ = 934)
$(Ph_3P)_2Pt(H)_2(SiAr_2H)_2$ $Ar_2 = C_{20}H_{24}$ (**18**)	^1H NMR data (223 K) 6.01 (br s, SiH)[b] -5.96 (br s, $^1J_{PtH}$ = 626, PtH) $^{31}P\{^1H\}$ NMR data (223 K) -9.1 (br s, $^1J_{PtP}$ = 1109)	 $Ar_2 = C_{20}H_{24}$ (**23**)	no hydrides $^{31}P\{^1H\}$ NMR data (300 K) 71.6 (s, $^1J_{PtP}$ = 3320, $^2J_{PtP}$ = 445, $^3J_{PP}$ = 81)
 $Ar_2 = C_{12}H_8$ (**10**)	no hydrides $^{31}P\{^1H\}$ NMR data (300 K) 29.5 (s, $^1J_{PtP}$ = 1708)		
 $Ar_2 = C_{20}H_{24}$ (**20**)	no hydrides $^{31}P\{^1H\}$ NMR data (300 K) 29.8 (s, $^1J_{PtP}$ = 1705)		

[a] In C_7D_8 solution unless otherwise noted. Chemical shifts are given in ppm and coupling constants in Hz. Si−H coupling was not resolved. [b] Pt satellites not resolved. [c] Resonance located by 2D $^1H-^{29}Si$ HMQC experiment. No hydrides were observed. [d] $^2J_{PtP}$ not resolved.

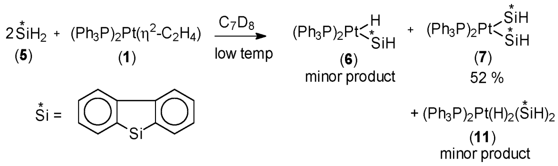
and after the sample was recooled to 223 K the spectral data indicated essentially quantitative formation of the unsymmetrical dinuclear complex **8** and PPh_3 as the major components in the reaction mixture. However, no signals were observed for the trinuclear complex $[(Ph_3P)Pt(\mu\text{-}SiC_{12}H_8)]_3$ (**9**) (eq 3).[6] When solutions containing **8** were kept for several weeks at room temperature and analyzed by ^{31}P NMR spectroscopy, a small resonance was observed for complex **9** as well as resonances for $OPPh_3$ and $(Ph_3P)_4Pt$.[12]

The ^1H NMR spectrum (300 K) collected immediately after the room-temperature addition of **5** to **1** showed sharp signals for the Pt−H resonance of the mononuclear product **6** and H_2. The resonances for the second mononuclear complex, **7**, were absent in both the ^1H and ^{31}P spectra (possibly due to fluxional behavior on the NMR time scale). In addition to the signals for **6** and unreacted **1**, the other major features in the $^{31}P\{^1H\}$ NMR spectrum were several broad, ill-defined signals between 10 and 55 ppm and a small signal for **9**. Cooling the solution to 223 K after 30 min showed broad ^1H and ^{31}P signals for **6**, sharp resonances for **7**, and peaks for the major species **8**. Small signals for the siloxane product $(Ph_3P)_2Pt[Si(C_{12}H_8)OSi(C_{12}H_8)]$ (**10**) (see below) and the hydrosilylation byproduct $HSi(C_{12}H_8)(CH_2CH_3)$ were also observed. Signals for the latter compound as well as for **6** and **7** were observed in the low-temperature $^{29}Si\{^1H\}$ NMR spectrum. From our previous studies, we found that the trinuclear complex **9** was gradually formed over a 2−3 h period in the room-temperature reaction of **1** with **5**, and the result above suggests that the formation of **9** is inhibited at lower temperature.

When the reaction of silafluorene **5** with **1** was performed at low temperature and then the mixture was warmed to room temperature and exposed to air for approximately 1 h, the dinuclear complex **8** was the major product, along with a minor amount of the trinuclear complex **9.** This result suggests that the products are possibly moderately air stable in solution for a short time.

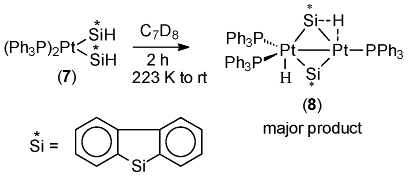
Attempts to isolate **6** have been unsuccessful. However, isolation of **7** was achieved from the reaction of **1** and **5** in a 1:2 ratio. After addition at 195 K, the major Pt−Si-containing product observed by $^{31}P\{^1H\}$ NMR spectroscopy was **7**. In addition, resonances for a species tentatively assigned to a six-coordinate complex, $(Ph_3P)_2Pt(H)_2[Si(C_{12}H_8)H]_2$ (**11**), were observed. Six-coordinate Pt(IV) phosphine complexes containing silyl ligands are uncommon. Only a few examples have been reported, and in some cases the complexes are thermally unstable.[13,14] One distinguishing feature of complexes of this type is a significantly smaller $^1J_{PtP}$ coupling value. Complex **11** exhibited an upfield shift of the $^{31}P\{^1H\}$ NMR resonance compared to the signals for the mononuclear complexes **6** and **7** as well as a reduced $^1J_{PtP}$ coupling value compared to the values obtained for **6** and **7**. Complexes such as **11** (or **18**; see eq 7) could be generated by a stepwise addition of two Si−H bonds in two molecules of **5** at one Pt center or by addition of H_2 to **7**. The NMR spectroscopic data from the low-temperature reaction of **1** with **5** exhibited signals assigned to **11** only in the earliest stage of the reaction. Complex **11** appeared to be unstable, and at later stages signals for both H_2 and **7** were observed, suggesting that the formation of **11** occurred by addition of two molecules of **5** to **1**.

After the solution from the reaction between **1** and 2 equiv of **5** was warmed and pentane was added, complex **7** was isolated in 52% yield as a golden yellow, air-sensitive solid (eq 4). Bis(silyl)platinum phosphine complexes have been reported previously.[14,15]



(eq 4)

When a solution prepared from the isolated complex **7** in C_7D_8 was warmed from 223 to 300 K, the dinuclear complex **8** was observed as the major product by $^{31}P\{^1H\}$ NMR spectroscopy (eq 5). After 1 day at room temperature the spectrum remained unchanged, except for the formation of a small resonance for the trinuclear complex **9**. However, heating a sample of **7** in C_7D_8 at 323 K resulted in nearly complete consumption of **7** and formation of **8** as the major product, along with a minor amount of the trinuclear complex **9.** Heating a solution of **7** for 1 h at 373 K produced only complex **8**, but no signals for **9** were observed at this higher temperature.



(eq 5)

In contrast, with **1** in excess (**1**:**5** = 2:1) the low-temperature addition reaction resulted in the formation of only the mononuclear complex **6** and unreacted **1**. However, when the mixture was warmed to room temperature complete consumption of **6** was accompanied by the formation of **8** as the major product and a trace of the trinuclear complex **9**.

Reaction of the deuterated silafluorene **5-*d*$_2$** with **1** was also monitored by ^2H NMR spectroscopy. NMR data were collected at 223 K, and then the temperature was raised to room temperature over a period of several hours. The variable-temperature ^2H NMR data are shown in Figure 1.

The ^2H NMR spectrum collected at 223 K immediately after addition of **5-*d*$_2$** to **1** in C_7H_8/C_6D_6 showed several new resonances. The major and prominent resonances were assigned to the terminal Pt−D and the remaining deuteride at silicon in **6-*d*$_2$**, and those resonances became better resolved after 1.5 h. Additional resonances were assigned to the minor products $(C_{12}H_8)Si(D)[C(H/D)_2C(H/D)_3]$ (from hydrosilylation),[11] D_2, and **11-*d*$_4$**. Approximately 1−1.5 h after addition, the region near 5 ppm became broad, consistent with the formation of the bis(silyl)platinum complex **7-*d*$_2$**. As the temperature was raised to 273 K, some signals became sharper, along with the gradual disappearance of the Pt−D resonance for **6-*d*$_2$** and the appearance of a new broad signal at −1 ppm assigned to the averaged signal for the two deuterides in the unsymmetrical dinuclear

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(12) Sen, A.; Halpern, J. *Inorg. Chem.* **1980**, 19, 1073.

(13) See for example: (a) Shimada, S.; Tanaka, M.; Honda, K. *J. Am. Chem. Soc.* **1995**, *117*, 8289. (b) Michalczyk, M. J.; Calabrese, J. C.; Recatto, C. A.; Fink, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 7955. (c) Grundy, S. L.; Holmes-Smith, R. D.; Stobart, S. R.; Williams, M. A. *Inorg. Chem.* **1991**, *30*, 3333.

(14) Heyn, R. R.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 1917.

(15) For some recent examples of bis(silyl)platinum complexes, see for example: (a) Kim, Y.-J.; Park, J.-I.; Lee, S.-C.; Osakada, K.; Tanabe, M.; Choi, J.-C.; Koizumi, T.; Yamamoto, T. *Organometallics* **1999**, *18*, 1349. (b) Ozawa, F. *J. Organomet. Chem.* **2000**, *611*, 332. (c) Lee, Y.-J.; Bae, J.-Y.; Kim, S.-J.: Ko, J.; Choi, M.-G.; Kang, S. O. *Organometallics* **2000**, *19*, 5546. (d) Tsuji, Y.; Nishiyama, K.; Hori, S.; Ebihara, M.; Kawamura, T. *Organometallics* **1998**, *17*, 507. (e) Yamashita, H.; Tanaka, M.; Goto, G. *Organometallics* **1992**, *11*, 3227.

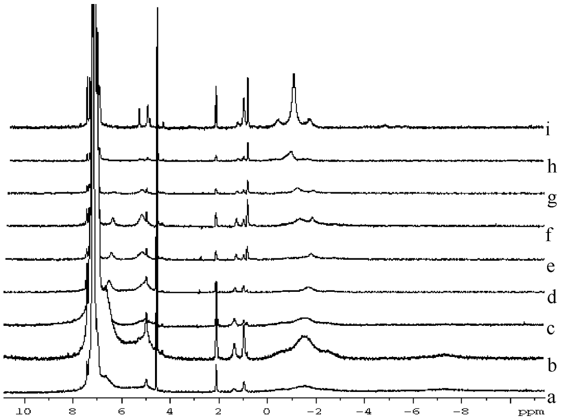


Figure 1. Variable-temperature ^{2}H NMR data for reaction of **1** with **5-*d*$_2$**: (a) just after mixing (223 K); (b) after 20 min (223 K); (c) after 1.5 h (223 K); (d) after 2.5 h (243 K); (e) after 3 h (263 K); (f) after 4 h (273 K); (g) after 4.5 h (283 K); (h) after 5 h (300 K); (i) after ca. 24 h (300 K).

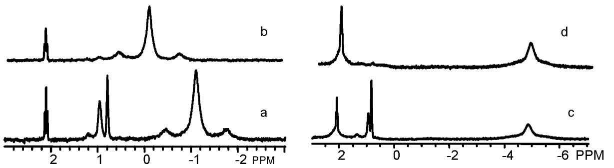


Figure 2. Selected ^{2}H NMR data (76 MHz, C_7D_8): (a) reaction solution containing **8-*d*$_2$** after 24 h at 300 K; (b) solution containing dissolved pure **8-*d*$_2$** at 300 K; (c) reaction solution containing **8-*d*$_2$** after 24 h at 223 K; (d) solution containing pure **8-*d*$_2$** at 223 K.

complex **8-*d*$_2$** present in the reaction mixture. When the sample was recooled to 223 K, the spectrum showed the presence of the terminal Pt–D in **8-*d*$_2$** and a broad unresolved region near 2 ppm for the bridging hydride (Pt···D···Si) in **8-*d*$_2$**.

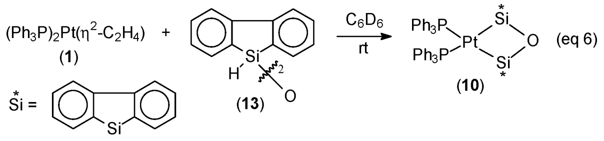
The room-temperature ^{2}H NMR spectrum taken after 24 h was comparable to the room-temperature spectrum obtained earlier but with a significantly enhanced averaged Pt–D signal for **8-*d*$_2$**. The ^{31}P{^{1}H} NMR spectrum for the reaction solution exhibited a broad resonance due to the averaged signal from the exchange between the phosphines in **8-*d*$_2$** with free PPh_3. No signals were observed for the trinuclear complex **9**. The solution was recooled to 223 K, and the ^{31}P{^{1}H} NMR spectrum exhibited resonances primarily for the unsymmetrical dinuclear complex **8-*d*$_2$** as well as for PPh_3 and $OPPh_3$. A minor resonance was present for the byproduct $(Ph_3P)_2Pt[Si(C_{12}H_8)OSi(C_{12}H_8)]$ (**10**).

An interesting comparison was noted for the ^{2}H NMR resonances for **8-*d*$_2$** found in solution compared to the spectrum for the isolated and redissolved pure sample of **8-*d*$_2$**. The room-temperature ^{2}H NMR spectrum for **8-*d*$_2$** in the reaction mixture showed an averaged Pt–D signal at −1.1 ppm ($^1J_{PtD}$ = 102 Hz), but the isolated sample is shifted downfield to −0.17 ppm ($^1J_{PtD}$ = 99 Hz) (Figure 2a,b). The low-temperature spectrum for **8-*d*$_2$** in the reaction mixture compared to the spectrum of the pure sample contained essentially identical resonances for the bridging and terminal deuterides (Figure 2c,d). The shifting of resonances observed at room temperature may be influenced by the presence (or absence) of free PPh_3 or other species in the reaction mixture.

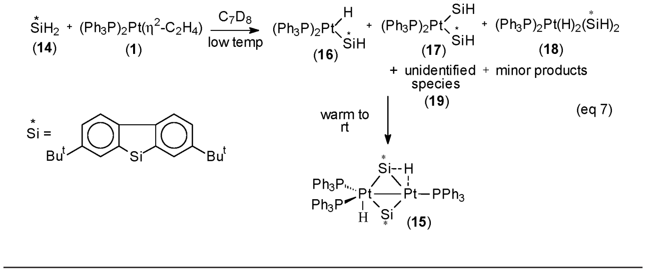
The room-temperature ^{1}H NMR spectrum for **8** in the reaction solution resulting from the mixing of **1** and **5** (or **5** and **12**; see below) exhibited a broad Pt–H resonance for the averaged hydride signals in **8**. However, a pure sample of **8** does not exhibit a well-defined signal for the hydrides under similar conditions, unlike the previously discussed **8-*d*$_2$** system (see VT NMR discussion below). However, when a solution containing **8** in C_7D_8 was treated with an excess (>2 equiv) of PPh_3, a broad signal near −1.3 ppm appeared, suggesting that the presence of free phosphine influences the ability to observe the resonance.

The low-temperature addition of silafluorene **5** to the Pt(0) phosphine complex $(Ph_3P)_4Pt$ (**12**) produced products similar to those observed in the reaction of **5** with **1**. For example, just after addition at 223 K, signals for both of the mononuclear complexes **6** and **7** (major product) were observed along with H_2. Additional minor resonances were also observed for the tentatively assigned six-coordinate[13] Pt complex **11**. When the solution was warmed to room temperature, the unsymmetrical dinuclear complex **8** became the major product, in addition to free PPh_3. No trinuclear complex **9** was detected in the reaction mixture.

One of the byproducts observed in the reaction of **1** with **5** was the complex $(Ph_3P)_2Pt[Si(C_{12}H_8)OSi(C_{12}H_8)]$ (**10**). The formation of **10** is probably due to the reaction of **7** with adventitious oxygen or water in the reaction vessel and is likely a consequence of the experimental procedure involved in the low-temperature reaction studies. Related platinum–disiloxy complexes have been described previously.[16,17] Complex **10** was prepared by an independent route from reaction of **1** with the 1,3-dihydrosiloxane $HSi(C_{12}H_8)OSi(C_{12}H_8)H$[18] (**13**; eq 6). Inevitably, minor ^{31}P resonances for **10** are observed in reaction mixtures after several hours following a variable-temperature experiment.



Reactions with $H_2SiC_{20}H_{24}$. We previously reported that the room-temperature reaction of the substituted silafluorene 3,7-di-*tert*-butylsilafluorene[18] (**14**) with complex **1** gave the unsymmetrical dinuclear complex $(Ph_3P)_2(H)Pt(\mu\text{-}SiC_{20}H_{24})(\mu\text{-}\eta^2\text{-}HSiC_{20}H_{24})Pt(PPh_3)$ (**15**) in 86% yield, whose structure was confirmed by X-ray crystallography.[6a] The direct Si–H addition product $(Ph_3P)_2Pt(H)(Si(C_{20}H_{24})H)$ (**16**) was not observed at room temperature. However, when the reaction was performed at 193–195 K and monitored by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy, resonances for **16** were observed just after addition, as the major product from the reaction (eq 7). In



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[16] (a) Goikhman, R.; Karakuz, T.; Shimon, L. J. W.; Leitus, G.; Milstein, D. *Can. J. Chem.* **2005**, *83*, 786. (b) Pham, E. K.; West, R. *J. Am. Chem. Soc.* **1989**, *11*, 7667. (c) Pham, E. K.; West, R. *Organometallics* **1990**, *9*, 1517. (d) Bell, L. G.; Gustavson, W. A.; Thanedar, S.; Curtis, M. D. *Organometallics* **1983**, *2*, 740. (e) Curtis, M. S.; Greene, J. *J. Am. Chem. Soc.* **1978**, *100*, 6362.

[17] Osakada, K.; Tanabe, M.; Tanase, T. *Angew. Chem., Int. Ed.* **2000**, *39*, 4053.

[18] Chang, L. S.; Corey, J. Y. *Organometallics* **1989**, *8*, 1885.

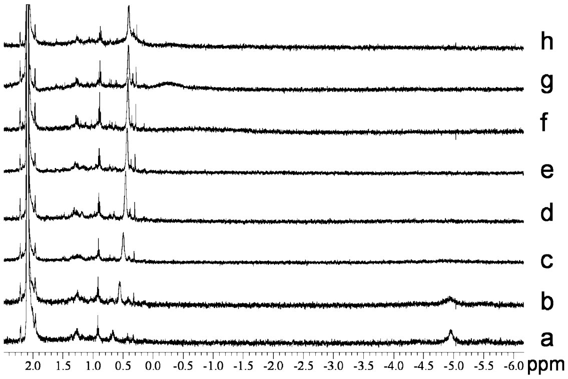

Figure 3. ^{1}H VT NMR data for **8** (500 MHz, C_7D_8): (a) 300 K; (b) 290 K; (c) 280 K; (d) 270 K; (e) 260 K; (f) 250 K; (g) 240 K; (h) 230 K.

addition, trace amounts of three other components were identified: the bis(silyl) complex *cis*-$(Ph_3P)_2Pt(Si(C_{20}H_{24})H)_2$ (**17**), a product tentatively assigned to a six-coordinate species similar to **10**, the complex $(Ph_3P)_2Pt(H)_2[Si(C_{20}H_{24})H]_2$ (**18**), and a third species **19**, which was unassigned.

After the mixture was warmed to room temperature, the major resonance in the $^{31}P\{^1H\}$ spectrum was a significantly broad region centered at 18 ppm due to the averaged signals for the unsymmetrical dinuclear complex **15**. A minor signal was assigned to the disiloxyplatinum complex $(Ph_3P)_2Pt[Si(C_{20}H_{24})\text{-}OSi(C_{20}H_{24})]$ (**20**), analogous to complex **10**. When the reaction was monitored by variable-temperature ^{1}H and $^{31}P\{^1H\}$ NMR spectroscopy, the signals for **16** began to broaden at 263 K, while those for **17** remained sharp. When the solution was then recooled to 223 K, signals for the dinuclear complex **15** were observed along with those for **16** and **17**. If the sample was warmed to room temperature for just a few minutes and then recooled to 223 K, signals for **16** disappeared and resonances for **15** and **17** remained.

Dynamic NMR Behavior of 8 and 15. Both of the dinuclear complexes **8** and **15** showed fluxional behavior on the NMR time scale. The ^{1}H NMR spectrum of pure **8** in C_7D_8 at room temperature showed a substantially broadened signal near 0 ppm for the two hydrides (Figure 3). When the temperature was lowered, the hydride resonance initially became more broadened and disappeared into the baseline by 270 K. At 250 K, a broad signal became visible near −5 ppm that sharpened considerably below 240 K due to the terminal hydride in **8**. The low-temperature resonance for the bridging hydride in **8** appears as a partially obscured doublet overlapping with the resonance for the solvent at 2 ppm (C_7D_8).

The coalescence temperature obtained from the variable-temperature $^{31}P\{^1H\}$ NMR spectra for complex **8** was $T_c = 260$ K, giving an approximate free energy of activation for $\Delta G^{\ddagger}$ of 11 kcal/mol. The coalescence temperature determined from variable-temperature $^{31}P\{^1H\}$ experiments for complex **15** was $T_c = 288$ K, providing an approximate value for $\Delta G^{\ddagger}$ of 12 kcal/mol. The variable-temperature ^{31}P NMR data for **15** are shown in Figure 4. The exchange of phosphorus sites was confirmed by a low-temperature 2D $^{31}P-^{31}P$ EXSY experiment. The low-temperature $^{31}P\{^1H\}$ NMR data for **15** at 183 K exhibited three broadened signals at 30, 22, and 20 ppm, each with Pt satellites for the three different phosphorus sites in the complex.

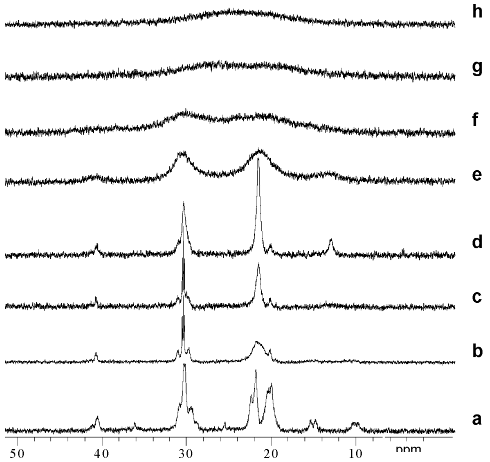

Figure 4. $^{31}P\{^1H\}$ VT NMR data for **15** (202 MHz, C_7D_8): (a) 183 K; (b) 203 K; (c) 213 K; (d) 243 K; (e) 263 K; (f) 273 K; (g) 284 K; (h) 292 K.

Upon heating a sample of **8** in C_7D_8 to 320 K, a new broad signal was observed in the ^{1}H NMR spectrum that was assigned to two equivalent bridging hydrides in the symmetrical dinuclear complex $[(Ph_3P)Pt(\mu\text{-}\eta^2\text{-}HSiC_{12}H_8)]_2$ (**21**). The sample was heated in 10 K increments to 370 K, and this resulted in a shift slightly downfield for the hydride resonance. These data are in good agreement with NMR data collected on a pure sample of **21** in CD_2Cl_2 (see below). Recooling the solution to 223 K showed ^{31}P resonances for **8**, **9**, PPh_3, and a minor amount of $OPPh_3$. In fact, heating a sample of **8** for 20 h at 358 K resulted in complete consumption of **8** and formation of the trimer **9** as the major Pt−Si-containing product. When the reaction of **1** and **5** was performed at room temperature followed by immediate heating to 323 K, the trinuclear complex **9** was formed (28% isolated yield) in a yield essentially identical with that obtained from the room-temperature reaction.[6a]

Approximately 15 h after a pure sample of **8** was dissolved in C_7D_8, a small amount of a peach-colored solid was often observed in the NMR tube. The solid was determined to be the symmetrical dinuclear complex **21**. Complex **21** is soluble in CD_2Cl_2, but no resonance was observed in the room-temperature ^{31}P NMR spectrum, indicating fluxional behavior on the NMR time scale. Examination of the ^{1}H NMR spectrum at 223 K revealed a resonance for the equivalent bridging hydrides with two sets of platinum satellites. The $^{31}P\{^1H\}$ spectrum displayed a resonance with a satellite pattern characteristic of a dinuclear Pt complex containing one phosphine at each platinum center.[19]

Heating a pure sample of **15** in C_7D_8 to 360 K did not show any significant decomposition, as determined by ^{1}H and $^{31}P\{^1H\}$ NMR spectroscopy. At 320 K, a broad signal was observed that was assigned to the equivalent bridging hydrides in the symmetrical dinuclear complex $[(Ph_3P)Pt(\mu\text{-}\eta^2\text{-}HSiC_{20}H_{24})]_2$ (**22**). At 360 K, the signal was shifted downfield and appeared as a sharp singlet with two sets of Pt satellites. The $^{31}P\{^1H\}$ NMR spectrum obtained at 223 K after heating the solution to 360 K exhibited the characteristic signals for **15** as the major species in solution. These results suggest that phosphine coordination is reversible and that, if decomposition occurs, it is to a minor extent. The molecular structure of **22** was determined by X-ray crystallography (see the Supporting Information); however, the structure was of low quality but confirmed the connectivity of the complex. The structural environment in **22** was similar to those of related symmetrical dinuclear complexes previously reported.[3e,g]

When a sample of **15** was heated to higher temperatures (368−373 K) in C_7D_8, the formation of several products was

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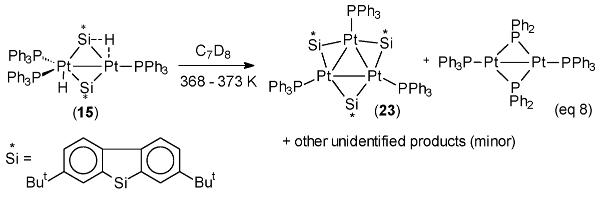
[19] Bender, R.; Braunstein, P.; Jud, J. M.; Dusausoy, Y. *Inorg. Chem.* **1984**, *23*, 4489.

observed. A new signal appeared at 71 ppm in the $^{31}P\{^{1}H\}$ NMR spectrum and was assigned to the symmetrical trinuclear complex $[(Ph_3P)Pt(\mu\text{-}SiC_{20}H_{24})]_3$ (**23**) (eq 8).[6] A resonance was also observed at 198 ppm (with Pt satellites) and was assigned to the bridging phosphido group in the complex $[(Ph_3P)Pt(\mu\text{-}PPh_2)]_2$. The phosphido complex was isolated from the mixture, and the structure was confirmed crystallographically to be identical with that in the published structure report.[20] The formation of the phosphido-bridged dinuclear complex resulted from a formal extrusion of the silicon moiety and loss of a phenyl group from the phosphorus center, but the fate of the silicon unit was not determined. Several other resonances were observed that are unassigned. Thus, the trinuclear complex **23** can be formed from the thermolysis of **15** but the more rigorous reaction conditions produced a mixture where several other minor products were formed in addition to the trimer **23**. However, the trimer **23** was isolated in 27% yield.

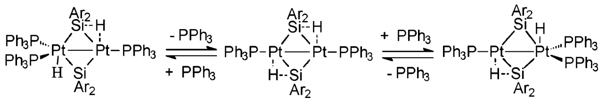


Discussion

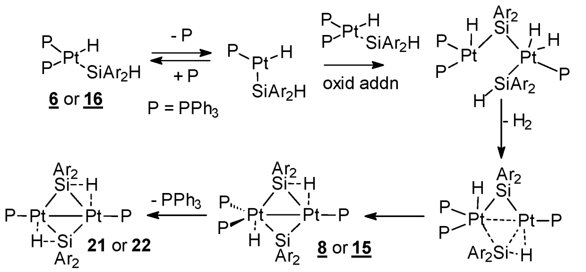
Addition of the Si−H bond of Ph_2SiH_2 (**2**) to $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ (**1**) produced the previously described mononuclear complex $(Ph_3P)_2Pt(H)(SiPh_2H)$ (**3**) as the major product.[8] In our examination of this reaction we found that the mononuclear complex **3** appeared to exhibit fluxional behavior on the NMR time scale, as evidenced by broad signals in both the ^{1}H and ^{31}P spectra at room temperature. Our studies also showed that **3** could be converted to the symmetrical dinuclear complex **4** upon heating. More recently, our studies have shown that reducing the spatial requirements of the diarylhydrosilane enhanced the reactivity of the Si−H-containing precursors. The reaction of silafluorene **5** with **1** also produced the expected Si−H bond activation product **6** as well as the bis(silyl) complex **7**, resulting from addition of two Si−H units to the Pt center. A minor amount of the unstable six-coordinate species **11** was observed by low-temperature NMR spectroscopy. None of the corresponding bis(silyl) or six-coordinate complexes were observed in the reaction of **1** with **2**. Complexes **6** and **7** were stable at low temperature only for several hours. Warming a C_7D_8 solution containing **6** and/or **7** resulted in the formation of the unsymmetrical dinuclear complex **8** as the major product, suggesting that the mononuclear compounds **6** and **7** are precursors to **8**. The room-temperature reaction of **1** with **5**, however, showed that the dinuclear product **8** was formed immediately, followed by the formation of the trinuclear complex **9** over a period of a few hours.[6a]

Compound **9** is a rare example of a trinuclear complex containing either a bridging $\mu\text{-}SiR_2$ or terminal SiR_3 ligand. Osakada et al. reported that the thermolysis of *cis*-$(Me_3P)_2Pt(SiPh_2H)_2$ at 100 °C produced the trinuclear system $[(Me_3P)Pt(\mu\text{-}SiPh_2)]_3$.[17] Two other related triplatinum complexes containing silicon ligands are known and were prepared from a preexisting Pt_3 cluster by Si−H bond activation.[21]

Scheme 1



Scheme 2



A proposed mechanism for the fluxional process responsible for the variable-temperature behavior of **8** and **15** is shown in Scheme 1. This mechanism involves loss of one of the two equivalent phosphines at the $(Ph_3P)_2(H)Pt$ site followed by coordination of phosphine at the other $Pt(PPh_3)$ site with concomitant transformation of the terminal Pt−H to a bridging hydride and bridging Pt···H···Si to a terminal Pt−H unit. This type of process would equilibrate the two different phosphorus and hydride sites in the complex. Exchange of the two different phosphorus and hydride sites was confirmed by low-temperature proton and phosphorus EXSY experiments. A similar mechanism has been proposed by Osakada et al. for related dipalladium and mixed platinum−palladium dinuclear complexes.[3a,h]

A possible mechanism for the formation of the dinuclear complex **8** (or **15**) from the mononuclear complex **6** (or **16**) is shown in Scheme 2. The initial step in the process would involve loss of the phosphine trans to the silicon center, producing a reactive three-coordinate (T- or Y-shaped) intermediate. Oxidative addition of the Si−H bond in **6** (or **16**) with the three-coordinate intermediate, followed by reductive elimination of H_2 and ring closure, would provide **8** (or **15**). Loss of PPh_3 from **8** would generate the symmetrical dinuclear complex **21** (or **22**).

The formation of complex **8** from the bis(silyl)platinum phosphine complex **7** may involve a similar process, where the first step involves loss of PPh_3 to give a three-coordinate species, $(Ph_3P)Pt(SiR_2H)_2$. A bimolecular reaction of this three-coordinate species with **7** followed by reductive elimination of a disilane ($HSiR_2-SiR_2H$, not observed by NMR spectroscopy) and cyclization would give **8**. An alternative mechanism could involve reductive elimination of silafluorene and formation of a platinum−silylene complex, $(Ph_3P)_2Pt{=}SiC_{12}H_8$. Formation of **8** from a Pt=Si species of this type would then require dimerization, loss of PPh_3, and incorporation of H_2 to give the unsymmetrical dinuclear complex. A signal at 4.9 ppm was observed in the early stages of the thermal decomposition of **7** to give **8**, which may be due to the formation of silafluorene **5**. No signals were observed in the ^{31}P NMR data that could be attributed to the formation of a Pt=Si species. The major pathway for the formation of the trinuclear complex **9** is probably due to a bimolecular reaction between **6** and **8**. Further studies are required to provide evidence in support of any mechanism.

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(20) The complex $[(Ph_3P)Pt(\mu\text{-}PPh_2)]_2$ was previously characterized by X-ray crystallography: Taylor, N. J.; Chieh, P. C.; Carty, A. J. *J. Chem. Soc., Chem. Commun*. **1975**, 448.

(21) (a) Itazaki, M.; Nishihara, Y.; Osakada, K. *Organometallics* **2004**, *23*, 1610. (b) Bender, R.; Braunstein, P.; Bouaoud, S.-E.; Merabet, N.; Rouag, D.; Zanello, P.; Fontani, M. *New J. Chem*. **1999**, *23*, 1045.

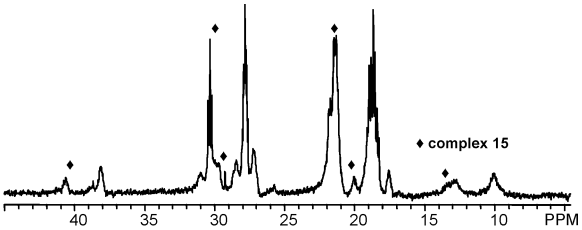
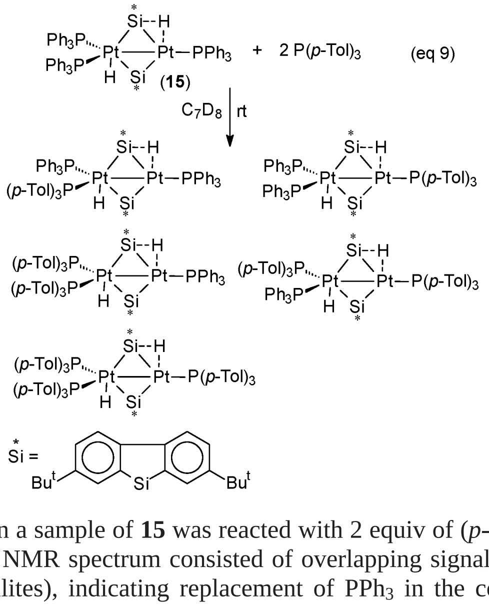


Figure 5. Partial $^{31}P\{^1H\}$ NMR spectrum of the mixture obtained from the reaction of **15** with $(p\text{-Tol})_3P$ (202 MHz, C_7D_8, 223 K).

The low-temperature experiments described above confirmed that the initial major products involved in the reactions shown in eqs 1, 3, 4, and 7 were mononuclear Pt−Si complexes of the types $P_2Pt(H)(SiAr_2H)$ and $P_2Pt(SiAr_2H)_2$. These complexes are thermally unstable, and when they are warmed to room temperature (or above), dinuclear complexes are produced. The formation of the dinuclear products can be rationalized by the mechanism shown in Scheme 2. No other intermediate species were observed by low-temperature NMR spectroscopy. Both mononuclear complexes appear to be precursors to the unsymmetrical Pt_2 complexes. Deuterium labeling studies between **5-*d*$_2$** and **1** support these observations. In contrast to the low-temperature reaction between **1** and **5**, the room-temperature reaction also produced the unsymmetrical dinuclear complex **8** as well as the trimer **9**.[6] These results suggest that **9** is probably formed from a bimolecular reaction involving mononuclear and dinuclear species. The observed fluxional behavior of the unsymmetrical dinuclear complexes prompted us to investigate their reactivity.

Reactivity Studies of Isolated Complexes. To evaluate the mechanism shown in Scheme 1, complex **15** was reacted with an external phosphine. Complex **15** was found to undergo exchange with added $(p\text{-Tol})_3P$. In theory, the reaction of **15** with 2 equiv of $(p\text{-Tol})_3P$ could produce a mixture of complexes incorporating one, two, or three $(p\text{-Tol})_3P$ ligands, as illustrated in eq 9.



When a sample of **15** was reacted with 2 equiv of $(p\text{-Tol})_3P$, the ^{31}P NMR spectrum consisted of overlapping signals (with Pt satellites), indicating replacement of PPh_3 in the complex with added $P(p\text{-Tol})_3$ (Figure 5). Signals for complex **15** were observed, but due to the complexity of the spectrum, it is probable that a number of products are formed. The spectrum remained unchanged after 24 h, and phosphine exchange was confirmed by a 2D $^{31}P-^{31}P$ EXSY experiment.

The low-temperature addition of the dinuclear complex **8** to the mononuclear complex **16** was performed to determine if exchange of silafluorenyl ligands could occur. The addition was performed at 223 K (due to the thermal instability of **16** at room temperature) followed by slow warming of the solution to room temperature. A mixture of three unsymmetrical dinuclear complexes, including unreacted **8**, **15**, and a new complex (eq 10) tentatively assigned to the mixed silafluorene system $(Ph_3P)_2(H)Pt(\mu\text{-}SiC_{20}H_{24})(\mu\text{-}\eta^2\text{-}H-SiC_{12}H_8)Pt(PPh_3)$ (**24**) were observed, as determined by $^{31}P\{^1H\}$ NMR spectroscopy (Figure 6). No trinuclear complexes were observed, as determined by the absence of any resonances in the region near 70 ppm, where signals are typically observed for a species of the type $[(Ph_3P)Pt(\mu\text{-}SiR_2)]_3$.[6]

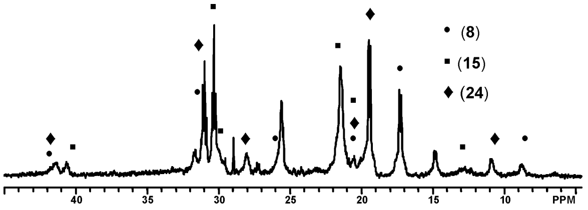
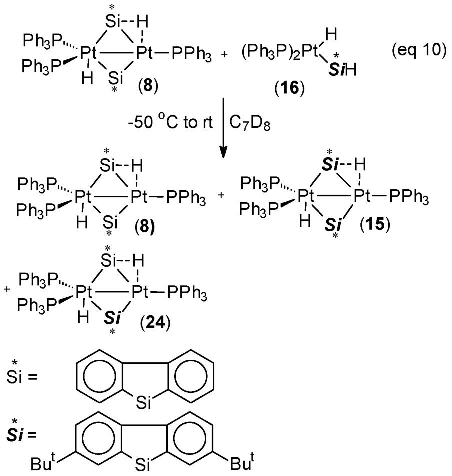
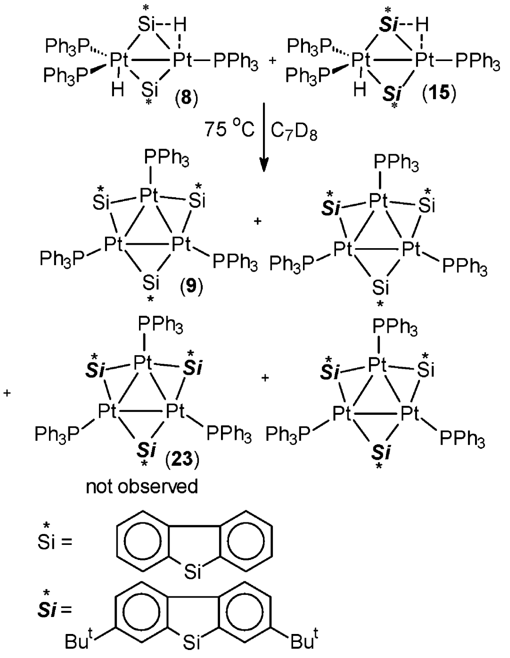


Figure 6. Partial $^{31}P\{^1H\}$ NMR spectrum (C_7D_8, 223 K) of the mixture obtained from the reaction between **8** and **15** after 24 h.



When the reaction was monitored by NMR spectroscopy at 223 K immediately after addition, signals for both **8** and **24** (but not **15**) were observed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, indicating that exchange takes place even at low temperature. Further warming of the reaction mixture to room temperature resulted in complete consumption of **16** and formation of the mixture of dinuclear complexes **8**, **15**, and **24**. A minor amount of an unassigned product was also observed (δ 15). In contrast, the room-temperature reaction between **5** and **15** gave a complex mixture of products, as shown by the $^{31}P\{^1H\}$ NMR spectrum.

The reaction between the two unsymmetrical dinuclear complexes **8** and **15** was performed, and upon mixing of the two complexes, no reaction was observed at room temperature or after heating to 330 K for 45 min. However, heating the mixture at 348 K for ca. 16 h resulted in the formation of several new resonances near 70 ppm (with Pt satellites) in the ^{31}P NMR spectrum (eq 11). In addition, several smaller resonances were observed near 30 and 65 ppm that have not been assigned. The low-temperature (223 K) ^{31}P NMR spectrum showed similar resonances in addition to unreacted **15** and PPh_3. The presence of several resonances near 70 ppm suggests that the thermal reaction between **8** and **15** produced not only the trinuclear complex **9** but possibly also mixed trinuclear complexes containing both bridging silafluorenyl and 3,7-di-*tert*-butylsi-



lafluorenyl ligands. No signal was observed for the trinuclear complex $[(Ph_3P)Pt(\mu\text{-}SiC_{20}H_{24})]_3$ (**23**).

Conclusions

Part of the current study involved the examination of the low-temperature reactions of diphenylsilane (**2**), silafluorene (**5**), silafluorene-d_2 (**5-*d*$_2$**), and 3,7-di-*tert*-butylsilafluorene (**14**) with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ (**1**). The major initial products obtained from these reactions were mononuclear complexes with the general formula $(Ph_3P)_2Pt(H)(SiAr_2H)$ and $(Ph_3P)_2Pt(SiAr_2H)_2$ (but not with Ar = Ph). Dinuclear complexes were obtained from these reactions by warming solutions to room temperature or above. Labeling studies involving **5-*d*$_2$** with **1** at low temperature provided additional evidence for the formation of mono- and dinuclear products. The proposed mechanism of formation of the unsymmetrical dinuclear complexes likely involves a bimolecular reaction involving the mononuclear complex $(Ph_3P)_2Pt(H)(SiAr_2H)$ with the related three-coordinate reactive intermediate. An important observation was that the formation of the trinuclear complex **9** appears to be inhibited when the reaction is performed at low temperature and probably involves a bimolecular reaction between mononuclear and dinuclear species.

VT-NMR studies of the unsymmetrical dinuclear complexes **8** and **15** suggested a fluxional process involving loss/recoordination of a PPh_3 ligand. This was confirmed by reaction of complex **15** with added $P(p\text{-}Tol)_3$ to produce a mixture of dinuclear products resulting from phosphine exchange. Exchange of silafluorenyl ligands was also observed from reactions between mononuclear and dinuclear complexes as well as between two different dinuclear complexes. Additional reactivity studies are in progress and will be reported in the future.

Experimental Section

General Considerations. All glassware was oven- or flame-dried prior to use. Reactions were performed (or samples prepared) under an argon or nitrogen atmosphere, either on a double-manifold Schlenk line or in an inert-atmosphere drybox. Silafluorene,[22] 3,7-di-*tert*-butylsilafluorene,[18] and diphenylsilane[23] were prepared as described previously. Tri-*p*-tolylphosphine and tetrakis(triphenylphosphine)platinum(0) were obtained from Strem Chemical Co. and used as received. Ethylenebis(triphenylphosphine)platinum(0) was purchased from Aldrich Chemical Co. and was used as received. Toluene-d_8, benzene-d_6, and methylene chloride-d_2 were purchased from Cambridge Isotopes, Inc., degassed by freeze−thaw vacuum cycles, and stored over activated molecular sieves.

NMR spectroscopic data were recorded on a Bruker ARX-500 spectrometer at 500 MHz for ^1H, 99 MHz for ^{29}Si, and 202 MHz for ^{31}P. Proton chemical shifts (δ) are reported relative to the residual protonated solvents C_7D_8 (2.09 ppm), C_6D_6 (7.15 ppm), and CD_2Cl_2 (5.32 ppm). Silicon chemical shifts (δ) are reported relative to external TMS (0 ppm). Phosphorus chemical shifts (δ) are reported relative to external H_3PO_4 (0 ppm). Chemical shifts are given in ppm and coupling constants in Hz. The majority of the NMR data listed in this section for reaction mixtures include selected key resonances that are characteristic for the particular product; resonances for aromatic protons, for example, are not included, since there are often many overlapping resonances. Compounds **3**,[7] **4**,[8] and **6**, **8**, **9**, **15**, and **16**[6] have been reported and/or characterized previously. Key NMR spectroscopic data for compounds **3**, **4**, **6**−**11**, **15**−**18**, and **20**−**23** are summarized in Table 1. Infrared spectra were recorded on a Thermo-Nicolet Avatar 360 E. S. P. FT-IR spectrometer. Elemental analysis determinations were performed by Atlantic Microlabs, Inc., Norcross, GA.

General Procedure for Low-Temperature Addition Reactions. The reactions are typically run on a 1:1 ratio between the platinum and hydrosilane precursors. A solution of the platinum precursor $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ (**1**) (or $Pt(PPh_3)_4$ (**12**)) was made 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 hydrosilane precursor in 0.25−0.5 mL of C_7D_8.. The solutions were then cooled in a dry ice/acetone bath (−78 °C unless otherwise noted), and the hydrosilane 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 then collected at various reaction times after addition.

Reaction of Diphenylsilane (2) with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ (1): Isolation of 4. (a) Low-Temperature Addition. The NMR tube containing **1** (40 mg, 0.054 mmol, 0.5 mL of C_7D_8) was cooled in a Dewar of liquid N_2. A solution of **2** (10 mg, 0.054 mmol, 0.25 mL of C_7D_8) was added slowly by syringe to the tube containing **1**, and then after approximately 5 min the tube was transferred to a cold bath (−78 °C) and then placed in the precooled magnet of the spectrometer. NMR data collection was started at 223 K approximately 5 min after mixing. After approximately 4.5 h the temperature was raised to 243 K and then gradually up to room temperature over ∼7 h. NMR signals for $(Ph_3P)_2(H)PtSiHPh_2$ (**3**) were observed within minutes after addition at 223 K, and no new resonances were observed in the NMR spectra as the temperature was raised, but the resonances broadened significantly above 243 K. After reaching room temperature, the NMR sample was then heated at 323 K for 0.5 h, after which no mononuclear complex was observed and white crystals of complex **4** (12 mg, 70%)[8] had formed in the NMR tube. The resulting solution was examined by $^{31}P\{^1H\}$ NMR spectroscopy at 193 K, and signals for PPh_3 (δ −7.7), $OPPh_3$ (25.8), and $Pt(PPh_3)_4$ (δ 10.3, $^1J_{PtP}$ = 3828, major component)[12] were observed as well as an unidentified resonance at 14.6 ppm ($^1J_{PtP}$ = 3612).

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[22] (a) Chang, L. S.; Corey, J. Y., *J. Organomet. Chem*. **1986**, *307*, 7. (b) For a recent report on the synthesis of dichlorosilafluorene see: Liu, Y.; Stringfellow, T. C.; Ballweg, T.; Guzei, I. A.; West, R., *J. Am. Chem. Soc*. **2002**, *124*, 49.

[23] Benkeser, R. A.; Landesman, H.; Foster, D. J. *J. Am. Chem. Soc*. **1952**, *74*, 648.

Selected NMR spectroscopic data for **3** are as follows. ^{1}H NMR (500 MHz, C_7D_8, 223 K, 5 min after mixing): *δ* 4.82 (br m, SiH), −1.0 (dd, $^1J_{PtH}$ = 1008, $^2J_{PH}$(trans) = 155, $^2J_{PH}$(cis) = 21, PtH). ^{31}P{^{1}H} NMR (202 MHz, C_7D_8, 223 K, 10 min): *δ* 35.5 (d, $^1J_{PtP}$ = 2506, $^2J_{PP}$ = 10, *cis*-P−Pt−Si), 35.2 (d, $^1J_{PtP}$ = 1785, *trans*-P−Pt−Si). ^{29}Si{^{1}H} NMR (99 MHz, C_7D_8, 223 K, 2.5 h after mixing, DEPT): *δ* 9.6 (dd, $^1J_{PtSi}$ = 1113, $^2J_{PSi}$ = 136 (trans), 15 (cis)).[7] Selected ^{1}H NMR (500 MHz, C_7D_8, 303 K, 7 h after addition): *δ* 4.74 (br s, SiH), −1.35 (br s, $^1J_{PtH}$ = 1018, PtH). Selected ^{31}P{^{1}H} NMR (202 MHz, C_7D_8, 303 K, 7 h after addition): *δ* 35.7 (br s, $^1J_{PtP}$ = 2494). Selected ^{1}H NMR (500 MHz, C_7D_8, 223 K, 5 days after addition): *δ* 4.83 (br s, SiH), −0.94 (br s, $^1J_{PtH}$ = 1016, PtH). Selected ^{31}P{^{1}H} NMR (202 MHz, C_7D_8, 223 K, 5 days after addition): *δ* 35.5 (br s, $^1J_{PtP}$ = 2466), 25.4, s, OPPh$_3$), −6.0 (br s, PPh$_3$); several minor unassigned resonances were observed between 10 and 44 ppm.

(b). Room-Temperature Addition. In a separate experiment at room temperature, a solution of **2** (12 mg, 0.065 mmol, 0.5 mL of C_6D_6) was added to **1** (47 mg, 0.063 mmol, 0.5 mL of C_6D_6). Vigorous bubbling was observed. ^{1}H NMR (500 MHz, C_6D_6, 300 K, 10 min after addition at room temperature): *δ* 4.8 (br, SiH), −1.2 (br with Pt satellites, $^1J_{PtH}$ = 1000 Hz). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6, 300 K, 10 min after addition): *δ* 35.6 (br with Pt satellites, $^1J_{PtP}$ = 2495 Hz). ^{29}Si{^{1}H} NMR (99 MHz, C_6D_6, 300 K, 1 h after mixing, DEPT): *δ* 8.0 ($^1J_{PtSi}$ = 1133 Hz). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6, 300 K, 5 h after addition): *δ* 10−50 (br, maximum peak height at 35 ppm), 25.1 (s, OPPh$_3$).

In a separate experiment at low temperature, a solution of **2** (5 mg, 0.027 mmol, ca. 0.5 mL of C_7D_8) was added to **1** (20 mg, 0.027 mmol, ca. 0.5 mL of C_7D_8). Formation of the mononuclear complex **3** was observed by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy at 223 K, and then the solution was heated to 323 K for 30 min. A white crystalline solid of **4** formed in the NMR tube and was isolated in 70% yield (12 mg). NMR spectroscopic data for isolated **4** are as follows. ^{1}H NMR (500 MHz, CD_2Cl_2, 223 K): *δ* 6.94−7.80 (m, aromatic region), 2.84 (s with Pt satellites, $^1J_{PtH}$ = 624, $^2J_{PtH}$ = 111, Pt···*H*···Si). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 223 K): *δ* 34.6 (s with Pt satellites, $^1J_{PtP}$ = 4242, $^2J_{PtP}$ = 282,$^3J_{PP}$ = 52). IR (neat, cm^{-1}): *ν* 1685 (Pt···*H*···Si).

Low-Temperature Reaction Studies of Silafluorene with (Ph$_3$P)$_2$Pt(η^2-C$_2$H$_4$). (a) Addition of Silafluorene to (Ph$_3$P)$_2$Pt(C$_2$H$_4$) at −50 °C: Observation of 6−8. A solution containing **5** (12 mg, 0.066 mmol, 0.25 mL of C_7D_8) was added to a cooled solution of **1** (50 mg, 0.067 mmol, 0.75 mL of C_7D_8). A small amount of bubbling was observed. The tube was then transferred to a precooled NMR magnet at 223 K. Experiments were begun within 5 min and were run continuously for 24 h at varying temperatures. After 24 h, the temperature was returned to 223 K and then to 183 K, and further measurements were obtained. The sample was checked again after approximately 48 h, and measurements were taken again at 300, 223, and 183 K, showing no change in comparison to data collected after 24 h.

^{1}H NMR data (C_7D_8, 500 MHz, 223 K, 5 min after mixing): *δ* 7.8−6.7 (aromatic resonances), 6.6 (s with Pt satellites, $^2J_{PtH}$ = 57, SiH for **6**), 5.2 (s, C$_2$H$_4$), 5.0 (m, overlapping SiH resonances for **7** and H(C$_{12}$H$_8$)SiCH$_2$CH$_3$), 4.5 (s, H$_2$), 0.98 (t, $^3J_{HH}$ = 7.5, HR$_2$SiCH$_2$C*H*$_3$), 0.76 (m, HR$_2$SiC*H*$_2$CH$_3$), −1.61 (br d, $^1J_{PtH}$ = 944,$^2J_{PH}$ = 139, PtH for **6**). ^{31}P{^{1}H} NMR (C_7D_8, 202 MHz, 223 K, 10 min after mixing): *δ* 37.5 (s, $^1J_{PtP}$ = 1953 Hz, **7**); small broad resonances observed at 38, 35, and 33 ppm (unassigned, but the last two resonances are probably due to **6**). Selected ^{1}H{^{31}P} NMR data (C_7D_8, 500 MHz, 223 K, 1.5 h after mixing): *δ* 6.56 (s, $^2J_{PtH}$ = 56, SiH for **6**), 4.98 (s, $^1J_{SiH}$ = 176 Hz,$^2J_{PtH}$ = 29, Si−H for **7**), −1.4 (s, $^1J_{PtH}$ = 973, PtH for unassigned minor product), −1.61 (s, $^1J_{PtH}$ = 944 Hz, PtH for **6**). ^{31}P{^{1}H} NMR (C_7D_8, 202 MHz, 183 K, 1.75 h after mixing): *δ* 37.5 (br, $^1J_{PtP}$ = 1948 Hz, **7**), 35.3 (br s with Pt satellites, $^1J_{PtP}$ = 1885, P trans to Si for **6**), 32.5 (br s with Pt satellites, $^1J_{PtP}$ = 2500, P cis to Si for **6**), 25.7 (s, OPPh$_3$).

After 2.5 h, the temperature was raised slowly by 20 K increments and broadening of the ^{1}H and ^{31}P resonances listed above was observed. Selected ^{31}P{^{1}H} NMR (C_7D_8, 202 MHz, 283 K, 4 h after mixing): *δ* 37.5 (br, $^1J_{PtP}$ = 1928, **7**), 29.2 (s, minor component, **10**), 24.9 (s, OPPh$_3$), 23.2 (unsassigned minor component), 15.0 (br, **8**). Selected ^{1}H NMR data (C_7D_8, 500 MHz, 300 K, 5 h after mixing): *δ* 4.88 (br, *H*R$_2$SiCH$_2$CH$_3$), 0.97 (t, HR$_2$SiCH$_2$C*H*$_3$), 0.81 (m, HR$_2$SiC*H*$_2$CH$_3$), −1.17 (br s, $^1J_{PtH}$ = 658, Pt···H···Si for **8**). ^{31}P{^{1}H} NMR data (C_7D_8, 202 MHz, 300 K, 5 h after mixing): *δ* 46.4 (s, unassigned minor product), 45.2 (m, unassigned minor product), 29.3 (s, $^1J_{PtP}$ = 1710, **10**), 24.8 (s, OPPh$_3$), 11 (br covering 4−18 ppm, major component, **8**). ^{31}P{^{1}H} NMR data (C_7D_8, 202 MHz, 300 K, 19.5 h after mixing): *δ* 24.8 (s with Pt satellites, $^1J_{PtP}$ = 2039, minor product), 24.3 (s, OPPh$_3$), 12.8 (br covering 4−18 ppm, major component, **8**). Selected ^{1}H NMR data (C_7D_8, 500 MHz, 223 K, 24 h after mixing): *δ* 2.0 (d, $^2J_{PH}$ = 12, Pt···H···Si for **8**), −4.9 (t, $^1J_{PtH}$ = 577, $^2J_{PtH}$ = 80, $^2J_{PH}$ = 10, Pt−H for **8**). ^{31}P{^{1}H} NMR (C_7D_8, 202 MHz, 223 K, 24 h after mixing): *δ* 31.1 (t, $^1J_{PtP}$ = 4260, $^2J_{PtP}$ = 265, $^3J_{PP}$ = 25, **8**), 25.1 (s, OPPh$_3$), 17.3 (d, $^1J_{PtP}$ = 3438, $^2J_{PtP}$ = 135, **8**), −6.8 (s, PPh$_3$).

After 48 h the 223 K ^{1}H and ^{31}P spectra remained essentially unchanged. Lowering the temperature to 183 K gave severely broadened resonances, and no new peaks were observed. Selected NMR data 3 weeks after addition for the soluble fraction of the reaction mixture are as follows. ^{31}P{^{1}H} NMR (C_7D_8, 202 MHz, 183 K): *δ* 69.7 (s, minor component, **9**), 30.9 (br, minor component, **8**), 25.5 (s, major component, OPPh$_3$), 17.4 (br, minor component, **8**), 10.3 (s, major component, Pt(PPh$_3$)$_4$, $^1J_{PtP}$ = 3832), −7.7 (s, major component, PPh$_3$). After 48 h, the sample was returned to the drybox, where several drops of pentane were added to the solution. Three weeks later, a small amount of a dark red-purple crystalline solid was present in the NMR tube (probably trinuclear complex **9**, yield not determined). The dark red soluble fraction was decanted and examined by low-temperature ^{31}P{^{1}H} NMR spectroscopy.

(b) Addition of Silafluorene to (Ph$_3$P)$_2$Pt(η^2-C$_2$H$_4$) at Room Temperature followed by Cooling to −50 °C: Observation of 6−8. A solution of silafluorene (12 mg, 0.066 mmol, 0.25 mL of C_7D_8) was added to a solution of (PPh$_3$)$_2$Pt(η^2-C$_2$H$_4$) (41 mg, 0.055 mmol, 0.75 mL of C_7D_8) at room temperature (significant bubbling was observed); the mixture was shaken vigorously and then immediately placed in the NMR magnet at 300 K. Selected ^{1}H NMR data (500 MHz, C_7D_8, 300 K, just after mixing): *δ* 5.25 (br, C$_2$H$_4$ and overlapping SiH resonance), 4.50 (s, H$_2$), 2.52 (br, coordinated C$_2$H$_4$ for **1**), −0.9 (br, Pt···H···Si for **8**), −1.73 (dd, $^1J_{PtH}$ = 956, $^2J_{PH}$ = 156 (trans), 21 (cis), PtH for **6**). ^{31}P{^{1}H} NMR data (202 MHz, C_7D_8, 300 K, just after mixing): *δ* 70.6 (s, minor component, **9**), 34.7 (br s, $^1J_{PtP}$ = 3746, unreacted **1**), 32.8 (d, $^1J_{PtP}$ = 1879, $^2J_{PP}$ = 8, P trans to Si for **6**), 32.6 (prob d, $^1J_{PtP}$ = 2539, P cis to Si for **6**), 29.7 (s, minor component, **10**), 24.8 (s, OPPh$_3$), 10−55 (br multiple resonances). Selected ^{1}H NMR data (500 MHz, C_7D_8, 223 K, 30 min after mixing): *δ* 5.29 (s, C$_2$H$_4$), 5.0 (m, overlapping Si−H resonance for **7** and *H*(C$_{12}$H$_8$)SiCH$_2$CH$_3$), 4.55 (s, H$_2$), 0.97 (t, HR$_2$Si−CH$_2$C*H*$_3$), 0.75 (m, HR$_2$Si−C*H*$_2$CH$_3$), −1.38 (br d, $^1J_{PtH}$ = 975, $^2J_{PH}$ = 149, unassigned Pt−H), −1.66 (br s, $^1J_{PtH}$ = 940, Pt−H for **6**), −4.95 (t, $^1J_{PtH}$ = 569, $^2J_{PtH}$ ≈ 90, $^2J_{PH}$ = 9, Pt−H for **8**). ^{29}Si{^{1}H} NMR data (99 MHz, 223K, DEPT, 30 min after mixing): *δ* −15.1 (s, HR$_2$SiCH$_2$CH$_3$), −17.2 (dd, Pt satellites not resolved, $^2J_{PSi}$ = 144 (trans), 20 (cis), **7**), −20.7 (br, Pt satellites not resolved, **6**). Selected ^{31}P{^{1}H} NMR data (202 MHz, C_7D_8, 223 K, 2.5 h after mixing): *δ* 37.7 (s, $^1J_{PtP}$ = 1952, **7**), 31.1 (t, $^1J_{PtP}$ = 4257, $^2J_{PtP}$ = 247, $^3J_{PP}$ = 26, **8**) 17.2 (d, $^1J_{PtP}$ = 3427,

$Pt(PPh_3)_2$, **8**); several minor resonances were also observed between 20 and 42 ppm but were not assigned, −7 (br, PPh_3).

Reaction of $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ with Silafluorene in a 1:2 Ratio of Pt to Si. Isolation of $(Ph_3P)_2Pt(SiHC_{12}H_8)_2$ (7). A cooled solution of **5** (11 mg, 0.054 mmol, 90% purity, 0.3 mL of C_7D_8) was added to a cooled solution of **1** (20 mg, 0.027 mmol, 0.5 mL of C_7D_8). The $^{31}P\{^1H\}$ and ^1H NMR spectra were recorded just after addition at 223 K, and resonances for **6** (broadened),[6a] **7** (major product, data for isolated **7** are given below), and a complex that has been tentatively assigned to the six-coordinate species $(Ph_3P)_2Pt(H)_2[Si(C_{12}H_8)H]_2$ (**11**) were observed. Selected NMR data for **11** obtained just after addition are as follows. ^1H NMR (C_7D_8, 500 MHz, 223 K): δ 5.58 (m, Si−H), −7.52 (t, $^1J_{PtH}$ = 672, $^2J_{PH}$ (cis) = 11, Pt−H). $^{31}P\{^1H\}$ NMR (C_7D_8, 202 MHz, 223 K) δ 10.1 (s, with Pt satellites, $^1J_{PtP}$ = 1330 Hz).

The temperature was kept at 223 K for 30 min, and then the solution was warmed to 273 K and maintained at that temperature for 30 min. The solution was then transferred to a Schlenk tube, and 10 mL of cold pentane was added, resulting in precipitation of a pale yellow solid. The sample was placed in a freezer (−50 °C) overnight. The solvent was removed by syringe and the solid dried under vacuum to give **7** (15 mg, 52%). NMR spectroscopic data for **7** are as follows. ^1H NMR (C_7D_8, 500 MHz, 223 K): δ 8.0−6.6 (aromatic resonances); 5.02 (m, Si−H). $^{31}P\{^1H\}$ NMR (C_7D_8, 202 MHz, 223 K): δ 37.7 (s, with Pt satellites, $^1J_{PtP}$ = 1952 Hz). Selected $^1H\{^{31}P\}$ NMR (500 MHz, C_7D_8, 223 K): δ 5.04 (s, $^1J_{SiH}$ = 176, $^2J_{PtH}$ = 29). Anal. Calcd for $C_{60}H_{48}P_2PtSi_2$: C, 66.59; H, 4.47. Found: C, 66.83; H, 4.91. Selected IR data for **7** (cm^{-1}): ν 2054 (Si−H).

A pure sample of **7** was dissolved in C_7D_8 at 223 K, kept at that temperature for 1 h, and then warmed to 300 K. The $^{31}P\{^1H\}$ NMR spectrum showed signals for the dinuclear complex **8** at 31.1 and 17.2 ppm.[6a] After 2 h the ^{31}P NMR resonance for **7** had nearly disappeared and signals for **8** (major Pt−Si containing product), as well as PPh_3, $OPPh_3$, and $(Ph_3P)_2Pt[Si(C_{12}H_8)OSi(C_{12}H_8)]$ (**10**, see below) were all present in addition to an unidentified resonance at 32.9 ppm ($^1J_{PtP}$ = 1753). After 1 day at room temperature the spectrum was essentially the same, except that a new resonance was observed for the trinuclear complex $[(Ph_3P)Pt(\mu\text{-}SiC_{12}H_8)]_3$ (**9**) at 70 ppm.[6] The relative ratio of the dinuclear (**8**) to the trinuclear complex (**9**) after 1 day was approximately 6:1.

Heating a pure sample of **7** in C_7D_8 at 323 K for ca. 1.5 h resulted in nearly complete consumption of **7** and the formation of **8** (major product), **10** (see below), PPh_3, $OPPh_3$, an unidentified peak at 32 ppm (minor), and a small amount of the trinuclear complex **9** (ratio of **8**:**9** = 20:1) as determined by $^{31}P\{^1H\}$ NMR spectroscopy. When a sample of **7** in C_7D_8 was heated to 373 K for 1 h, all of **7** had been consumed and the major product observed by $^{31}P\{^1H\}$ NMR spectroscopy was the dinuclear complex **8**, along with PPh_3 and $OPPh_3$. No signals for the trinuclear complex **9** were observed. A minor unidentified product appeared at 21.2 ppm.

Reaction of $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ with Silafluorene in a 2:1 Ratio of Pt to Si. A cooled solution of **5** (2 mg, 0.01 mmol, 0.4 mL of C_7D_8) was added to a cooled solution of **1** (16 mg, 0.021 mmol, 0.5 mL of C_7D_8). The sample was then transferred to a precooled NMR magnet at 223 K, and then the temperature immediately decreased to 193 K. Only the mononuclear complex **6** (δ 35.3 and 32.7), unreacted **1** (δ 33.7),[12] and a small amount of $OPPh_3$ (δ 25.9) were observed by $^{31}P\{^1H\}$ NMR spectroscopy. However, complex **6** was thermally unstable, and when the temperature was maintained at 253 K for 1 h, signals for the dinuclear complex **8** were then observed (δ 30.1, 17.2) along with a trace amount of complex **7** (δ 37.4). The intensity of the signals for **8** increased with time, and the resonances for complex **6** disappeared. Warming the sample to 300 K for 40 min followed by examination of the mixture by $^{31}P\{^1H\}$ NMR spectroscopy at 223 K showed signals for the dinuclear complex **8** (major component), a small amount of the trinuclear complex **9** (δ 69.7), and some remaining unreacted complex **1**.

Reaction of Silafluorene-d_2 with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$. Silafluorene-$d_2$ (10 mg, 0.054 mmol, 0.5 mL of C_7H_8) was added to a cooled NMR tube containing **1** (40 mg, 0.054 mmol, 0.5 mL of C_7H_8 and 1 drop of C_6D_6). NMR spectroscopic data were collected at 223 K immediately after addition and at multiple time intervals for several hours thereafter with warming to room temperature.

^2H NMR (76 MHz, C_7D_8, 223 K, immediately after mixing): δ 6.6 (br shoulder overlapping C_6D_6 resonance, SiD for **6-*d*₂**), 5.5−5.0 (br), 4.9 (br s, unreacted **5-*d*₂**), 4.5 (s, D_2), 2.0 (t, *J* = 2, probably due to toluene with deuterium incorporation),[24] 1.3 (br s, assigned to $D(C_{12}H_8)Si[C(H/D)_2C(H/D)_3]$), 0.9 (br s, assigned to $D(C_{12}H_8)Si[C(H/D)_2C(H/D)_3]$), −1.6 (br, PtD for **6-*d*₂**), −7.3 (br, PtD for **11-*d*₄**).

At *T* = 223 K for the time interval from *t* = 20 min to 1.5 h the region near 4.9 ppm (for **5-*d*₂**) broadened and increased in intensity and a new small peak (s) appeared at 0.8 ppm (possibly due to deuterioethane). In addition, the broad resonance centered at −7 ppm for **11-*d*₄** disappeared.

At *T* = 243 K (*t* = 2.5 h) the ^2H NMR spectrum showed a peak at 6.5 ppm for **6-*d*₂** and a more defined broad peak centered at approximately 5.1 ppm (probably due to **7-*d*₂**) overlapping with a decreased amount of **5-*d*₂** at 4.9 ppm. Essentially the same spectral features were observed at *T* = 263 K (*t* = 3 h).

At *T* = 273−283 K (*t* = 4−4.5 h) the following changes were observed in the ^2H NMR spectrum. Resonances at 6.5, 5.1, and 4.9 ppm were less broad (latter peak also lower intensity) and the peak at 0.8 ppm became more intense. In addition, a new broad resonance was now prominent at −1.3 ppm (assigned to Pt−D in **8-*d*₂**) overlapping with the now less intense (but slightly sharper) peak at −1.9 ppm for **6-*d*₂**.

When the temperature had reached 300 K (*t* = 5 h), the signals for the products **6-*d*₂** and **7-*d*₂** were absent. The resonance at −1.2 remained but had shifted to −1.0 ppm with partially defined Pt satellites.

The reaction solution was then cooled to 223 K (*t* = 5.25 h) to confirm the presence of the unsymmetrical dinuclear complex **8-*d*₂**. Two new broad resonances were now present near 2.1 ppm overlapping with the triplet peak at 2.08 ppm (assigned to the partially deuterated toluene) and −4.9 ppm (with broad Pt satellite shoulder) assigned to **8-*d*₂**. The ^2H spectrum collected after 24 h at 223 K was essentially identical. $^{31}P\{^1H\}$ NMR (202 MHz, C_7H_8/C_6D_6, 223 K, 24 h): δ 31.2 (t, Pt−PPh_3, $^1J_{PtP}$ = 4267, $^2J_{PtP}$ = 264, $^3J_{PP}$ = 28, for **8-*d*₂**), 17.4 (d, $Pt(PPh_3)_2$, $^1J_{PtP}$ = 3441, $^2J_{PtP}$ = 135, for **8-*d*₂**). Minor resonances were observed for $OPPh_3$ (25 ppm), PPh_3 (−6 ppm), and a trace amount of **10** (29 ppm).

The ^2H NMR spectrum was also collected after 24 h at 300 K. The spectrum obtained was essentially the same as that collected at *t* = 5 h at 300 K, but the resonance at − 1 ppm (for **8-*d*₂**) was now better resolved, with clearly defined Pt satellites ($^1J_{PtD}$ = 101).

The NMR sample containing the reaction mixture was treated with approximately 5 mL of pentane and the solution placed in a low-temperature freezer (−35 °C). After several hours a red-brown solid (**8-*d*₂**) was obtained. The solid was washed with additional pentane, dried in vacuo, and then redissolved in fresh C_7H_8 with 1 drop of C_6D_6 and analyzed by ^2H NMR at 223 and 300 K. ^2H NMR (76 MHz, C_7H_8/C_6D_6, 300 K): δ −0.8 (s with Pt satellites, $^1J_{PtD}$ = 100, for **8-*d*₂**); a small amount of the toluene with D incorporation was observed at 2.1 ppm. ^2H NMR (76 MHz, C_7H_8/C_6D_6, 223 K): δ 2.07 (br s, Pt···D···Si, for **8-*d*₂**), −4.8 (br, Pt-D, for **8-*d*₂**) observed in approximately 1:1 ratio by NMR integration.

Low-Temperature Reaction of Silafluorene with $(Ph_3P)_4Pt$. Silafluorene (**5**; 8 mg, 0.04 mmol, 0.25 mL of C_7D_8) was added to a cooled solution of $(Ph_3P)_4Pt$ (**12**; 48 mg, 0.039 mmol, 0.75 mL

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[24] The signal could be due to C_7D_8 vapors present in the drybox atmosphere that were introduced during sample preparation.

of C_7D_8). NMR data collection was performed immediately after addition at 223 K and at multiple time intervals and temperatures during an approximately 24 h time period.

Selected ^{1}H NMR data (500 MHz, C_7D_8, 223 K, immediately after mixing): δ 6.60 (s, SiH overlapping with aromatic region, **6**), 5.59 (m, SiH, minor product, tentative assignment **11**), 5.05 (m, SiH for **7**), 4.46 (s, H_2), −1.75 (br, $^1J_{PtH}$ = 938, Pt−H, **6**), −7.51 (t, $^1J_{PtH}$ = 673, $^2J_{PH}$ = 11, PtH for **11**). ^{31}P{^{1}H} NMR (202 MHz, C_7D_8, 223 K, 1−2 h after mixing): δ 40−10 (br), 37.7 (s, $^1J_{PtP}$ = 1953, **7**), 10.1 (s, $^1J_{PtP}$ = 1330, assigned to **11**), −5.9 (br, PPh_3); distinct signals were not observed for **6**, possibly due to exchange. ^{29}Si{^{1}H} NMR (99 MHz, C_7D_8, 223 K, 3.5 h after mixing): δ − 17.2 (dd, $^1J_{PtSi}$ = 1095, $^2J_{PSi}$ = 144, 20, **7**), −20.8 (br s, $^1J_{PtSi}$ = 1128, **6**). After 7 h at 223 K, ^{1}H and ^{31}P NMR data were essentially identical with the data collected just after mixing. After 7 h the solution was slowly warmed to room temperature over a period of several hours. When the temperature had reached 283 K, the ^{1}H and ^{31}P resonances for **6** and **7** were substantially reduced in intensity and disappeared as the sample reached room temperature.

Selected ^{1}H NMR (500 MHz, 303 K, 13 h after mixing): δ −1.3 ppm ($J_{PtH} \approx 650$, averaged PtH for **8**). Selected ^{31}P{^{1}H} NMR data (202 MHz, C_7D_8, 303 K, 13 h after mixing): δ 46.4 (s unassigned minor product), 45.1 (d, unassigned minor product), 24.4 (s, $OPPh_3$), −1 ppm (covering region from +5 to −10 ppm, **8**). Selected ^{1}H NMR data (500 MHz, 223 K, 24 h after mixing): δ 2.04 (d, $^2J_{PH}$ = 13, Pt···H···Si for **8**), − 4.94 ppm (t, $^1J_{PtH}$ = 574, $^2J_{PH} \approx$ 10, Pt−H for **8**). Selected ^{31}P{^{1}H} NMR data (202 MHz, C_7D_8, 223 K, 24 h after mixing): δ 31.0 (t, $^1J_{PtP}$ = 4260, $^2J_{PtP}$ = 257, $^3J_{PP}$ = 28, Pt−PPh_3 for **8**), 25.2 (s, $OPPh_3$), 17.3 (d, $^1J_{PtP}$ = 3434, $Pt(PPh_3)_2$ for **8**), −6.8 (s, PPh_3).

Synthesis of $(Ph_3P)_2Pt[Si(C_{12}H_8)OSi(C_{12}H_8)]$ (10). A low-temperature solution of $[H(C_{12}H_8Si)]_2O$ (**13**; 8 mg, 0.02 mmol, 0.3 mL of C_7D_8) was added to a low-temperature solution of **1** (16 mg, 0.021 mmol, 0.5 mL of C_7D_8). The reaction tube was shaken several times to mix the contents, and after approximately 10 min, the^{31}P{^{1}H} and ^{1}H NMR data showed the presence of **10** as the major species. Pentane (5 mL) was added, and a yellow precipitate formed. The yellow solid was dried under vacuum to give **10** (13 mg, 56%). ^{1}H NMR (C_7D_8, 500 MHz, 300 K): δ 8.4−6.5 (aromatic resonances). ^{31}P{^{1}H} NMR (C_7D_8, 202 MHz, 300 K): δ 29.5 (s, $^1J_{PtP}$ = 1708 Hz). Anal. Calcd for $C_{60}H_{46}P_2PtSi_2O$: C, 65.74; H, 4.23. Found: C, 61.68; H, 4.12.

Low-Temperature Reaction of 3,7-Di-*tert*-butylsilafluorene (14) with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ (1). At low temperature, a solution of **14** (20 mg, 0.068 mmol, 0.3 mL of C_7D_8) was added to **1** (50 mg, 0.068 mmol, 0.5 mL of C_7D_8). ^{31}P{^{1}H} NMR (202 MHz, C_7D_8, 193 K, immediately after addition): δ 38.5 (s, trace amount of **17**), 35.4 (br d, $^1J_{PtP}$ = 1890, P trans to Si in **16**), 33.7 (br d, $^1J_{PtP}$ = 2543, P trans to H in **16**), 33.6 (small amount of unreacted **1**, $^1J_{PtP}$ = 3702), 24.5 (s, $OPPh_3$), 5.5 (br s, $^1J_{PtP}$ = 1846, **19**), −8.4 (br s, $^1J_{PtP}$ = 1109, **18**). Three hours after addition the solution was warmed to 300 K. ^{31}P{^{1}H} NMR (202 MHz, C_7D_8, 300 K, 3 h after addition, major resonances): δ 29.8 (s, $^1J_{PtP}$ = 1705, **20**), 24.8 (s, $OPPh_3$), 18 (br, **15**).

In a separate experiment at low temperature, a solution of **14** (10 mg, 0.034 mmol, ca. 0.5 mL of C_7D_8) was added to **1** (25 mg, 0.034 mmol, ca. 0.5 mL of C_7D_8). ^{1}H NMR (500 MHz, C_7D_8, 195 K, immediately after addition): δ 7.22 (br, SiH for **16**, tentative assignment), 6.31 (br, SiH in **18**, tentative assignment), 6.12 (br, SiH in **19**, tentative assignment), 5.29 (s, C_2H_4), 5.18 (br, overlapping with C_2H_4, SiH for **17**), 5.00 (br, SiH for **14**), 4.5 (s, H_2), 2.81 (br s, with Pt satellites, C_2H_4 for **1**), −1.02 (dd, $^1J_{PtH}$ = 942, $^2J_{PH}$ = 150 (trans), 17 (cis), Pt−H for **16**), −5.92 (br s, $^1J_{PtH}$ = 628, PtH for **19**, tentative assignment), − 9.35 (br dd, $^1J_{PtH}$ = 799, $^2J_{PH}$ = 188, PtH for **18**, tentative assignment). After 2.5−3 h, the temperature was raised to 263 K. Selected ^{1}H NMR data (500 MHz, C_7D_8, 263 K): δ 7.04 (s, SiH for **16**, tentative assignment), 5.27 (s, C_2H_4), 5.03 (m, SiH for **17**), 4.53 (s, H_2), 2.58 (br, C_2H_4 for **1**), −1.44 (br d, $^1J_{PtH}$ = 950, $^2J_{PH}$ = 149, PtH for **16**). ^{31}P{^{1}H} NMR data (202 MHz, C_7D_8, 263 K): δ 38.8 (s, $^1J_{PtP}$ = 1965, **17**), 36−33 (br, overlapping **16** and unreacted **1**), 25.0 (s, $OPPh_3$). The solution was kept at 263 K for 30 min and then recooled to 223 K. Selected ^{1}H NMR data after warming to 263 K for 30 min (500 MHz, C_7D_8, 223 K): δ 7.07 (s, SiH for **16**), 5.29 (s, C_2H_4), 5.09 (m, SiH for **17**), 4.55 (s, H_2), 2.70 (br, C_2H_4 for **1**), 1.92 (d, Pt···H···Si for **15**), −1.21 (br d, **16**), −5.22 (t, $^1J_{PtH}$ = 561, $^2J_{PH}$ = 8, PtH for **15**). ^{31}P{^{1}H} NMR data after warming to 263 K for 30 min (202 MHz, C_7D_8, 223 K): δ 38.6 (s, **17**), 35.1 (br s, **16**), 34.0 (s, **1**), 33. 5 (br s, **16**), 30.3 (t, **15**), 25.4 (s, $OPPh_3$), 21.5 (br, **15**). NMR data were collected after the solution was warmed to room temperature for a few minutes and then recooled to 223 K. Selected ^{1}H NMR data (500 MHz, C_7D_8, 223 K, after warming to room temperature): δ 5.29 (s, C_2H_4), 5.10 (m, SiH for **17**), 4.55 (s, H_2), 2.70 (s, C_2H_4 for **1**), 1.93 (d, Pt···H···Si, $^2J_{PH}$ = 12, **15**), −5.20 (t, **15**). ^{31}P{^{1}H} NMR (202 MHz, C_7D_8, 223 K, after warming to room temperature): δ 38.1 (**17**), 30.3 (t, **15**), 29.5 (**20**), 25.4 ($OPPh_3$), 21.5 (br, **15**), −6.8 (PPh_3).

NMR data were collected from a similar low-temperature experiment 45 min after addition at low temperature. ^{1}H−^{31}P-COSY (500 MHz, C_7D_8, 223 K): correlations observed between (^{1}H, ^{31}P) resonances at (5.1, 38.4) for **17**, (−1.26, 33.7) for **16**, (−5.96, −8.4) for **18**, and (−9.35, 5.4) for **19**. ^{1}H−^{29}Si HMQC (500 MHz, C_7D_8, 223 K): correlation observed between (^{1}H, ^{29}Si) resonances at (7.07, −18.5) for **16**, (5.1, −17.2) for **17**, and (4.9, −42.7) for **14**. Selected ^{29}Si{^{1}H} NMR (99 MHz, 223 K, 2.5 h after addition): δ −17.2 (dd, for **17**, $^1J_{PtSi}$ not resolved, $^2J_{PSi}$ = 141 (trans), 19 (cis)), −18.5 (dd, for **16**, $^1J_{PtSi}$ = 1105, $^2J_{PSi}$ = 154 (trans), 11 (cis)).[6a]

Variable-Temperature NMR Study of $(Ph_3P)_2(H)Pt(\mu\text{-}SiC_{12}H_8)(\mu\text{-}\eta^2\text{-}HSiC_{12}H_8)Pt(PPh_3)$ (8). A sample of **8** (10 mg) in 0.75 mL of C_7D_8 was monitored by VT-^{31}P{^{1}H} NMR spectroscopy over the temperature range between 300 and 223 K. The coalescence temperature was determined to be T_c = 260 K. A separate sample of **8** (6 mg) in ca. 0.75 mL of C_7D_8 was examined by ^{1}H NMR spectroscopy from 310 to 370 K. Selected ^{1}H NMR data for Pt···H···Si for **21** (500 MHz, C_7D_8): T = 320 K, δ 2.53 (br with broad flanking Pt satellites (J not resolved); T = 330 K, δ 2.85 (br with broad flanking Pt satellites (J not resolved)); T = 340 K, δ 3.03 (br); T = 350 K, δ 3.17 (br); T = 360 K, δ 3.22 (br); T = 370 K, δ 3.24 (br). ^{31}P{^{1}H} NMR data after heating to 370 K (202 MHz, C_7D_8, 223 K): δ 69.7 (s, **9**), 31.2 (t, **8**), 28.9 (minor component, **20**), 25.3 (minor component, $OPPh_3$), 17.2 (d, **8**), −6.8 (s, PPh_3).

The ^{1}H−^{1}H EXSY (500 MHz, C_7D_8, 223 K, mixing time 0.025 s) experiment showed a correlation between the two distinct hydride sites in **8** at 2.0 and −4.9 ppm, indicating exchange between the two sites. The ^{31}P−^{31}P EXSY experiment (202 MHz, C_7D_8, 223 K, mixing time 0.80 s) showed a correlation between the two phosphorus sites in complex **8** at 31 and 17 ppm, indicating exchange between the two different sites.

After ca. 20 h, the C_7D_8 solution containing **8** showed the formation of a peach-colored solid identified as the symmetrical dinuclear complex $[(Ph_3P)Pt(\mu\text{-}\eta^2\text{-}HSiC_{12}H_8)]_2$ (**21**; 1 mg, 12%). Selected ^{1}H NMR data for **21** (500 MHz, CD_2Cl_2, 223 K): δ 2.83 (br s, $^1J_{PtH}$ = 696, $^2J_{PtH}$ = 123). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 223 K): δ 35.7 (s, $^1J_{PtP}$ = 4302, $^2J_{PtP}$ = 303, $^3J_{PP}$ = 56).

Elevated-Temperature Reaction of Silafluorene (5) with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ (1). A solution of **5** (6 mg, 0.03 mmol, 0.2 mL of C_7D_8) was added to a solution of **1** (23 mg, 0.031 mmol, 0.3 mL of C_7D_8) at room temperature. The reaction mixture was transferred immediately to a preheated NMR magnet at 323 K. Selected ^{31}P{^{1}H} NMR data (202 MHz, 323 K, 10 min after mixing): δ 70.8 (s, **9**), 29.5 (s, **10**), 24.1 (s, $OPPh_3$), 14.4 (br s, major component, **8**). After 6 h the ^{31}P NMR spectrum was identical, except the signal for **9** had increased and **8** had decreased.

The reaction mixture was heated for a total of 6 h, and after cooling to room temperature, red crystalline **9** was isolated in 27% yield (6 mg).

Variable-Temperature NMR Study of $(Ph_3P)_2(H)Pt(\mu\text{-}SiC_{20}H_{24})(\mu\text{-}\eta^2\text{-}HSiC_{20}H_{24})Pt(PPh_3)$ (15). A sample of **15** (approximately 10 mg) in 0.75 mL of C_7D_8 was monitored by VT-$^{31}P\{^1H\}$ NMR spectroscopy over the temperature range between 300 and 223 K, and the coalescence temperature $T_c = 288$ K was observed. $^{31}P\{^1H\}$ NMR data for **15** (202 MHz, C_7D_8, 183 K): δ 30, 22, 20 (with overlapping Pt satellites). The VT-^1H NMR data (246−300 K) for **15** are provided in the Supporting Information.

A separate sample of **15** in C_7D_8 was examined by ^1H NMR spectroscopy from 320 to 360 K. Selected NMR data for **22** are as follows. $T = 320$ K: ^1H NMR data (500 MHz, C_7D_8) δ 2.21 (br with broad flanking Pt satellites (*J* not resolved); $^{31}P\{^1H\}$ NMR data (202 MHz, C_7D_8) δ 24 (br). $T = 340$ K: ^1H NMR data (500 MHz, C_7D_8) δ 3.22 (br s with flanking Pt satellites); $^{31}P\{^1H\}$ NMR data (202 MHz, C_7D_8) δ 24 (br). $T = 360$ K: ^1H NMR data (500 MHz, C_7D_8) δ 3.27 (s, $^1J_{PtH} = 684$, $^2J_{PtH} = 117$); $^{31}P\{^1H\}$ NMR data (202 MHz, C_7D_8) δ 24 (br). $^{31}P\{^1H\}$ NMR data after heating to 360 K (202 MHz, C_7D_8, 223 K): δ 30.2 (t, **15**), 21.4 (br, **15**). An X-ray crystal structure was determined for **22** on an aged sample from a room-temperature reaction of **1** with **14** (see the Supporting Information). The X-ray crystallographic structure for **22** was of poor quality but was used to confirm the connectivity of the complex.

$^1H-^1H$ EXSY (500 MHz, C_7D_8, 223 K, mixing time 0.90 s) experiment showed a correlation between the two distinct hydride sites in **15** at 1.9 and −5.2 ppm, indicating exchange between the two sites. The $^{31}P-^{31}P$ EXSY experiment (202 MHz, C_7D_8, 223 K, mixing time 0.80 s) showed a correlation between the two phosphorus sites for **15** at 30.3 and 21.5 ppm, indicating exchange between the two different sites.

Elevated-Temperature Study of $(Ph_3P)_2(H)Pt(\mu\text{-}SiC_{20}H_{24})(\mu\text{-}\eta^2\text{-}H\text{-}SiC_{20}H_{24})Pt(PPh_3)$ (15). In a NMR tube were placed **15** (8 mg, 0.004 mmol) and $OPPh_3$ (1 mg, 0.004 mmol, as internal standard) in C_7D_8 (1 mL). The sample was heated for 12 h at 363 K, followed by additional heating at 368 (30 h) and 373 K (17 h). NMR spectroscopic data were recorded at room temperature and at 223 K to monitor the disappearance of **15** and formation of new signals with intensities relative to $OPPh_3$. A minor amount of the trinuclear complex **23** was observed after 3 h at 368 K. The highest amount of **23** was observed after heating to 373 K for 17 h, where the ratio $OPPh_3$:**23**:**16** was ca. 12.5:1:1.5. Selected $^{31}P\{^1H\}$ NMR spectroscopic data for the reaction mixture after heating to 373 K for 17 h (202 MHz, C_7D_8, 300 K): δ 198.3 (s, $^1J_{PtP} = 2787$, $[(Ph_3P)Pt(\mu\text{-}PPh_2)]_2$), 71.6 (s, $^1J_{PtP} = 3320$, $^2J_{PtP} = 445$, $^3J_{PP} = 81$, **23**), 61.6 (s, $^1J_{PtP} = 2268$, unassigned), 99 (m), 54.1, 52.7, 21.0, 19.5 (unassigned resonances). In a separate experiment, a C_7D_8 solution of **15** was heated at 348 K for approximately 1 week. Analysis by $^{31}P\{^1H\}$ NMR spectroscopy at 223 K showed a resonance at 24.6 ppm for $OPPh_3$ and a resonance assigned to **22** at 36.6 ppm (s, $^1J_{PtP} = 4290$, $^2J_{PtP} = 252$, $^3J_{PP} = 60$), as well as a number of minor unassigned resonances.

In a separate experiment, complex **15** (40 mg, 0.023 mmol) was dissolved in 1.0 mL of C_7D_8 and placed in a NMR tube. The sample was heated for a total of 19 h at 373 K, after which a bright orange-red crystalline solid had formed in the tube. The solid was washed with pentane and dried to give 9 mg of complex **23** (27% based on Pt). NMR spectroscopic data for isolated **23** are as follows. ^1H NMR data (500 MHz, CD_2Cl_2, 300 K): δ 7.0−6.2 (aromatic CH), 1.3 (s, *t*-Bu), 1.2, (s, *t*-Bu). $^{31}P\{^1H\}$ NMR data (202 MHz, CD_2Cl_2, 300 K): δ 70.0 (s, $^1J_{PtP} = 3327$, $^2J_{PtP} = 448$, $^3J_{PP} = 82$).

Phosphine Exchange with $(Ph_3P)_2(H)Pt(\mu\text{-}SiC_{20}H_{24})(\mu\text{-}\eta^2\text{-}HSiC_{20}H_{24})Pt(PPh_3)$ (15). In a J. Young NMR tube were placed **15** (11 mg, 0.0062 mmol) and P(*p*-Tol)$_3$ (4 mg, 0.01 mmol) in 0.75 mL of C_7D_8. The solution was monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy just after mixing and after 24 h. Selected ^1H NMR data for the reaction mixture (500 MHz, 223 K, just after mixing): δ 1.9 (m, overlapping resonances, Pt···H···Si), −5.0 (m, overlapping resonances, $^1J_{PtH} = 530$ (combined), Pt−H). $^{31}P\{^1H\}$ NMR (202 MHz, 223 K, just after mixing): δ 30.3 (t, **15**), 27.7 (m, overlapping resonances), 21.3 (m, overlapping resonances for **15** and other mixed dinuclear species), 18.6 (m, overlapping resonances), −6.8 (s, PPh_3), −15.9 (s, P(*p*-Tol)$_3$). The $^{31}P\{^1H\}$ NMR spectrum after 24 h (223 K) was identical with the ^{31}P NMR spectrum collected just after addition. The $^{31}P-^{31}P$ EXSY experiment collected after 24 h (202 MHz, 223 K, mixing time 0.80 s) exhibited correlation peaks between all resonances at 30.3, 27.7, 21.3, and 18.6 ppm and with free PPh_3 and P(*p*-Tol)$_3$.

Addition of $(Ph_3P)_2Pt(H)[Si(C_{20}H_{24})H]$ (16) to $(Ph_3P)_2(H)Pt(\mu\text{-}SiC_{12}H_8)(\mu\text{-}\eta^2\text{-}HSiC_{12}H_8)Pt(PPh_3)$ (8). To a cooled solution of **1** (4 mg, 0.006 mmol, ca. 0.5 mL of C_7D_8) was added a solution of **14** (2 mg, 0.007 mmol, ca. 0.25 mL of C_7D_8), and the resulting mixture was then analyzed by $^{31}P\{^1H\}$ NMR (223 K) spectroscopy, which indicated the formation of **16**.[6a] A solution of **8** (8 mg, 0.005 mmol, ca. 0.25 mL of C_7D_8) was added to the above reaction mixture at 195 K. The reaction mixture was analyzed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy just after addition (223 K). After 1 h the temperature was raised to room temperature for several minutes and then returned to 223 K for NMR data collection. After 24 h at room temperature, the ^1H and $^{31}P\{^1H\}$ NMR spectra (223 K) were essentially identical. Selected ^1H NMR (500 MHz, 223 K, immediately after addition): δ 5.29 (s, C_2H_4), 4.94 (br s, small amount of unreacted **14**), 4.5 (s, H_2), −1.21 (br d, Pt−H for **16**), −1.59 (br d, Pt−H, unassigned), −4.96 (br m, Pt−H for **8**), −5.19 (br t, Pt−H for **24**). Selected $^{31}P\{^1H\}$ NMR (202 MHz, 223 K, immediately after addition): δ 35.1 (d, **16**), 33.6 (d, **16**), 31.1 (t, $Pt(PPh_3)$ for **8**), 30.9 (t, $^1J_{PtP} = 4200$, $^3J_{PP} = 25$, $Pt(PPh_3)$ for **24**), 25.4 (s, $OPPh_3$), 19.4 (d, $^1J_{PtP} = 3454$, $Pt(PPh_3)_2$ for **24**), 17.2 (d, $Pt(PPh_3)_2$ for **8**). Selected ^1H NMR (500 MHz, 223 K, after 24 h at room temperature): δ 2.0 (m, overlapping with C_7D_8 resonance, Pt···H···Si for **8**, **15**, **24**), −4.9 (m, Pt−H for **8**), −5.15 (m, overlapping Pt−H for **15** and **24**). Selected $^{31}P\{^1H\}$ NMR (202 MHz, 223 K, after 24 h at room temperature): δ 31.1 (t, for **8**), 30.9 (t, for **24**), 30.3 (t, for **15**), 21.4 (br d, for **15**), 19.4 (d, for **24**), 17.2 (d, for **8**). Signals were also observed for PPh_3 (−6.8 ppm) and $OPPh_3$ (25.5 ppm); a minor amount of **10** (28.9 ppm) and an unidentified resonance at 14.8 ppm (d) were also observed. The approximate ratio of the three dinuclear complexes **8**, **15**, and **24** after 24 h was 1:1.6:1.4 by integration of the $^{31}P\{^1H\}$ NMR spectrum using the $Pt(PPh_3)$ resonances for each complex.

Reaction between $(Ph_3P)_2(H)Pt(\mu\text{-}SiC_{12}H_8)(\mu\text{-}\eta^2\text{-}HSiC_{12}H_8)Pt(PPh_3)$ (8) and $(Ph_3P)_2Pt(H)(\mu\text{-}SiC_{20}H_{24})(\mu\text{-}\eta^2\text{-}HSiC_{20}H_{24})Pt(PPh_3)$ (15). In a NMR tube were placed **8** (5 mg, 0.003 mmol) and **15** (6 mg, 0.003 mmol) in ca. 0.75 mL of C_7D_8. The orange solution was heated in an oil bath at 348 K for approximately 16 h to give a red solution that was analyzed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. Selected $^{31}P\{^1H\}$ NMR spectroscopy (202 MHz, 300 K, 16 h after heating to 348 K): δ 71.2, 70.8, 70.5 (**9**), 70.1, 65.2, 64.8, 64.4, 30.6−28.9, 24.8, 24.5 ($OPPh_3$). Selected $^{31}P\{^1H\}$ NMR spectroscopy (202 MHz, 223 K, 16 h after heating to 348 K): δ 71.2, 70.5, 70.0, 69.4, 69.2, 69.0, 63.2, 62.8, 62.4, 59.0, 30.1 (t, **16**), 21.4 (br d, **16**), −6.6 (PPh_3).

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Supporting Information Available: Figures giving selected VT and 2D NMR spectroscopic data for **8** and **15** and $^{31}P\{^1H\}$ NMR data for the elevated-temperature reaction between **8** and **15** and a CIF file containing X-ray crystallographic data for complex **22**. This material is available free of charge via the Internet at http://pubs.acs.org.

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