Spectroscopic and Structural Studies of Thermally Unstable Intermediates Generated in the Reaction of $[Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)]$ with Dihydrodisilanes

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The reaction of $[Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)]$ (**1**) with 1,2-dihydrodisilane $HSiR_2SiR_2H$ (R = Ph, Me) was investigated by NMR spectroscopy and X-ray diffraction analysis. In the case of R = Ph, the treatment of **1** with $HSiPh_2SiPh_2H$ at −60 °C afforded the disilanylplatinum hydride $[Pt(PPh_3)_2(H)(SiPh_2SiPh_2H)]$ (**2a**) by an oxidative addition of Si−H to the Pt center. Complex **2a** was converted to the bis(silyl)platinum complex $[Pt(PPh_3)_2(SiHPh_2)_2]$ (**3a**) by 1,2-migration of the silyl group with a first-order rate constant of $5.5(2) \times 10^{-4}\ s^{-1}$ at –40 °C. The silylplatinum hydride $[Pt(PPh_3)_2(H)(SiHPh_2)]$ (**4a**) was formed by the elimination of a $SiPh_2$ unit from the toluene solution of **3a** maintained at –20 °C for 2 days. Then, the dimerization and reductive elimination of dihydrogen of **4a** at room temperature afforded the symmetrical dinuclear complex $[Pt(PPh_3)(\mu\text{-}SiHPh_2)]_2$ (**6a**). Complex **6a** also was obtained by an alternative method wherein **1** reacted with $HSiPh_2SiPh_2H$ at room temperature. In the case of R = Me, the bis(silyl)platinum complex $[Pt(PPh_3)_2(SiHMe_2)_2]$ (**3b**) was formed even at a temperature as low as −70 °C; this formation reaction was considerably faster than that of **3a**, and no disilanylplatinum hydride was detected. While **3b** was stable below 0 °C, it underwent dimerization at room temperature to afford the unsymmetrical dinuclear complex $[(PPh_3)_2Pt(H)(\mu\text{-}SiMe_2)(\mu\text{-}SiHMe_2)Pt(PPh_3)]$ (**5b**), in which one hydride of the $Pt(PPh_3)_2$ site binds to the Pt center in a terminal binding mode and the other hydride of the $Pt(PPh_3)$ site bridges between the Pt and the Si atoms in a nonclassical 3c−2e interaction. The liberation of one PPh_3 from the $Pt(PPh_3)_2$ site in **5b** afforded $[Pt(PPh_3)(\mu\text{-}SiHMe_2)]_2$ (**6b**), which was similar to **6a**; the ^1H and $^{31}P\{^1H\}$ NMR data after the addition of excess PPh_3 to **6b** indicated the equilibrium between **5b** and **6b**. These results suggest that the reaction in the **1**/$HSiR_2SiR_2H$ system proceeds in the following order: an oxidative addition of Si−H, 1,2-migration, elimination of SiR_2, dimerization accompanying the reductive elimination of dihydrogen, and liberation of PPh_3.

Introduction

The activation of the Si−H and Si−Si bonds by metal complexes is one of the important steps in the syntheses of new organosilane compounds.[1,2] A zerovalent platinum complex is well known as a catalyst for the insertion reaction. A silylplatinum species is considered as an intermediate during the reaction and has been synthesized by a Si−H oxidative addition of hydrosilanes to Pt(0) complexes and a salt elimination from Pt(II) halide complexes on reaction with silyllithium compounds.[3] The treatment of Pt(0) complexes with SiH_nR_{4-n} in various molar ratios affords silylplatinum(II) hydride and bis(silyl)platinum(II) complexes by the oxidative addition of the Si−H bond. Di- and trinuclear platinum complexes are synthesized by the reactions of Pt(0) complexes with primary silanes SiH_3R and secondary silanes SiH_2R_2 via intermediates such as silylplatinum(II) hydride and bis(silyl)platinum(II) complexes, respectively.[4,5]

Furthermore, the reactions of Pt(0) complexes with disilanes $H_nSiR_{3-n}SiR_{3-n}H_n$ containing a Si−Si bond as well as a Si−H bond have been studied.[6] On the basis of the ^1H NMR signals, Fink and Michalczyk et al. have reported that the mononuclear $[Pt(dcpe)(SiH_2SiH_3)_2]$ (dcpe = 1,2-bis(dicyclohexylphosphino)-ethane) and dinuclear complexes $[Pt(dcpe)(\mu\text{-}1,2\text{-}SiH_2SiH_2)]_2$ were generated in a 4:1 ratio when H_3SiSiH_3 is rapidly added to a solution of $[Pt(dcpe)(H)_2]$ in toluene and that the structures of both

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[1] Sharma, H. K.; Pannell, K. H. *Chem. Rev.* **1995**, *95*, 1351–1374.

[2] Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175–292.

[3] (a) Ozawa, F.; Kamite, J. *Organometallics* **1998**, *17*, 5630–5639. (b) Roy, A. K.; Taylor, R. B. *J. Am. Chem. Soc.* **2002**, *124*, 9510–952. (c) Kang, Y.; Kang, S.; Ko, J. *Organometallics* **2000**, *19*, 1216–1224. (d) Tsuji, Y.; Nishiyama, K.; Hori, S.; Ebihara, M.; Kawamura, T. *Organometallics* **1998**, *17*, 507–512. (e) Hashimoto, H.; Sekiguchi, A.; Iwamoto, T.; Kabuto, C.; Kira, M. *Organometallics* **2002**, *21*, 454–456. (f) Kim, Y.-J.; Choi, E.-H.; Lee, S. W. *Organometallics* **2003**, *22*, 3316–3319. (g) Shimada, S.; Rao, M. L. N.; Li, Y.-H.; Tanaka, M. *Organometallics* **2005**, *24*, 6029–6036. (h) Goikhman, R.; Karakuz, T.; Shimon, L. J. W.; Leitus, G.; Milstein, D. *Can. J. Chem.* **2005**, *83*, 786–792. (i) Sagawa, T.; Asano, Y.; Ozawa, F. *Organometallics* **2002**, *21*, 5879–5886.

[4] (a) Zarete, E. A.; Tessier-Youngs, C. A.; Youngs, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 4068–4070. (b) 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*, 192–205. (c) Tanabe, M.; Yamada, T.; Osakada, K. *Organometallics* **2003**, *22*, 2190–2192. (d) Tanabe, M.; Ito, D.; Osakada, K. *Organometallics* **2007**, *26*, 459–462. (e) Braddock-Wilking, J.; Levchinsky, Y.; Rath, N. P. *Organometallics* **2000**, *19*, 5500–5510. (f) Shimada, S.; Li, Y.-H.; Rao, M. L.; Tanaka, M. *Organometallics* **2006**, *25*, 3796–3798.

[5] (a) Osakada, K.; Tanabe, M.; Tanase, T. *Angew. Chem., Int. Ed.* **2000**, *39*, 4053–4055. (b) Braddock-Wilking, J.; Corey, J. Y.; Dill, K.; Rath, N. P. *Organometallics* **2002**, *21*, 5467–5469.

[6] (a) Michalczyk, M. J.; Recatto, C. A.; Calabrese, J. C.; Fink, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 7955–7957. (b) Pham, E. K.; West, R. *J. Am. Chem. Soc.* **1989**, *111*, 7667–7668. (c) Yamashita, H.; Tanaka, M.; Goto, M. *Organometallics* **1992**, *11*, 3227–3232. (d) Heyn, R. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 1917–1919.

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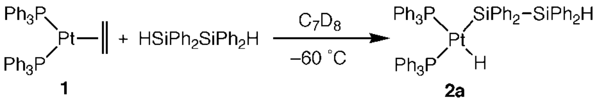
the complexes were identified by X-ray diffraction (XRD) analysis. Moreover, it was confirmed by ^{1}H NMR spectroscopy that the treatment of [Pt(dcpe)(H)$_2$] with $H_2SiMeSiMeH_2$ afforded the bis(silyl)platinum(II) complex [Pt(dcpe)(SiH$_2$Me)$_2$] via the disilanylplatinum(II) hydride complex [Pt(dcpe)(H)(SiHMeSiH$_2$Me)].[6a] It has been clarified by West and co-workers that the η^2-disilene platinum complex [Pt(dppe)(η^2-Si$_2{}^i$Pr$_4$)] (dppe = 1,2-bis(diphenylphosphino)ethane) was obtained when the Pt(0)−olefin complex [Pt(dppe)(η^2-C$_2$H$_4$)] reacted with HSi^{i}Pr$_2$Si^{i}Pr$_2$H in toluene.[6b]

We are eager to study the reaction behavior of a zerovalent platinum complex with compounds of group 14 elements and have synthesized many silylplatinum and germylplatinum complexes.[7] Among them, the reaction of [Pt(PPh$_3$)$_2$(η^2-C$_2$H$_4$)] with a silylgermyl compound HGePh$_2$(SiMe$_2$)$_2$GePh$_2$H afforded [Pt(PPh$_3$)$_2${GePh$_2$(SiMe$_2$)$_2$GePh$_2$}] with a five-membered ring of PtSi$_2$Ge$_2$.[8] In this paper, we report the resolution of the structures of the intermediates in the reaction of [Pt(PPh$_3$)$_2$(η^2-C$_2$H$_4$)] (**1**) with 1,2-dihydrodisilane HSiR$_2$SiR$_2$H (R = Ph, Me) from −60 °C to room temperature by NMR spectroscopy and XRD analysis.

Results and Discussion

Reaction of Complex 1 with HSiR$_2$SiR$_2$H below −30 °C. When complex **1** was reacted with HSiPh$_2$SiPh$_2$H in toluene-d_8 at −60 °C, a new species was formed during the progress of the reaction. In the ^{1}H NMR spectra, multiple peaks were observed in the aromatic region of 7–8 ppm (Figures S1, S2). A new intense peak at 5.30 ppm exhibited the evolution of free ethylene gas attributed to the liberation from the platinum center in **1**, and the new Si−H peak at 5.71 ppm with ^{195}Pt satellites appeared at a lower magnetic field than the Si−H peak in the starting material HSiPh$_2$SiPh$_2$H. A Pt−H peak was observed centered at −1.83 ppm as a doublet of doublets with ^{195}Pt satellites and was similar to that of the platinum hydride complexes reported hitherto.[9] One of the two Si−H bonds in the disilane permits the platinum atom to undergo oxidative addition, and the other remains on the second silicon atom, consistent with the formation of the disilanylplatinum(II) hydride complex [Pt(PPh$_3$)$_2$(H)(SiPh$_2$SiPh$_2$H)] (**2a**; eq 1). In the ^{31}P{^{1}H} NMR spectrum (Figure 1), two doublets with ^{195}Pt satellites were observed at 37.4 and 31.5 ppm, indicating that the phosphine atoms of PPh$_3$ are nonequivalent. Complex **2a** is thermally unstable and is converted slowly at −60 °C and rapidly at −30 °C to the bis(silyl)platinum complex [Pt(PPh$_3$)$_2$(SiHPh$_2$)$_2$] (**3a**; eq 2). The conversion of **2a** to **3a** obeyed a first-order rate law, and the rate constant was estimated at 5.5(2) × 10^{-4} s^{-1} from the ratio of the area of the peak at 7.82 ppm of **2a** to that of a residual protio toluene-d_8 at 2.09 ppm (Figure S3). In the ^{1}H NMR spectra for the conversion of **2a** to **3a** (Figure S1), the peaks in the aromatic region showed two phenyl groups, of which one was attached on the P atoms and the other is on the Si atoms. The terminal Si−H and Pt−H signals disappeared, and a new Si−H signal appeared at 5.80 ppm as a triplet with ^{195}Pt satellites, although it resembled a septet due to an overlay of the satellites. Furthermore, a peak due to the dihydrogen was not detected around 4.5 ppm. In the ^{31}P{^{1}H} NMR spectra (Figure 1), two doublets disappeared and a singlet with the ^{195}Pt satellites appeared at 31.6 ppm. The Si−H signal and no detection of dihydrogen in the ^{1}H NMR spectral change of the toluene-d_8 solution of **2a** support that **3a** is assigned not to an η^2-disilene platinum complex but to a bis(silyl)platinum complex.



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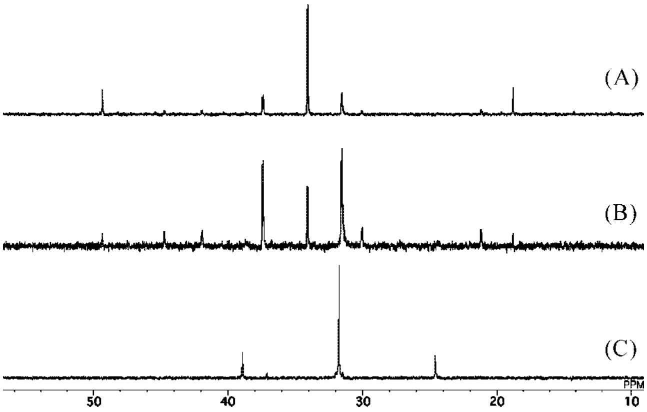
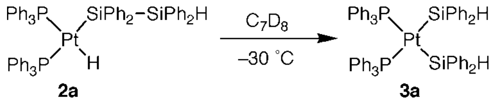


Figure 1. ^{31}P{^{1}H} NMR spectra for the reaction of **1** with HSiPh$_2$SiPh$_2$H at −60 °C for 10 min after mixing (A) and for 3 h after mixing (B). The solution B was standing at –30 °C for 10 min (C).



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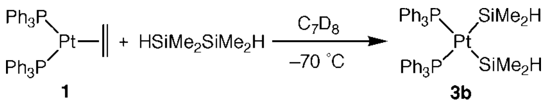
On the other hand, **1** reacted with HSiMe$_2$SiMe$_2$H rapidly even at −70 °C to obtain the bis(silyl)platinum(II) complex [Pt(PPh$_3$)$_2$(SiHMe$_2$)$_2$] (**3b**; eq 3) without the any evidence for the formation of a disilanylplatinum(II) hydride similar to **2a**. The small methyl groups on the Si atom make the silyl groups SiHMe$_2$ more reactive to the Pt center as compared with the SiHPh$_2$ units; due to this, **2b** is converted to **3b** more rapidly than **2a** to **3a**. In the NMR spectrum of **3b**, the Si−H signal appeared as a triplet of septets at 4.42 ppm, and the Si−Me signals appeared as a doublet with the ^{195}Pt satellites. The signals for the ^{31}P nuclei were observed as a singlet at 34.9 ppm with the ^{195}Pt satellites. Moreover, both **3a** and **3b** were less thermally stable in contrast to other bis(silyl)platinum complexes reported hitherto, which were stable at room temperature.[3a,6a,d,7a,10] The conversions of **3a** and **3b** commenced above −20 and 0 °C, respectively, which are described in the next section. It is proposed that an arylphosphine PPh$_3$ causes the low thermal stability because complexes with high thermal stability contain



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[7] (a) Mochida, K.; Wada, T.; Suzuki, K.; Hatanaka, W.; Nishiyama, Y.; Nanjo, M.; Sekine, A.; Ohashi, Y.; Sakamoto, M.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 123–137. (b) Usui, Y.; Fukushima, T.; Nanjo, M.; Mochida, K.; Akasaka, K.; Kudo, T.; Komiya, S. *Chem. Lett.* **2006**, *35*, 810–811. (c) Mochida, K.; Fukushima, T.; Suzuki, M.; Hatanaka, W.; Takayama, M.; Usui, Y.; Nanjo, M.; Akasaka, K.; Kudo, T.; Komiya, S. *J. Organomet. Chem.* **2007**, *692*, 395–401.

[8] Usui, Y.; Hosotani, S.; Ogawa, A.; Nanjo, M.; Mochida, K. *Organometallics* **2005**, *24*, 4337–4339.

[9] (a) Azizian, H.; Dixon, K. R.; Eaborn, C.; Pidcock, A.; Shuaib, N. M.; Vinaixa, J. *J. Chem. Soc., Chem. Commun.* **1982**, 1020–1022. (b) Packett, D. L.; Syed, A.; Trogler, W. C. *Organometallics* **1988**, *7*, 159–166. (c) Chan, D.; Duckett, S. B.; Heath, S. L.; Khazal, I. G.; Perutz, R. N.; Sabo-Etienne, S.; Timmins, P. L. *Organometallics* **2004**, *23*, 5744–5756.

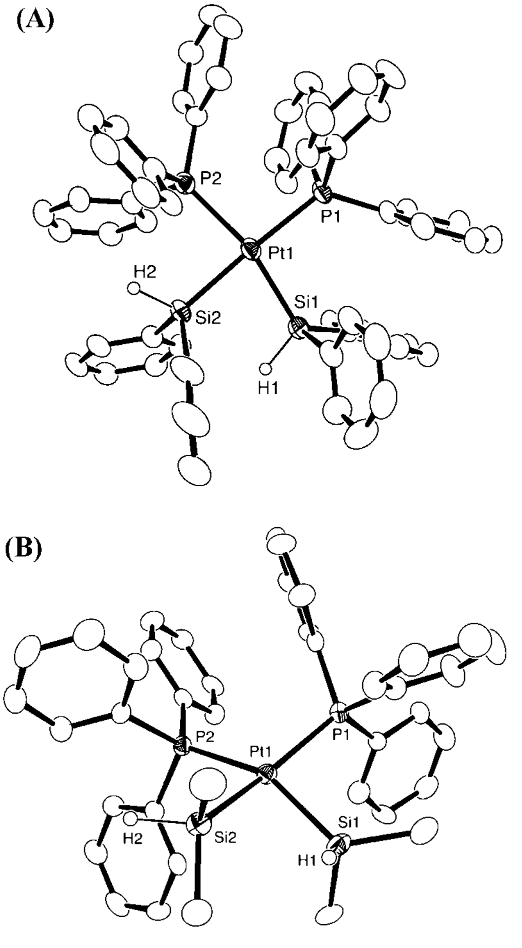


Figure 2. Crystal structure of **3a** (A) and **3b** (B) showing 50% probability thermal ellipsoids. The hydrogen atoms except for one on Si are omitted for clarity. Selected bond lengths (Å) and angles (deg), **3a**: Pt(1)−P(1) 2.3599(17), Pt(1)−P(2) 2.3767(18), Pt(1)−Si(1) 2.358(2), Pt(1)−Si(2) 2.3973(19), Si(1)−Si(2) 3.069(3); P(1)−Pt(1)−P(2) 96.54(6), P(1)−Pt(1)−Si(1) 96.98(7), P(1)−Pt(1)−Si(2) 177.20(7), P(2)−Pt(1)−Si(1) 165.94(6), P(2)−Pt(1)−Si(2) 86.16(6), Si(1)−Pt(1)−Si(2) 80.37(7); **3b**: Pt(1)−P(1) 2.3382(18), Pt(1)−P(2) 2.3452(16), Pt(1)−Si(1) 2.3828(19), Pt(1)−Si(2) 2.4019(19), Si(1)−Si(2) 3.134(3); P(1)−Pt(1)−P(2) 104.17(6), P(1)−Pt(1)−Si(1) 93.57(7), P(1)−Pt(1)−Si(2) 159.82(6), P(2)−Pt(1)−Si(1) 155.49(6), P(2)−Pt(1)−Si(2) 86.72(6), Si(1)−Pt(1)−Si(2) 81.85(7).

aliphatic alkylphosphines such as PEt_3 and dcpe. Both **3a** and **3b** were obtained as crystals suitable for XRD analysis due to its thermal stability below −30 °C.

The Pt atom in the crystal structures of both **3a** and **3b** has a four-coordinate square-planar geometry with a P_2Si_2 donor set (Figure 2), and the bond lengths of Pt−Si are similar to those of bis(silyl)platinum(II) complexes reported previously.[7a,10] The bond distances between platinum and the hydrides on the Si atoms in **3a** and **3b** are more than 3 Å, and the two hydrides are not bridged between the Pt and Si atoms but are localized on each Si atom. The bond distances of Si(1)−Si(2) in **3a**and **3b** are 3.07 and 3.14 Å, respectively; these are beyond the range of a Si−Si single bond in cyclic compounds (2.21–2.51 Å),[11] indicating that there is no interaction between the two Si atoms.

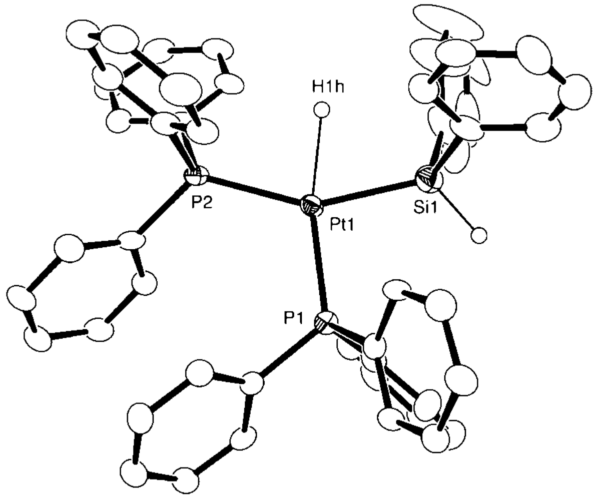
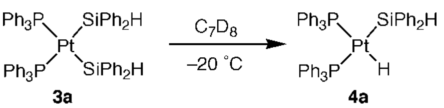


Figure 3. Crystal structure of **4a**, showing 50% probability thermal ellipsoids. The hydrogen atoms except for ones on Si and Pt are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt(1)−P(1) 2.2900(14), Pt(1)−P(2) 2.3140(14), Pt(1)−Si(1) 2.3368(17), Pt(1)−H(1h) 1.885(3), P(1)−Pt(1)−P(2) 111.98(5), P(1)−Pt(1)−Si(1) 95.95(6), P(1)−Pt(1)−H(1h) 166.4(7), P(2)−Pt(1)−Si(1) 152.08(6), P(2)−Pt(1)−H(1h) 80.97(10), Si(1)−Pt(1)−H(1h) 71.19(9).

The P−Pt−Si(trans to P) bond angles in **3b** are 160° and 155° less than that of **3a** and the reported bis(silyl)platinum complexes, which implies that the coordination plane in **3b** is rather distorted.

Hence, the single Si−H oxidative addition of $HSiPh_2SiPh_2H$ to the Pt center in **1** affords **2a** with the elimination of ethylene; subsequently, the terminal $SiHPh_2$ of the disilanyl unit in **2a** is transferred to the Pt center to generate complex **3a**. The bis(silyl)platinum complex **3b** is rapidly generated even at −70 °C during the reaction of **1** with $HSiMe_2SiMe_2H$, although **2b** could not be detected. It is possible that **2b** is formed transiently and rapidly converted to **3b** by analogy to the results for $HSiPh_2SiPh_2H$.

Change in $[Pt(PPh_3)_2(SiHR_2)_2]$ (3a, 3b). We attempted to examine the change in **3a** at −20 °C in toluene-d_8. The ^{1}H NMR spectrum of the aromatic region in the toluene-d_8 solution of **3a** (after allowing the solution to stand for 2 days at −20 °C) showed the presence of the silylplatinum(II) hydride complex *cis*-$[Pt(PPh_3)_2(H)(SiHPh_2)]$ (**4a**; eq 4) and a few minor products (Figure S4). The NMR data of **4a** are consistent with that reported by Braddock-Wilking et al. in a reaction of **1** with a monosilane SiH_2Ph_2.[12]



(4)

4a (Figure 3) is determined to be the silylplatinum(II) hydride complex *cis*-$[Pt(PPh_3)_2(H)(SiHPh_2)]$ by XRD analysis, wherein formally one of the two silyl groups in **3a** is liberated as a silylene group $:SiPh_2$ and the hydride remains on Pt. The two hydrides H(1h) and H(1s) determined by difference Fourier maps are localized on Pt(1) and Si(1), respectively. The bond length of Pt(1)−Si(1) is shorter than that in the silylplatinum

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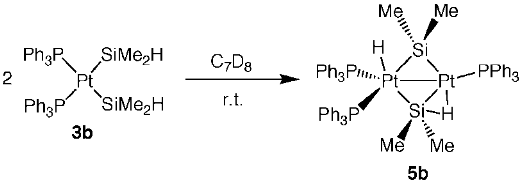
(10) (a) Pham, E. K.; West, R. *Organometallics* **1990**, *9*, 1517–1523. (b) Kim, Y.-J.; Park, J.-I.; Lee, S.-C.; Osakada, K.; Tanabe, M.; Choi, J.-C.; Koizumi, T.; Yamamoto, T. *Organometallics* **1999**, *18*, 1349–1352.

(11) Kaftory, M.; Kapon, M.; Botoshansky, M. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1998; Vol. 2, Part 1, p 202.

(12) Braddock-Wilking, J.; Corey, J. Y.; Trankler, K. A.; Xu, H.; French, L. M.; Praingam, N.; White, C.; Rath, N. P. *Organometallics* **2006**, *25*, 2859–2871.

hydride complexes with a tertiary silane reported previously, although the Pt–P bond lengths are similar to them.[13] The terminal Pt–H bond is 1.885(3) Å, longer than that found in the platinum complexes with a terminal hydride.[9c,12,14,15b] Complex **4a** has been already synthesized by Pidcock et al. in 1974, but it could not be isolated as a powder or crystals owing to its low thermal stability.[16] We have succeeded in isolating **4a** as single crystals as well as in synthesizing it by an alternative method using the dihydrodisilane $HSiPh_2SiPh_2H$. Unfortunately, we have no proof for the silylene elimination, which is a key step in the conversion.

In the case of complex **3b**, the ^1H and $^{31}P\{^1H\}$ NMR spectra showed few changes in the range −20 to 0 °C. After the solution was allowed to stand at room temperature overnight, the ^1H and $^{31}P\{^1H\}$ NMR spectra indicated a loss of **3b** and formation of the unsymmetrical diplatinum complex $[(PPh_3)_2Pt(H)(\mu\text{-}SiMe_2)(\mu\text{-}SiHMe_2)Pt(PPh_3)]$ (**5b**; eq 5), and no silylplatinum(II) hydride complex was observed. In the ^1H NMR spectrum of **5b** measured at −70 °C in CD_2Cl_2 (Figure S5), the Si–Me signals were observed as two resonances of a singlet at 0.11 and −0.43 ppm, and the Pt–H signals were observed as a doublet at 0.70 ppm in the region of the hydride bridged between Pt and Si and a triplet with two sets of satellites at −7.05 ppm in the region of the terminal hydride on Pt. These resonances were observed at a magnetic field higher than that of the unsymmetrical diplatinum complex bearing silafluorenyl units,[17] causing an electronic deficiency on the Si atom included in the aromatic ring. The variable-temperature ^1H NMR data of **5b** from −80 to 20 °C showed a dynamic behavior, and the coalescence temperature was determined to be –30 °C (Figure 4). The behavior concerns an intra- or intermolecular exchange of PPh_3 between the $Pt(PPh_3)_2$ and $Pt(PPh_3)$ sites. The trialkylphosphine exchange has been reported in related unsymmetrical dinuclear palladium complexes.[18] The $^{31}P\{^1H\}$ NMR spectra (Figure S5) showed a triplet at 31.7 ppm assignable to the resonance of the ^{31}P nuclei on the $Pt(PPh_3)$ side and a doublet at 22.4 ppm for the P nuclei on the $Pt(PPh_3)_2$ side.



3b **5b**

(5)

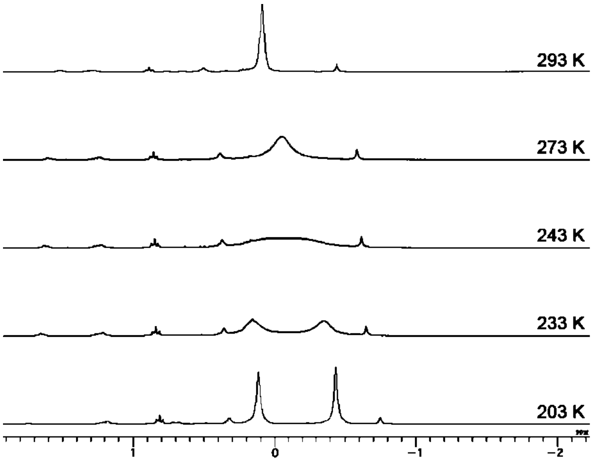


Figure 4. Variable-temperature ^1H NMR spectra in the Si–Me region of **5b**.

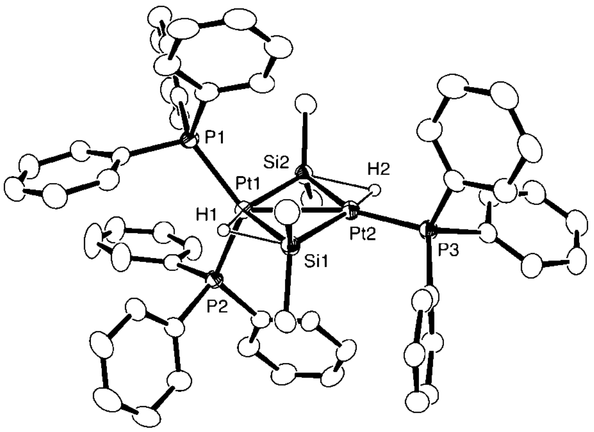


Figure 5. Crystal structure of **5b**, showing 50% probability thermal ellipsoids. The hydrogen atoms except for H1 and H2 are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt(1)–Pt(2) 2.7518(2), Pt(1)–P(1) 2.2826(11), Pt(1)–P(2) 2.3268(12), Pt(1)–Si(1) 2.4602(12), Pt(1)–Si(2) 2.3509(13), Pt(1)–H(1) 1.57(5), Pt(2)–P(3) 2.2477(11), Pt(2)–Si(1) 2.3464(12), Pt(2)–Si(2) 2.4241(12), Pt(2)–H(2) 1.63(5), Si(1)–H(1) 1.79(5), Si(2)–H(2) 1.95(5); P(1)–Pt(1)–P(2) 118.49(4), P(1)–Pt(1)–Si(1) 118.35(4), P(1)–Pt(1)–Si(2) 99.21(4), P(1)–Pt(1)–Pt(2) 125.34(3), P(2)–Pt(1)–Si(1) 107.23(4), P(2)–Pt(1)–Si(2) 102.53(4), P(2)–Pt(1)–Pt(2) 114.51(3), Si(1)–Pt(1)–Si(2) 109.18(4), P(3)–Pt(2)–Si(1) 98.63(4), P(3)–Pt(2)–Si(2) 150.80(4), Si(1)–Pt(2)–Si(2) 110.57(4), P(3)–Pt(2)–Pt(1) 155.59(3).

In the crystal structure of **5b** (Figure 5), Pt(1) has a tetrahedral geometry with a P_2Si_2 donor set, and Pt(2) has a planar geometry with a PSi_2 donor set. The two platinum atoms are bridged by two $SiHMe_2$ groups, and the bond distance of Pt(1)–Pt(2) is 2.7535(5) Å longer than that of the symmetrical diplatinum complexes containing Pt–Pt single bonds.[4,19] The two hydrides are determined by difference Fourier maps and are bridged between Pt and Si. **5b** exhibits two alternating long/short Pt–Si bonds in which the long Pt–Si bonds are associated with a nonclassical 3c–2e interaction. However, one of the two hydrides binds to the Pt center as a terminal hydride, as determined from NMR experiments, wherein the Pt–H signals were observed at an upfield resonance of –7.05 ppm. Braddock-Wilking and co-workers have reported that the hydride of the $Pt(PPh_3)_2$ site is a terminal binding mode in the unsymmetrical diplatinum complex with silafluorenyl units.[17] From a ^1H–^{31}P HMBC experiment of **5b** (Figure S6), the terminal hydride at −7.05 ppm correlated to the doublet signal of the $Pt(PPh_3)_2$ site, and the bridged hydride at 0.70 ppm correlated to the triplet signal of the $Pt(PPh_3)$ site. Hence, in solution, the hydride (H1)

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[13] (a) Latif, L. A.; Eaborn, C.; Pidcock, A. P.; Weng, N. S. *J. Organomet. Chem.* **1994**, *474*, 217–221. (b) Koizumi, T.; Osakada, K.; Yamamoto, T. *Organometallics* **1997**, *16*, 6014–6016.

[14] White, C. P.; Braddock-Wilking, J.; Corey, J. Y.; Xu, H.; Redekop, E.; Sedinkin, S.; Rath, N. P. *Organometallics* **2007**, *26*, 1996–2004.

[15] Kloek, S. M.; Goldberg, K. I. *J. Am. Chem. Soc.* **2007**, *129*, 3460–3461.

[16] Eaborn, C.; Ratcliff, B.; Pidcock, A. *J. Organomet. Chem.* **1974**, *65*, 181.

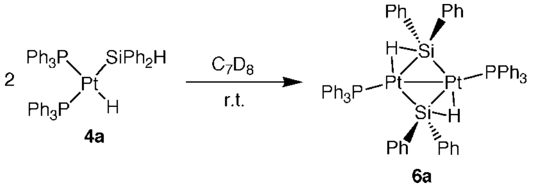
[17] (a) Braddock-Wilking, J.; Corey, J. Y.; Trankler, K. A.; Dill, K. M.; French, L. M.; Rath, N. M. *Organometallics* **2004**, *23*, 4576–4584. (b) Braddock-Wilking, J.; Corey, J. Y.; French, L. M.; Choi, E.; Speedie, V. J.; Rutherford, M. F.; Yao, S.; Xu, H.; Rath, N. P. *Organometallics* **2006**, *25*, 3974–3988.

[18] Kim, Y.-J.; Lee, S.-C.; Park, J.-I.; Osakada, K.; Choi, J.-C.; Yamamoto, T. *Organometallics* **1998**, *17*, 4929–4931.

[19] Taylor, N. J.; Chieh, P. C.; Carty, A. J. *J. Chem. Soc., Chem. Commun.* **1975**, 448–449.

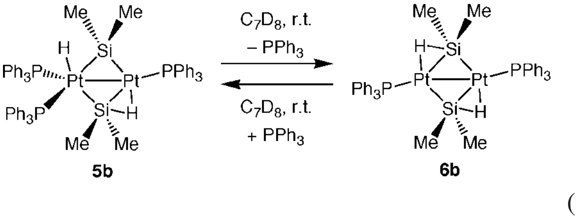
of the Pt(PPh$_3$)$_2$ site of **5b** is localized on the Pt atom as a terminal hydride.

Conversion to Symmetrical Dinuclear Complexes [Pt(PPh$_3$)(μ-SiHR$_2$)]$_2$ (6a, 6b). When the ^{1}H NMR signal of **4a** recorded after allowing it to stand in toluene-d_8 or CD$_2$Cl$_2$ at room temperature overnight decreased, the symmetrical diplatinum complex [Pt(PPh$_3$)(μ-SiHPh$_2$)]$_2$ (**6a**; eq 6) was crystallized in the NMR tube due to the its low solubility in toluene. Complex **4a** is converted into **6a** by dimerization and reductive elimination of dihydrogen on Pt. Complex **6a** was also afforded by the treatment of **1** with HSiPh$_2$SiPh$_2$H in toluene at room temperature, which implies that **2a**, **3a**, and **4a** are intermediates in the process when **1** is reacted with HSiPh$_2$SiPh$_2$H to form **6a**. The structure of **6a** was confirmed by XRD analysis, wherein the hydride of SiHPh$_2$ is bridged between Pt and Si in an η^2-binding fashion, and is consistent with the crystal structural data reported previously.[20] The bis(silyl)platinum complex with silafluorenyl units and **3b** provided the corresponding unsymmetrical dinuclear complexes,[17] but the unsymmetrical dinuclear complex [(PPh$_3$)$_2$Pt(H)(μ-SiPh$_2$)(μ-SiHPh$_2$)Pt(PPh$_3$)] (**5a**) during the conversion of **4a** into **6a** could not be detected with ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. The steric repulsion between PPh$_3$ and SiHPh$_2$ is expected to increase if [(PPh$_3$)$_2$Pt(H)(μ-SiPh$_2$)(μ-SiHPh$_2$)-Pt(PPh$_3$)] (**5a**) was generated transiently. Therefore, one PPh$_3$ group of the Pt(PPh$_3$)$_2$ site is liberated from the Pt atom to minimize the repulsion; due to this, the symmetrical dinuclear complex **6a** is generated from **4a** without the detection of the unsymmetrical one. In fact, when [Pt(PMePh$_2$)$_2$(μ-SiH(IMP))]$_2$ (IMP = 2-isopropyl-6-methylphenyl), which is stable in the solid state, is dissolved in organic solvents, one PMePh$_2$ group was liberated from the Pt atom despite the expected lower hindrance of the phosphine, PMePh$_2$, as compared to PPh$_3$ to form [Pt-(PMePh$_2$)(μ-SiH(IMP))]$_2$.[21]



(6)

In the case of R = Me, **5b** is converted into the symmetrical diplatinum complex [Pt(PPh$_3$)(μ-SiHMe$_2$)]$_2$ (**6b**; eq 7) by the liberation of one PPh$_3$ from the Pt(PPh$_3$)$_2$ site. In the ^{1}H NMR spectra of **6b**, the Pt−H−Si and Si−Me signals were observed as a singlet at 1.58 and 0.22 ppm, respectively. The ^{31}P{^{1}H} NMR data of **6b** exhibited part of an AA′XX′ spin system pattern associated with a diplatinum complex. Moreover, when excess PPh$_3$ was added to **6b**, the ^{1}H and ^{31}P{^{1}H} spectra showed only regeneration of **5b** without the formation of other species. The conversion of **5b** to **6b** in solution indicates the equilibrium between them for the liberation/rebinding of PPh$_3$ to the Pt(PPh$_3$)$_2$ center. The Pt centers in the crystal structure of **6b** (Figure 6) have a three-coordinate planar geometry and are bridged by two SiHMe$_2$ groups. The bond lengths and angles are similar to those of the symmetrical dipalladium and diplatinum complexes.[4,22] Complex **6b** was synthesized by the reaction of **1** with the monosilane Me$_2$SiH$_2$ at a molar ratio of 1:4,[20a] but the crystal structure has not been reported yet. The treatment of **1** with HSiMe$_2$SiMe$_2$H at room temperature does not afford the symmetrical complex **6b**, but an unsymmetrical complex **5b**; this is in contrast to the HSiPh$_2$SiPh$_2$H system, where the symmetrical complex **6a** is obtained as the product. The difference in the products formed may be due to the steric repulsion between the alkyl groups on Si and P. The substitution of the phenyl group on Si with a methyl group decreases the steric repulsion and keeps PPh$_3$ bound to the Pt(PPh$_3$)$_2$ center in order to maintain the unsymmetrical structure of **5b**.



(7)

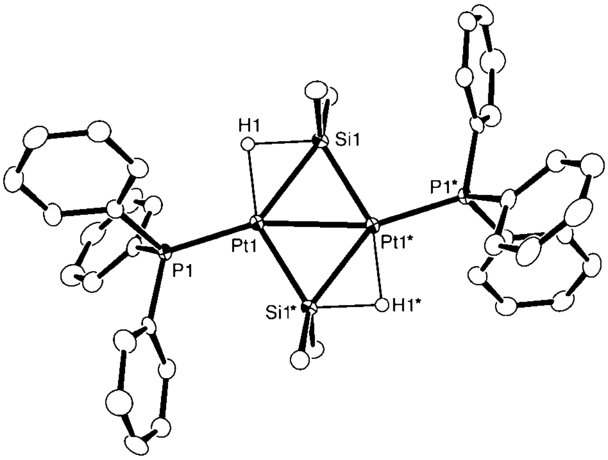


Figure 6. Crystal structure of **6b**, showing 50% probability thermal ellipsoids. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt(1)−Pt(1)* 2.7010(4), Pt(1)−P(1) 2.2537(15), Pt(1)−Si(1) 2.4273(16), Pt(1)−Si(1)* 2.3304(16), Pt(1)−H(1) 1.86(8), Si(1)−H(1) 1.70(8); P(1)−Pt(1)−Si(1) 145.12(6), P(1)−Pt(1)−Si(1)* 103.78(6), Si(1)−Pt(1)−Si(1)* 110.85(4), P(1)−Pt(1)−Pt(1)* 160.52(4).

Hence, the reaction scheme of **1** with general dihydrodisilanes can be described as follows (Scheme 1): A disilanyl platinum hydride complex **2** is generated by the oxidative addition of one Si−H in HSiR$_2$SiR$_2$H to the Pt center of **1**. Complex **2** rapidly converts into the bis(silyl)platinum complex **3** by 1,2-migration. The elimination of silylene leads to the conversion of **3** into the silylplatinum hydride complex **4**. The unsymmetrical dinuclear complex **5** is generated by dimerization and reductive elimination of H$_2$ of **4**. One PPh$_3$ is liberated from the Pt(PPh$_3$)$_2$ site of **5** in order to decrease the steric repulsion between PPh$_3$ and SiR$_2$; finally, the symmetrical dinuclear complex **6** is generated.

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(20) (a) 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**, 659–666. (b) White, C. P.; Braddock-Wilking, J.; Corey, J. Y.; Xu, H.; Redekop, E.; Sedinkin, S.; Rath, N. M. *Organometallics* **2007**, *26*, 1996–3988.

(21) Braddock-Wilking, J.; Levchinsky, Y.; Rath, N. P. *Organometallics* **2001**, *20*, 474–480.

(22) Kim, Y.-J.; Lee, S.-C.; Park, J.-I.; Osakada, K.; Choi, J.-C.; Yamamoto, T. *J. Chem. Soc., Dalton Trans.* **2000**, 417–421.

(23) (a) Cook, C. D.; Jauhal, G. S. *J. Am. Chem. Soc.* **1968**, *90*, 1464–1467. (b) Ugo, R.; Caliati, F.; LaMonica, G. *Inorg. Synth.* **1968**, *11*, 106.

(24) Boudjouk, P.; Han, B. H. *Tetrahedron Lett.* **1981**, *22*, 3813–3814.

(25) (a) Sakurai, H.; Tominaga, K.; Watanabe, T.; Kumada, M. *Tetrahedron Lett.* **1966**, *7*, 5493–5497. (b) Nares, K. E.; Harris, M. E.; Ring, M. A.; O'Neal, H. E. *Organometallics* **1989**, *8*, 1964–1967.

Scheme 1

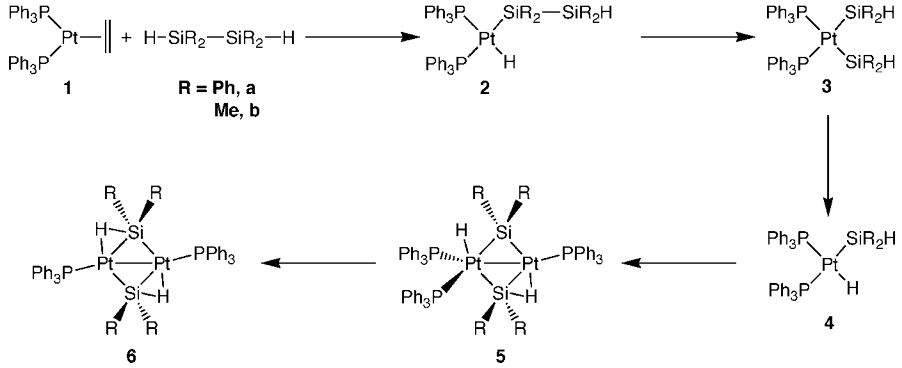

Table 1. Crystallographic Data

	3a·C_7H_8	**3b**	**4a**·C_7H_8	**5b**·C_7H_8	**6b**
formula	$C_{67}H_{60}P_2PtSi_2$	$C_{40}H_{44}P_2PtSi_2$	$C_{55}H_{50}P_2PtSi$	$C_{65}H_{67}P_3Pt_2Si_3$	$C_{20}H_{22}PPtSi$
fw	1178.36	837.96	996.07	1387.46	516.53
cryst syst	triclinic	monoclinic	triclinic	monoclinic	triclinic
space group	$P\bar{1}$ (#2)	$P2_1/n$ (#14)	$P\bar{1}$ (#2)	$P2_1/c$ (#14)	$P\bar{1}$ (#2)
a, Å	12.6440(13)	11.1420(9)	9.5937(2)	16.7770(7)	8.8370(3)
b, Å	14.1320(11)	15.2450(5)	11.1677(2)	21.2150(9)	9.8380(6)
c, Å	17.0186(15)	21.5240(14)	21.3492(3)	16.8200(5)	13.3330(8)
α, deg	73.490(5)	90	97.0400(10)	90	80.115(3)
β, deg	86.090(5)	91.594(3)	94.1000(10)	106.959(3)	73.335(4)
γ, deg	83.673(5)	90	98.4360(10)	90	82.170(4)
V, Å^3	2895.2(5)	3654.6(4)	2236.19(7)	5726.3(4)	1089.32(10)
Z	2	4	2	4	2
ρ_{calcd}, g cm^{-3}	1.352	1.523	1.479	1.609	1.575
μ(Mo Kα), cm^{-1}	2.559	4.020	3.273	5.046	6.566
total no. of data	27 413	32 727	17 514	52 978	10 112
no. of unique data	12 593	8545	10 680	13 701	4746
no. of params	655	412	541	655	211
R1[a]	0.0632	0.0503	0.0505	0.0404	0.0438
wR2 (all data)[b]	0.1794	0.1306	0.1238	0.1186	0.1420

[a] $I > 2.00\sigma(I)$. $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum(w(|F_o| - |F_c|)^2)/\sum wF_o^2\}^{1/2}$.

In the conversion of disilanylplatinum hydride complexes, West and co-workers have reported that two Si−H oxidative additions occur in the reaction of [Pt(dppe)(η^2-C_2H_4)] with $HSiR_2SiR_2H$ (R = Me, ^{i}Pr) to afford the η^2-disilene platinum complex [Pt(dppe)(η^2-Si_2R_4)] as a major product and 1,2-migration product [Pt(dppe)($SiHR_2$)$_2$] as the minor one.[10a] In contrast, Tilley and co-workers proved on the basis of NMR analysis that the treatment of [Pt(PEt_3)$_3$] with $H_2SiPhSiPhH_2$ yields only one product, *cis*-[Pt(PEt_3)$_2$(SiH_2Ph)$_2$].[6d] In our system, the bis(silyl)platinum complex is obtained as the major product below −30 °C, and the other products could not be detected by NMR.

Conclusion

The reaction of [Pt(PPh_3)$_2$(η^2-C_2H_4)] (**1**) with disilanes $HSiR_2SiR_2H$ (R = Ph, Me) was investigated by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy and XRD analysis. In the case of $HSiPh_2SiPh_2H$, complex **1** changed to the symmetrical diplatinum complex [Pt(PPh_3)(μ-$SiHPh_2$)]$_2$ (**6a**) via three intermediates in the following order: the disilanylplatinum hydride (**2a**), the bis(silyl)platinum (**3a**), and the silylplatinum hydride (**4a**). **4a** was obtained from the toluene solution of **3a** by the elimination of a $SiPh_2$ unit, although it has been synthesized by the treatment of **1** with Ph_2SiH_2. In $HSiMe_2SiMe_2H$, the sterically minimized alkyl substituents, methyl groups, caused the conversion of **1** to the unsymmetrical diplatinum complex **5b** and the observation of only the intermediate **3b** in the reaction. These mononuclear silylplatinum complexes bearing PPh_3 were more thermally unstable than that of aliphatic alkylphosphine ligands.

Experimental Section

General Procedure. All the experiments were carried out using a standard vacuum line and Schlenk techniques or in an M. Braun inert atmosphere drybox. All the reagents were of the highest grade available and were used without further purification. All the solvents used for the syntheses were distilled according to the general procedure. Benzene-d_6 and toluene-d_8 were distilled from potassium metal under Ar atmosphere. CD_2Cl_2 was dried over activated 4 Å molecular sieves. Complex **1**[23] and $HSiR_2SiR_2H$ (R = Ph,[24] Me[25]) were synthesized according to the previously reported method. The ^1H NMR spectral measurements were performed on a JEOL AL-300 NMR spectrometer at 300 MHz for ^1H and 122 MHz for ^{31}P. The chemical shifts of the protons are reported relative to the residual protonated solvents benzene-d_6 (7.15 ppm), toluene-d_8 (2.09 ppm), and CD_2Cl_2 (5.32 ppm). The chemical shifts of phosphine are corrected relative to external H_3PO_4 (0 ppm). Elemental analysis was performed on a CE Instruments EA1110 corrected by acetoanilide.

Syntheses of Platinum Complexes. [Pt(PPh_3)$_2$(H)($SiPh_2$-$SiHPh_2$)] (2a). To an H-shape glass tube attached to an NMR tube was added a toluene solution (0.3 mL) of $HSiPh_2SiPh_2H$ (7.4 mg, 0.020 mmol) to the NMR tube side, and a toluene solution (0.4 mL) of [Pt(PPh_3)$_2$(η^2-C_2H_4)] (**1**) (15 mg, 0.020 mmol) was added to the other side. After the disilane solution was frozen by liquid N_2, a small portion of the solution of **1** was poured into the NMR tube side so that the disilane solution did not melt. The NMR tube was sealed with the solution frozen by liquid N_2 and then was stored in a cold methanol bath at −80 °C. The solution was mixed by shaking carefully and placed into the NMR probe controlled at −60 °C. ^1H NMR (toluene-d_8, 300 MHz, −60 °C): δ 7.82 (d, $^3J_{HH}$ = 6.6 Hz), 7.66 (m, ArH), 7.5–7.3 (m, ArH), 7.2–6.6 (m, ArH), 5.71 (s, $^2J_{PtH}$ = 56 Hz, SiH), 5.30 (s, C_2H_4), −1.83 (dd, $^1J_{PtH}$ = 923

Hz, $^2J_{PH}$ = 153 Hz (trans), 20 Hz (cis), PtH). ^{31}P{^{1}H} NMR (toluene-d_8, 122 MHz, −60 °C): δ 37.4 (d, $^1J_{PtP}$ = 1785 Hz, $^2J_{PP}$ = 11 Hz, PPh$_3$ cis to H), 31.5 (d, $^1J_{PtP}$ = 2521 Hz, $^2J_{PP}$ = 10 Hz, PPh$_3$ trans to H).

[Pt(PPh$_3$)$_2$(SiHPh$_2$)$_2$] (3a). To a toluene solution (2 mL) of **1** (100 mg, 0.134 mmol) was added a toluene solution (2 mL) of HSiPh$_2$SiPh$_2$H (49.0 mg, 0.134 mmol) at −30 °C, and the resulting solution was stored in a chilled box at −30 °C overnight. Pentane (2 mL) was added to the resulting solution. The solution was allowed to stand for 2 days in the chilled box to afford light yellow crystals. Yield: 70.5 mg (45%). ^{1}H NMR (toluene-d_8, 300 MHz, –30 °C): δ 7.60 (d, 8H, $^3J_{HH}$ = 6.0 Hz, SiPh), 7.35 (m, 12H, PPh), 7.2–7.0 (m, SiPh), 6.9–6.7 (m, 18H, PPh), 5.80 (t, 2H, $^2J_{PtH}$ = 71 Hz, $^3J_{PH}$ = 18 Hz, SiH). ^{31}P{^{1}H} NMR (toluene-d_8, 122 MHz, −30 °C): δ 31.6 (s, $^1J_{PtP}$ = 1743 Hz). Anal. Calcd for **3a** ($C_{60}H_{52}P_2PtSi_2$): C, 66.34; H, 4.83. Found: C, 66.08; H, 4.59.

[Pt(PPh$_3$)$_2$(SiHMe$_2$)$_2$] (3b). Complex **3b** was synthesized by the same method as that used for **3a**, except for HSiMe$_2$SiMe$_2$H. Yield: 110 mg (49%). ^{1}H NMR (toluene-d_8, 300 MHz, 0 °C): δ 7.45 (m, 12H, PPh), 7.0–6.8 (m, 18H, PPh), 4.42 (ts, 2H, $^3J_{PH}$ = 20 Hz, $^3J_{HH}$ = 3.9 Hz, SiH), 0.72 (d, 12H, $^3J_{PtH}$ = 29 Hz, $^3J_{HH}$ = 3.6 Hz, SiMe). ^{31}P{^{1}H} NMR (toluene-d_8, 122 MHz, 0 °C): δ 34.9 (s, $^1J_{PtP}$ = 1679 Hz). Anal. Calcd for **3b**$\cdot$0.5C$_7$H$_8$ ($C_{43.5}H_{48}P_2PtSi_2$): C, 59.10; H, 5.47. Found: C, 59.45; H, 5.58.

[Pt(PPh$_3$)$_2$(H)(SiHPh$_2$)] (4a). To a toluene solution (2 mL) of **1** (150 mg, 0.200 mmol) was added a toluene solution (2 mL) of HSiPh$_2$SiPh$_2$H (73.5 mg, 0.200 mmol) at −30 °C, and the mixture was stirred at −10 to −5 °C for 1 h. Pentane (2 mL) was added to the resulting solution. The solution was allowed to stand in a chilled box at −30 °C to afford colorless crystals. Yield: 74.3 mg (37%). ^{1}H NMR (toluene-d_8, 300 MHz, −30 °C): δ 8.02 (d, 4H, $^3J_{HH}$ = 6.6 Hz, SiPh), 7.5–7.4 (m, 12H, PPh), 7.25 (t, 4H, $^3J_{HH}$ = 6.9 Hz, SiPh), 7.19 (d, 2H, $^3J_{HH}$ = 7.2 Hz, SiPh), 7.0–6.85 (m, 18H, PPh), 4.79 (br, 1H, SiH), −1.08 (dd, $^1J_{PtH}$ = 1009 Hz, $^2J_{PH}$ = 151 Hz (trans), 17 Hz (cis), PtH). ^{31}P{^{1}H} NMR (toluene-d_8, 122 MHz, −30 °C): δ 35.8 (s, $^1J_{PtP}$ = 2518 Hz, PPh$_3$ trans to H), 35.2 (s, $^1J_{PtP}$ = 1768 Hz, PPh$_3$ cis to H). ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz, −50 °C): δ 7.55–7.4 (m, 4H, SiPh), 7.4–7.0 (m, 36H), 4.00 (ddd, 1H, $^3J_{PH}$ = 21 Hz (trans), 14 Hz (cis), $^3J_{(Pt)HH}$ = 2.4 Hz, SiH), −1.89 (ddd, $^1J_{PtH}$ = 996 Hz, $^2J_{PH}$ = 152 Hz (trans), 20 Hz (cis), $^3J_{(Si)HH}$ = 2.4 Hz, PtH). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 122 MHz, −50 °C): δ 35.7 (d, $^1J_{PtP}$ = 1800 Hz, $^2J_{PP}$ = 11 Hz, PPh$_3$ cis to H), 34.5 (d, $^1J_{PtP}$ = 2477 Hz, $^2J_{PP}$ = 11 Hz, PPh$_3$ trans to H). IR (KBr, cm^{-1}): 2037 (PtH), 1956 (SiH). Anal. Calcd for **4a**$\cdot$C$_7$H$_8$ ($C_{55}H_{50}P_2PtSi$): C, 66.32; H, 5.06. Found: C, 66.72; H, 4.96.

[(PPh$_3$)$_2$Pt(H)(μ-SiMe$_2$)(μ-SiHMe$_2$)$_2$Pt(PPh$_3$)] (5b). Method A. To a toluene solution (2 mL) of **1** (202 mg, 0.271 mmol) was added HSiMe$_2$SiMe$_2$H (31.8 mg, 0.269 mmol) at room temperature, and the mixture was allowed to stand overnight. Pentane (4 mL) was added slowly to the toluene solution, and then the resulting solution was allowed to stand for 2 days at room temperature to afford yellow crystals. Yield: 145 mg (83%).

Method B. Complex **3b** (50 mg, 0.060 mmol) was dissolved in toluene at room temperature. The resulting solution was allowed to stand for 2 days at room temperature, and then pentane was added to the solution. **5b** crystallized as colorless crystals from a toluene/pentane solution after allowing the solution to stand for 2 days. Yield: 20.7 mg (53%). ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz, −70 °C): δ 7.7–7.5 (m, 12H, PPh), 7.5–6.8 (m, 33H, PPh), 0.70 (d, 1H, $^2J_{PH}$ = 6.5 Hz, Si−H−Pt), 0.11 (s, 6H, SiMe), −0.43 (s, 6H, SiMe), −7.05 (t, 1H, $^1J_{PtH}$ = 553 Hz, $^2J_{PtH}$ = 86 Hz, $^2J_{PH}$ = 14 Hz, PtH). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 122 MHz, −70 °C): δ 31.7 (t, $^1J_{PtP}$ = 4111 Hz, $^2J_{PtP}$ = 309 Hz, $^3J_{PP}$ = 29 Hz), 22.4 (d, $^1J_{PtP}$ = 3704 Hz, $^2J_{PtP}$ = 121 Hz, $^3J_{PP}$ = 29 Hz). Calcd for **5b**$\cdot$C$_7$H$_8$ ($C_{65}H_{67}P_3Pt_2Si_2$): C, 56.27; H, 4.87. Found: C, 56.10; H, 4.90.

[Pt(PPh$_3$)(μ-SiHPh$_2$)]$_2$ (6a). Method A. To a toluene solution (3 mL) of **1** (150 mg, 0.200 mmol) was added HSiPh$_2$SiPh$_2$H (73.5 mg, 0.200 mmol) at room temperature, and the mixture was stirred for 10 min. The resulting solution was allowed to stand for 2 days at room temperature to afford colorless microcrystals. Yield: 64.7 mg (51%).

Method B. Complex **4a** (10 mg, 0.011 mmol) was dissolved in toluene-d_8 at room temperature. The resulting solution was allowed to stand overnight at room temperature to afford colorless crystals. Anal. Calcd for **6a** ($C_{60}H_{52}P_2Pt_2Si_2$): C, 56.24; H, 4.09. Found: C, 56.07; H, 3.87.

[Pt(PPh$_3$)(μ-SiHMe$_2$)]$_2$ (6b). Complex **5b** (50.2 mg, 0.0388 mmol) was dissolved in toluene/pentane at room temperature. The resulting solution was allowed to stand for a few days at room temperature to afford colorless crystals. Yield: 13.9 mg (36%). ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz, −70 °C): δ 7.56 (br, 12H, PPh), 7.34 (br, 18H, PPh), 1.58 (s, 2H, $^1J_{PtH}$ = 641 Hz, $^2J_{PtH}$ = 131 Hz, Si−H−Pt), 0.22 (s, 12H, SiMe). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 122 MHz, −70 °C): δ 31.6 (s, $^1J_{PtP}$ = 4197 Hz, $^2J_{PtP}$ = 311 Hz, $^3J_{PP}$ = 62 Hz). Anal. Calcd for **6b**$\cdot$C$_7$H$_8$ ($C_{47}H_{52}P_2Pt_2Si_2$): C, 50.17; H, 4.66. Found: C, 51.93; H, 4.82.

Kinetics. The formation of complex **2a** was confirmed by increasing the peak intensity at 7.82 ppm in the ^{1}H NMR spectra. A residual protonated solvent at 2.09 ppm in toluene-d_8 was used as an internal standard, and the conversion rate of **2a** was estimated from the area ratio of the peak at 7.82 ppm to that at 2.09 ppm. The data collection was performed at 5 or 10 min intervals at −40 °C for 90 min (over 3 times the half-life). The data were analyzed with Igor (WaveMatrics, Inc.) on a Macintosh computer and fitted to an exponential function by a nonlinear least-squares method.

X-ray Crystallography. Single crystals of **3a**, **3b**, **4a**, **5b**, **6a**, and **6b** suitable for XRD analyses were obtained by allowing their corresponding toluene/pentane solutions to stand for a few days. Each crystal was mounted on a glass fiber, and the diffraction data of all the complexes except **4a** were collected on a Bruker-AXS M06X^{CE} imaging plate using graphite-monochromated Mo Kα radiation at 120 K. The diffraction data of **4a** were collected on a Bruker-AXS SMART APEXII. The crystal data and experimental details are listed in Table 1. The number of solvent molecules in the crystal structure of **3a**, **4a**, and **5b** was determined in the XRD analyses.

All the structures were solved by the combination of the direct method and Fourier techniques, and all the non-hydrogen atoms were anisotropically refined by full-matrix least-squares calculations. The atomic scattering factors and anomalous dispersion terms were obtained from the International Tables for X-ray Crystallography IV.[26] Since the numbers of reflection data for the above-mentioned crystals were insufficient for refining all the parameters of the hydrogen atoms, they were not included for further refinement; their positions were obtained from difference Fourier maps. All the calculations were carried out on a Silicon Graphics workstation by the maXus program.

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Supporting Information Available: Selected ^{1}H and ^{31}P{^{1}H} NMR data and kinetics. This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) Ibers, J. A., Hamilton, W. C. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.