



Article

Si–H Bond Activation of a Primary Silane with a Pt(0) Complex: Synthesis and Structures of Mononuclear (Hyrido)(dihydrosilyl) Platinum(II) Complexes

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Abstract: A hydrido platinum(II) complex with a dihydrosilyl ligand, [*cis*-PtH(SiH₂Trip)(PPh₃)₂] (**2**) was prepared by oxidative addition of an overcrowded primary silane, TripSiH₃ (**1**, Trip = 9-triptycyl) with [Pt(η²-C₂H₄)(PPh₃)₂] in toluene. The ligand-exchange reactions of complex **2** with free phosphine ligands resulted in the formation of a series of (hydrido)(dihydrosilyl) complexes (**3–5**). Thus, the replacement of two PPh₃ ligands in **2** with a bidentate bis(phosphine) ligand such as DPPF [1,2-bis(diphenylphosphino)ferrocene] or DCPE [1,2-bis(dicyclohexylphosphino)ethane] gave the corresponding complexes [PtH(SiH₂Trip)(L-L)] (**3**: L-L = dppf, **4**: L-L = dcpe). In contrast, the ligand-exchange reaction of **2** with an excess amount of PMe₃ in toluene quantitatively produced [PtH(SiH₂Trip)(PMe₃)(PPh₃)] (**5**), where the PMe₃ ligand is adopting *trans* to the hydrido ligand. The structures of complexes **2–5** were fully determined on the basis of their NMR and IR spectra, and elemental analyses. Moreover, the low-temperature X-ray crystallography of **2**, **3**, and **5** revealed that the platinum center has a distorted square planar environment, which is probably due to the steric requirement of the *cis*-coordinated phosphine ligands and the bulky 9-triptycyl group on the silicon atom.

Keywords: platinum; primary silane; hydrido complex; oxidative addition; ligand-exchange reaction; X-ray crystallography

1. Introduction

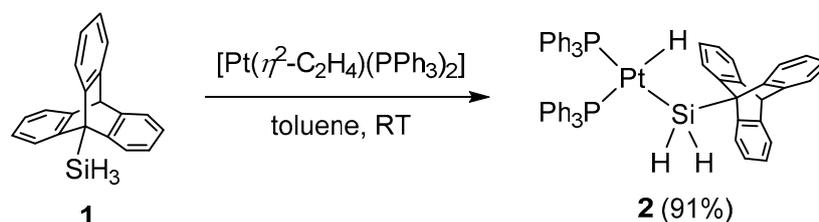
The transition metal catalyzed synthesis of functionalized organosilicon compounds gained substantial momentum during the past few decades [1]. Among these catalytic conversions, the oxidative addition of hydrosilanes with platinum(0) complexes is an efficient method for the generation of the platinum(II) hydride species, which has been proposed as a key intermediate in platinum-catalyzed hydrosilylations [2–6] and bis-silylations [7,8], as well as the dehydrogenative couplings of hydrosilanes [9–13]. While a number of reactions of hydrosilanes with platinum(0) complexes affording mononuclear bis(silyl) [14–18] and silyl-bridged multinuclear complexes [19–29] have been described so far, the isolation of mononuclear hydrido(silyl) complexes has been less well studied due to the high reactivity of a Pt–H bond [30–34]. In particular, the synthesis of hydrido(dihydrosilyl) platinum(II) complexes, which are anticipated as the initial products in the Si–H bond activation reactions of primary silanes with platinum(0) complexes, is quite rare. Indeed, only two publications have previously reported the characterization of hydrido(dihydrosilyl) platinum(II) complexes. In 2000, Tessier et al. reported that the reaction of a primary silane with a bulky *m*-terphenyl group with [Pt(PPr)₃] produced the first example of a stable hydrido(dihydrosilyl) complex [*cis*-PtH(SiH₂Ar)(PPr₃)₂] (Ar = 2,6-MesC₆H₃) [35]. Quite recently, Lai et al. also

described the synthesis of a bis(phosphine) hydrido(dihydrosilyl) complex [PtH(SiH₂Si^tBu₂Me)(dcpe)] (dcpe = 1,2-bis(dicyclohexylphosphino)ethane) containing a Si–Si bond [36]. Meanwhile, we succeeded in the first isolation of a series of hydrido(dihydrogermyl) platinum(II) complexes [PtH(GeH₂Trip)(L)] (Trip = 9-triptycyl) using a bulky substituent, 9-triptycyl group [37]. In addition, we reported the first syntheses and structural characterizations of hydrido palladium(II) complexes with a dihydrosilyl- or dihydrogermyl ligand, [PdH(EH₂Trip)(dcpe)] (E = Si, Ge) [38]. Very recently, we also found that hydride-abstraction reactions of [MH(EH₂Trip)(dcpe)] (M = Pt, Pd, E = Si, Ge) with B(C₆F₅)₃ led to the formations of new cationic dinuclear complexes with bridging hydrogermylene and hydrido ligands, [{M(dcpe)}₂(μ-GeHTrip)(μ-H)]⁺ [39]. As an extension of our previous work and taking into account the interest devoted to hydrido platinum(II) complexes, we present here the synthesis and characterization of a series of mononuclear (hydrido)(dihydrosilyl) complexes [PtH(SiH₂Trip)(L)₂].

2. Results

2.1. Synthesis and Characterization of [cis-PtH(SiH₂Trip)(PPh₃)₂] (2)

The reaction of TripSiH₃ **1** with [Pt(η²-C₂H₄)(PPh₃)₂] in toluene proceeded efficiently at room temperature under inert atmosphere to form the corresponding complex [cis-PtH(SiH₂Trip)(PPh₃)₂] (**2**) in 91% yield as colorless crystals (Scheme 1). In the ¹H NMR spectrum of **2**, the characteristic signals of the platinum hydride were observed at δ = −2.15, which were split by 19 and 157 Hz of ³¹P–¹H couplings accompanying 958 Hz of satellite signals from the ¹⁹⁵Pt isotope. This chemical shift is comparable with those of the related (hydrido)(dihydrosilyl) complexes, [cis-PtH(SiH₂Ar)(PPr₃)₂] (Ar = 2,6-MesC₆H₃) (δ = −3.40) [35] and [cis-PtH(SiH₂Si^tBu₂Me)(dcpe)] (δ = −0.89) [36]. The SiH₂ resonance appeared as a multiplet at δ = 4.68 ppm. The ³¹P{¹H} NMR spectrum of **2** exhibited two doublets (²J_{P–P} = 15 Hz) at δ = 33.8 and 34.5 with ¹⁹⁵Pt–³¹P coupling constants, 2183 and 1963 Hz, which were assigned to the phosphorus atoms lying *trans* to the hydrido and dihydrosilyl ligands, respectively, in agreement with the NMR data for reported germanium congener [cis-PtH(GeH₂Trip)(PPh₃)₂] [δ = 31.2 (¹J_{Pt–P} = 2317 Hz) and 31.6 (¹J_{Pt–P} = 2252 Hz)] [37]. The silicon atom of **2** gave rise to a resonance around δ = −40.6 with splitting due to ³¹P–²⁹Si couplings (²J_{P(trans)–Si} = 161, ²J_{P(cis)–Si} = 15 Hz) and ¹⁹⁵Pt satellites (¹J_{Pt–Si} = 1220 Hz) in the ²⁹Si{¹H} NMR spectrum. In the solid state IR spectrum for **2**, Pt–H and Si–H stretching vibrations were observed at 2041 and 2080 cm^{−1}, respectively. Complex **2** is thermally and air stable in the solid state (melting point: 123 °C (dec.)) or in solution, and no dimerization or dissociation of phosphine ligands was observed.



Scheme 1. Synthesis of [cis-PtH(SiH₂Trip)(PPh₃)₂] **2**.

The molecular structure of **2** was determined unambiguously by X-ray crystallographic analysis, as depicted in Figure 1. The X-ray crystallographic analysis of **2** revealed that the platinum center attains a distorted square-planar environment, which was probably due to the steric requirement of the *cis*-coordinated PPh₃ ligands and the bulky 9-triptycyl group on the silicon atom. The P1–Pt1–P2 angle of 101.63(3)° and P1–Pt1–Si1 angle of 96.17(3)° deviated considerably from the ideal 90° of square-planar geometry. The Pt–Si bond length is 2.3458(9) Å, which is comparable to those ranging from 2.321 to 2.406 Å observed in the related mononuclear platinum(II) complexes bearing silyl ligands [1]. The hydrogen atom on the platinum atom was located in the electron density map and has

a Pt–H distance of 1.59(4) Å. The Pt1–P1 bond length [2.2945(8) Å] is slightly shorter than the Pt1–P2 bond length [2.3401(8) Å], which indicates the stronger *trans* influence of the silicon atom compared with that of the hydride in this complex. This result is consistent with the ^{195}Pt – ^{31}P coupling constants (2183 and 1963 Hz) observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum.

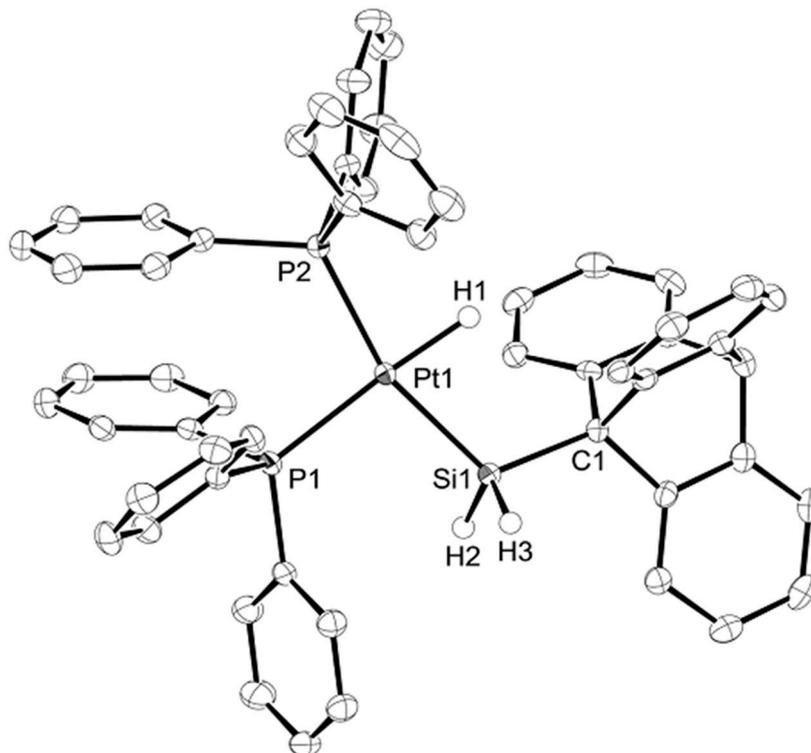
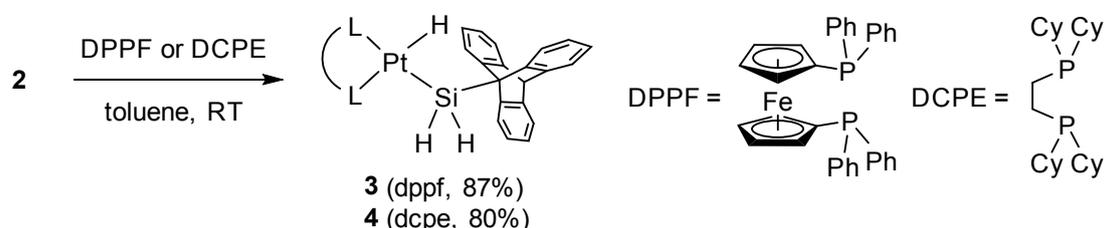


Figure 1. ORTEP of $[\text{cis-PtH}(\text{SiH}_2\text{Trip})(\text{PPh}_3)_2]$ **2** (50% thermal ellipsoids, a solvation toluene molecule, and hydrogen atoms, except H1, H2, and H3 were omitted for clarity). Selected bond lengths (Å) and bond angles ($^\circ$): Pt1–Si1 = 2.3458(9), Pt1–P1 = 2.2945(8), Pt1–P2 = 2.3401(8), Pt1–H1 = 1.59(4), Si1–C1 = 1.918(3), P1–Pt1–P2 = 101.63(3), Si1–Pt1–P1 = 96.17(3), Si1–Pt1–H1 = 79.7(16), P2–Pt1–H1 = 82.5(16), Si1–Pt1–P2 = 162.13(3), P1–Pt1–H1 = 175.8(16).

2.2. Ligand Exchange Reactions of **2** with Free Phosphine Ligands

We next examined the ligand-exchange reactions of complex **2** with free phosphine ligands. The replacement of two PPh_3 ligands in **2** with a bidentate bis(phosphine) ligand such as DPPF (1,2-bis(diphenylphosphino)ferrocene) or DCPE gave the corresponding complexes $[\text{PtH}(\text{SiH}_2\text{Trip})(\text{L-L})]$ (**3**: L-L = dppf, **4**: L-L = dcpe) in 87% and 80% yields, respectively (Scheme 2). In the ^1H NMR spectra of **3** and **4**, the hydride resonated as a doublet of doublets at $\delta = -1.62$ ($^2J_{\text{P-H}} = 20, 164$, $^1J_{\text{Pt-H}} = 995$ Hz) for **3** and -0.46 ($^2J_{\text{P-H}} = 13, 166$, $^1J_{\text{Pt-H}} = 1004$ Hz) for **4**. These chemical shifts are shifted downfield in comparison with that of the starting complex **2** ($\delta = -2.15$), which is probably due to the stronger electron-donating ability of chelating phosphines compared with PPh_3 . The spectrum for **3** also displayed a multiplet signal centering at $\delta = 4.61$ corresponding to the SiH_2 protons, which is shifted upfield by 0.89 ppm in comparison with that of **4**. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3** showed two doublets ($^2J_{\text{P-P}} = 21$ Hz) with ^{195}Pt satellites at $\delta = 30.5$ ($^1J_{\text{Pt-P}} = 2247$ Hz) and 34.5 ($^1J_{\text{Pt-P}} = 1837$ Hz), which are close to those of **2** [$\delta = 33.8$ ($^1J_{\text{Pt-P}} = 2183$ Hz) and 34.5 ($^1J_{\text{Pt-P}} = 1963$ Hz)]. The observation of P–P coupling indicates a large deviation of the P–Pt–P angle from 90° of the ideal square planar geometry around the Pt(II) center (vide infra). In contrast, the $^{31}\text{P}\{^1\text{H}\}$ resonances for **4** were observed as two singlets at $\delta = 69.2$ ($^1J_{\text{Pt-P}} = 1809$ Hz) and 85.3 ($^1J_{\text{Pt-P}} = 1678$ Hz), respectively, which are relatively shifted downfield relative to those of **2** and **3**. The larger $^1J_{\text{Pt-P}}$ values

(2183 Hz for **3**, 1809 Hz for **4**) are assigned to the phosphorus atom *trans* to the hydrido ligand, as in the case of **2**. Furthermore, the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of **3** and **4** showed a doublet of doublets signals at $\delta = -39.0$ ($^2J_{\text{Si-P}} = 167, 12$ Hz) for **3**, and -44.6 ($^2J_{\text{Si-P}} = 173, 11$ Hz) for **4**, which were accompanied by ^{195}Pt satellites of 1207 Hz for **3** and 1253 Hz for **4**, respectively.



Scheme 2. Ligand-exchange reaction of $[\text{cis-PtH}(\text{SiH}_2\text{Trip})(\text{PPh}_3)_2]$ **2** with chelating bis(phosphine)s.

The molecular structure of DPPF-derivative **3** in the crystalline state was confirmed by X-ray crystallography (Figure 2). The platinum atom lies in a distorted square-planar geometry; the sum of the bond angles around the platinum atom is 360.48° . The P1–Pt1–P2 angle is $102.29(9)^\circ$, and other angles around the platinum atom are less than 90° , except the P1–Pt1–Si1 angle [$95.19(9)^\circ$]. The Pt–Si [$2.331(3)$ Å] and two Pt–P bond lengths [$2.286(2)$, $2.319(2)$ Å] are comparable to those of the corresponding DPPF-ligated hydrido complex $[\text{PtH}(\text{SiHPh}_2)(\text{dppf})]$ [$2.3366(4)$, $2.2830(4)$, and $2.3192(4)$ Å, respectively] [40].

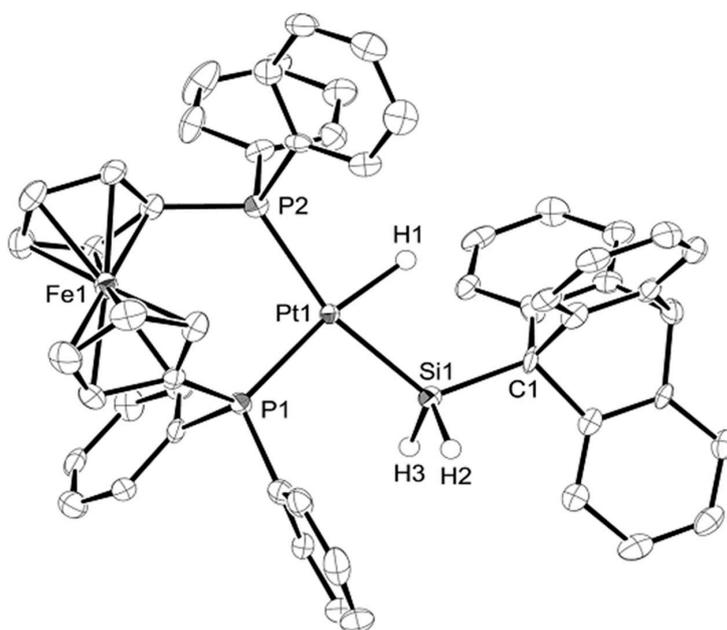
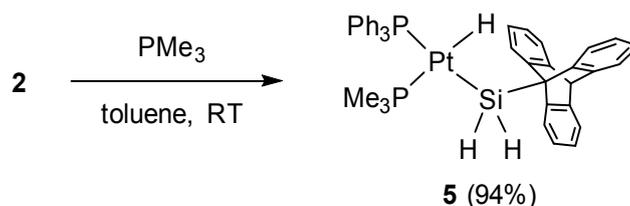


Figure 2. ORTEP of $[\text{PtH}(\text{SiH}_2\text{Trip})(\text{dppf})]$ **3** 50% thermal ellipsoids, a solvation CH_2Cl_2 molecule, and hydrogen atoms, except H1, H2, and H3 were omitted for clarity. Selected bond lengths (Å) and bond angles ($^\circ$): Pt1–Si1 = $2.331(3)$, Pt1–P1 = $2.286(2)$, Pt1–P2 = $2.319(2)$, Pt1–H1 = $1.687(10)$, Si1–C1 = $1.920(10)$, P1–Pt1–P2 = $102.29(9)$, Si1–Pt1–P1 = $95.19(9)$, Si1–Pt1–H1 = $76(5)$, P2–Pt1–H1 = $87(5)$, Si1–Pt1–P2 = $162.10(9)$, P1–Pt1–H1 = $171(5)$.

It is well known that trimethylphosphine (PMe_3) is a strong σ -donating ligand for a wide variety of transition-metal complexes. Therefore, one can reasonably expect the formation of $[\text{PtH}(\text{SiH}_2\text{Trip})(\text{PMe}_3)_2]$ in a similar ligand-exchange reaction of **2** with PMe_3 . However, we found that the reaction of **2** with 2.2 equivalents of PMe_3 in toluene at room temperature did not proceed completely, which resulted in the formation of $[\text{PtH}(\text{SiH}_2\text{Trip})(\text{PMe}_3)(\text{PPh}_3)]$ (**5**), where the PPh_3 ligand *trans* to hydrido in **2** is exchanged with a PMe_3 ligand (Scheme 3). Complex **5** was isolated as colorless

crystals in quantitative yield after workup. In the ^1H NMR spectrum of **5** at 298 K, the characteristic broad doublet signal due to the platinum hydride was observed centering at $\delta = -1.91$ with splitting by $^{31}\text{P}-^1\text{H}$ ($^2J_{\text{P}(\text{trans})-\text{H}} = 157$ Hz) and $^{195}\text{Pt}-^1\text{H}$ ($^1J_{\text{Pt}-\text{H}} = 899$ Hz) couplings. The SiH_2 protons also appeared as a broad multiplet at $\delta = 5.95$, which is shifted downfield relative to those of the above complexes **2–4** ($\delta = 4.68\text{--}5.50$). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **5** at 298 K exhibited two nonequivalent broad singlet signals at $\delta = -22.9$ and 37.4 , with two sets of ^{195}Pt satellites of 2115 and 1833 Hz. The former signal was assigned to the PMe_3 *trans* to the hydrido ligand using a non ^1H -decoupled ^{31}P NMR technique at 253 K. The $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **5** at 223 K featured one ^{29}Si resonance as a broad doublet signal at $\delta = -43.9$ ($^2J_{\text{Si}-\text{P}} = 151$ Hz). The broadening of NMR signals possibly implies the existence of the $\text{Si}-\text{H}$ σ -complex intermediate **6** in the NMR time scale [38,41,42]. Unfortunately, attempts to probe further the fluxional behavior of **5** by VT (variable temperature)-NMR in solution revealed no appreciable changes in spectroscopic features by ^1H and ^{31}P NMR spectroscopy. The molecular structure of **5** is also determined by X-ray analysis, as shown in Figure 3. Distortions from square planar geometry at the platinum center were observed, similar to the cases of **2** and **4**. The Pt–Si bond length of **5** [2.3414(13) Å] is almost equal to those of **2** [2.3458(9) Å] and **4** [2.331(3) Å]. As expected, the Pt1–P1 bond length for the PMe_3 ligand of **5** [2.2978(12) Å] is shortened compared with the Pt1–P2 bond length for the PPh_3 ligand of **5** [2.3203(11) Å] due to the different ligands in the *trans* positions of the phosphorus atoms. While only a few cationic platinum complexes containing different phosphine ligands have been reported [43–45], complex **5** is the first example of a neutral platinum complex bearing a weakly electron-donating PPh_3 and strongly electron-donating PMe_3 .



Scheme 3. Ligand-exchange reaction of $[\text{cis-PtH}(\text{SiH}_2\text{Trip})(\text{PPh}_3)_2]$ **2** with trimethylphosphine (PMe_3).

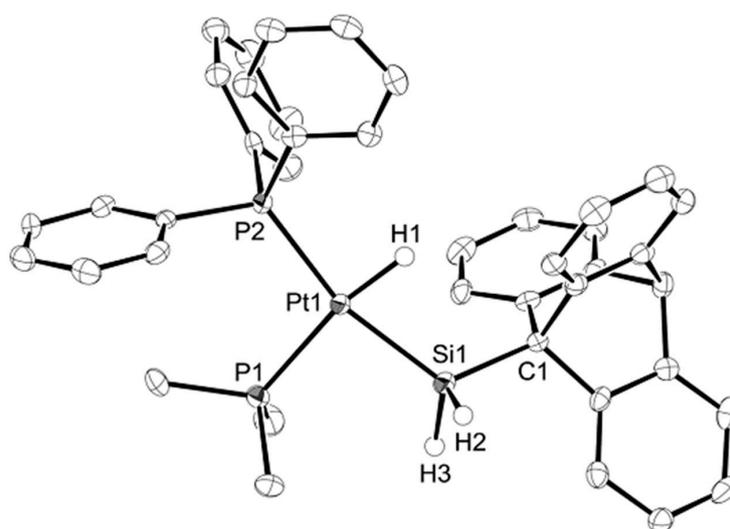
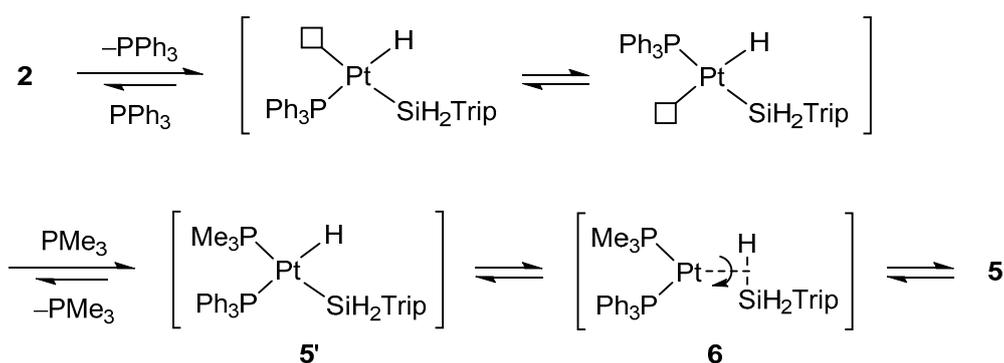


Figure 3. ORTEP of $[\text{PtH}(\text{SiH}_2\text{Trip})(\text{PMe}_3)(\text{PPh}_3)]$ **5** 50% thermal ellipsoids, a solvation CH_2Cl_2 molecule, and hydrogen atoms, except H1, H2, and H3 were omitted for clarity. Selected bond lengths (Å) and bond angles ($^\circ$): Pt1–Si1 = 2.3414(13), Pt1–P1 = 2.2978(12), Pt1–P2 = 2.3203(11), Pt1–H1 = 1.44(6), Si1–C1 = 1.930(5), P1–Pt1–P2 = 103.47(4), Si1–Pt1–P1 = 92.34(4), Si1–Pt1–H1 = 75(2), P2–Pt1–H1 = 89(2), Si1–Pt1–P2 = 164.19(4), P1–Pt1–H1 = 167(2).

A plausible formation mechanism for **5** is shown in Scheme 4. According to the stronger *trans* influence of the silyl ligand than that of the hydrido ligand, the ligand-exchange of a PPh₃ *trans* to silyl ligand takes place to yield the intermediate **5'** in the first step, while **5** might be formed directly from the corresponding coordinatively unsaturated intermediate (3-coordinated 14-electron complexes) [46,47]. Then, the intramolecular interchange of coordination environments between the silyl and hydrido ligands through the Si–H σ -complex intermediate **6** would occur, probably due to the steric repulsion between the bulky 9-triptycyl group on the silicon atom and the *cis*-PPh₃ ligand in **5'**. Finally, the corresponding complex **5** was obtained as the thermodynamic product. As another pathway, it is likely that the direct formation of **5** is caused by an initial dissociation of the PPh₃ ligand at the *trans* position of the hydrido ligand in **2** due to steric reason.



Scheme 4. Plausible reaction pathway for the formation of [PtH(SiH₂Trip)(PMe₃)(PPh₃)] **5**.

3. Materials and Methods

3.1. General Procedures

All of the experiments were performed under an argon atmosphere unless otherwise noted. Solvents were dried by standard methods and freshly distilled prior to use. ¹H, ¹³C, and ³¹P NMR spectra were recorded on Bruker DPX-400 or DRX-400 (400, 101 and 162 MHz, respectively), Avance-500 (500, 126 and 202 MHz, respectively) (Karlsruhe, Germany) spectrometers using CDCl₃ or C₆D₆ as the solvent at room temperature. ²⁹Si NMR spectra were recorded on Bruker Avance-500 (Karlsruhe, Germany) or JEOL EX-400 (Tokyo, Japan) (99.4 and 79.3 MHz, respectively) spectrometers using CDCl₃, CD₂Cl₂, C₆D₆, or THF-*d*₈ as the solvent at room temperature, unless otherwise noted. IR spectra were obtained on a Perkin-Elmer System 2000 FT-IR spectrometer (Walham, MA, USA). Elemental analyses were carried out at the Molecular Analysis and Life Science Center of Saitama University. All of the melting points were determined on a Mel-Temp capillary tube apparatus (Stafford, UK) and are uncorrected. 9-Triptycylsilane (TripSiH₃, **1**) [48] and [Pt(η²-C₂H₄)(PPh₃)₂] [49] were prepared according to the reported procedures.

3.1.1. [cis-PtH(SiH₂Trip)(PPh₃)₂] (**2**)

A solution of TripSiH₃ **1** (50.9 mg, 0.179 mmol) and [Pt(η²-C₂H₄)(PPh₃)₂] (149.3 mg, 0.199 mmol) in toluene (3 mL) was stirred at room temperature for 1 h to form a pale yellow solution. After the removal of the solvent in vacuo, the residual colorless solid was purified by washing with hexane to give [cis-PtH(SiH₂Trip)(PPh₃)₂] (**2**) (164.3 mg, 91%) as colorless crystals.

¹H NMR (400 MHz, CDCl₃): δ = −2.15 (dd, ²J_{H-P(trans)} = 157, ²J_{H-P(cis)} = 19, ¹J_{H-Pt} = 958 Hz, 1H, PtH), 4.68 (m, 2H, SiH₂), 5.28 (s, 1H, TripCH), 6.83–6.89 (m, 6H, Ar), 7.02–7.06 (m, 6H, Ar), 7.15–7.31 (m, 21H, Ar), 7.49 (t, J = 7 Hz, 6H, Ar), 7.81 (d, J = 7 Hz, 3H, Ar). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ = 46.6 (TripC), 55.3 (TripCH), 122.7 (Ar(CH)), 123.7 (Ar(CH) × 2), 126.2 (Ar(CH)), 127.8 (Ar(CH)), 127.9 (Ar(CH)), 129.4 (Ar(CH)), 129.6 (Ar(CH)), 134.1 (Ar(CH)), 134.2 (Ar(CH)),

133.7–134.8 (m, Ar(C)), 135.5 (d, $^1J_{C-P} = 38$ Hz, Ar(C)), 148.4 (Ar(C)), 149.5 (Ar(C)). $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$): $\delta = 33.8$ (d, $^2J_{P-P} = 15$, $^1J_{P-Pt} = 2183$ Hz), 34.5 (d, $^2J_{P-P} = 15$, $^1J_{P-Pt} = 1963$ Hz). $^{29}Si\{^1H\}$ NMR (79.3 MHz, CD_2Cl_2): $\delta = -40.6$ (dd, $^2J_{Si-P(trans)} = 161$, $^2J_{Si-P(cis)} = 15$, $^1J_{Si-Pt} = 1220$ Hz). IR (KBr, cm^{-1}): $\nu = 2041$ (Pt–H), 2080 (Si–H). Anal. Calcd. for $C_{56}H_{46}P_2PtSi$: C, 66.99; H, 4.62. Found: C, 66.55; H, 4.61. Melting point: 123 °C (dec.).

3.1.2. [PtH(SiH₂Trip)(dppf)] (3)

A solution of **2** (40.5 mg, 0.040 mmol) and DPPF (28.2 mg, 0.048 mmol) in toluene (3 mL) was stirred at room temperature for 5 h. After the removal of the solvent in vacuo, the residual colorless solid was purified by washing with Et_2O and hexane to give [PtH(SiH₂Trip)(dppf)] (**3**) (37.1 mg, 0.035 mmol, 87%) as yellow crystals.

1H NMR (400 MHz, $CDCl_3$): $\delta = -1.62$ (dd, $^2J_{H-P(trans)} = 164$, $^2J_{H-P(cis)} = 20$, $^1J_{H-Pt} = 995$ Hz, 1H, PtH), 3.86 (s, 2H, Cp), 4.20 (s, 2H, Cp), 4.37 (s, 2H, Cp), 4.58–4.64 (m, 4H, Cp and SiH₂), 5.30 (s, 1H, TripCH), 6.87–6.89 (m, 6H, Ar), 7.26 (m, 6H, Ar), 7.41 (br, 6 H, Ar), 7.66–7.81 (m, 14H, Ar). $^{13}C\{^1H\}$ NMR (101 Hz, $CDCl_3$): $\delta = 46.5$ (m, TripC), 55.2 (TripCH), 71.3 (d, $^3J_{C-P} = 5$ Hz, Cp(CH)), 72.1 (d, $^3J_{C-P} = 6$ Hz, Cp(CH)), 74.5 (d, $^2J_{C-P} = 7$ Hz, Cp(CH)), 75.6 (d, $^2J_{C-P} = 8$ Hz, Cp(CH)), 79.3 (dd, $^1J_{C-P} = 42$, $^3J_{C-P} = 5$ Hz, Cp(C)), 80.7 (dd, $^1J_{C-P} = 47$, $^3J_{C-P} = 6$ Hz, Cp(C)), 122.7 (Ar(CH)), 123.71 (Ar(CH)), 123.68 (Ar(CH)), 126.4 (Ar(CH)), 127.7 (d, $^3J_{C-P} = 11$ Hz, Ar(CH)), 128.0 (d, $^3J_{C-P} = 10$ Hz, Ar(CH)), 129.9 (Ar(CH)), 130.1 (Ar(CH)), 134.3 (d, $^2J_{C-P} = 13$ Hz, Ar(CH)), 134.6 (d, $^2J_{C-P} = 14$ Hz, Ar(CH)), 134.8–135.5 (m, Ar(C)), 136.2 (d, $^1J_{C-P} = 43$ Hz, Ar(C)), 148.4 (Ar(C)), 149.7 (Ar(C)). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): $\delta = 30.5$ (d, $^2J_{P-P} = 21$ Hz, $^1J_{Pt-P} = 2247$ Hz), 34.5 (d, $^2J_{P-P} = 21$, $^1J_{Pt-P} = 1837$ Hz). $^{29}Si\{^1H\}$ NMR (79.3 MHz, $CDCl_3$): $\delta = -39.0$ (dd, $^2J_{Si-P(trans)} = 167$, $^2J_{Si-P(cis)} = 12$, $^1J_{Si-Pt} = 1207$ Hz). IR (KBr, cm^{-1}): $\nu = 2055$ (Pt–H), 2081 (Si–H). Anal. Calcd. for $C_{54}H_{44}FeP_2PtSi$: C, 62.73; H, 4.29. Found: C, 62.70; H, 4.27. Melting point: 183 °C (dec.).

3.1.3. [PtH(SiH₂Trip)(dcpe)] (4)

A solution of **2** (35.6 mg, 0.035 mmol) and DCPE (18.8 mg, 0.044 mmol) in toluene (3 mL) was stirred at room temperature for 5 h. After the removal of the solvent in vacuo, the residual colorless solid was purified by washing with Et_2O and hexane to give [PtH(SiH₂Trip)(dcpe)] (**4**) (25.5 mg, 0.028 mmol, 80%) as colorless crystals.

1H NMR (500 MHz, $CDCl_3$): $\delta = -0.45$ (dd, $^2J_{H-P(trans)} = 165$, $^2J_{H-P(cis)} = 13$, $^1J_{Pt-H} = 1004$ Hz, 1H, PtH), 1.16–1.51 (m, 20H, Cy), 1.65–1.86 (m, 24H, Cy), 2.16–2.19 (m, 2H, Cy), 2.30–2.37 (m, 2H, Cy), 5.32 (s, 1H, TripCH), 5.50 (dd, $^2J_{H-H} = 15$, $^3J_{H-P(trans)} = 6$, $^2J_{Pt-H} = 31$ Hz, 2H, SiH₂), 6.84–6.90 (m, 6H, Ar), 7.30–7.32 (d, $J = 7$ Hz, 3H, Ar), 7.94–7.96 (d, $J = 7$ Hz, 3H, Ar). $^{13}C\{^1H\}$ NMR (101 Hz, $CDCl_3$): $\delta = 23.2$ (dd, $^3J_{C-P} = 21$, 16 Hz, PCH₂), 26.2 (dd, $^3J_{C-P} = 23$, 21 Hz, PCH₂), 26.9 (d, $^3J_{C-P} = 14$ Hz, PCy(CH₂)), 26.4 (d, $^3J_{C-P} = 13$ Hz, PCy(CH₂)), 26.8 (d, $^3J_{C-P} = 10$ Hz, PCy(CH₂)), 27.0 (d, $^3J_{C-P} = 12$ Hz, PCy(CH₂)), 28.9 (m, PCy(CH₂) × 2), 29.7 (m, PCy(CH₂)), 35.3–35.8 (m, PCy(CH) × 2), 46.8 (TripC), 55.4 (TripCH), 122.7 (Ar(CH)), 123.6 (Ar(CH)), 126.9 (Ar(CH)), 148.6 (Ar(C)), 159.2 (Ar(C)). $^{31}P\{^1H\}$ NMR (162 Hz, $CDCl_3$): $\delta = 69.2$ (s, $^1J_{Pt-P} = 1809$ Hz), 85.3 (s, $^1J_{Pt-P} = 1678$ Hz). $^{29}Si\{^1H\}$ NMR (79.3 MHz, CD_2Cl_2): $\delta = -44.6$ (dd, $^2J_{Si-P(trans)} = 173$, $^2J_{Si-P(cis)} = 11$, $^1J_{Si-Pt} = 1253$ Hz). IR (KBr, cm^{-1}): $\nu = 2057$ (Pt–H), 2081 (Si–H). Anal. Calcd for $C_{46}H_{64}P_2PtSi$: C, 61.24; H, 7.15. Found: C, 61.10; H, 7.10. Melting point: 134 °C (dec.).

3.1.4. [PtH(SiH₂Trip)(PMe₃)(PPh₃)] (5)

A toluene solution of PMe_3 (1.0 M, 0.2 mL, 0.200 mmol) was added to a solution of **2** (98.0 mg, 0.098 mmol) in toluene (3.5 mL) at room temperature. The reaction mixture was stirred at room temperature for 30 min. After the removal of the solvent in vacuo, the residual colorless solid was purified by washing with Et_2O and hexane to give [PtH(SiH₂Trip)(PMe₃)(PPh₃)] (**5**) (75.6 mg, 94%) as colorless crystals.

^1H NMR (400 MHz, C_6D_6): $\delta = -1.91$ (d, $^2J_{\text{H-P}(\text{trans})} = 157$, $^1J_{\text{H-Pt}} = 899$ Hz, 1H, PtH), 1.03–1.11 (m, 9H, PMe), 5.34 (s, 1H, TripCH), 5.95–5.97 (m, 2H, SiH_2), 6.82–6.97 (m, 15H, Ar), 7.31 (d, $J = 7$ Hz, 3H, Ar), 7.57 (br, 6H, Ar), 8.50 (d, $J = 7$ Hz, 3H, Ar). $^{13}\text{C}\{^1\text{H}\}$ -NMR (101 Hz, CDCl_3): $\delta = 16.4$ – 17.1 (m, PMe), 53.6 (TripC), 55.4 (TripCH), 123.0 (Ar(CH)), 123.9 (Ar(CH)), 124.1 (Ar(CH)), 126.5 (Ar(CH)), 128.5 (d, $^3J_{\text{C-P}} = 10$ Hz, Ar(CH)), 130.0 (Ar(CH)), 134.4 (d, $^2J_{\text{C-P}} = 13$ Hz, Ar(CH)), 135.6 (d, $^1J_{\text{C-P}} = 36$ Hz, Ar(CH), 148.5 (Ar(C)), 149.7 (Ar(C)). $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 Hz, C_6D_6): $\delta = -22.9$ (s, $^1J_{\text{Pt-P}} = 2115$ Hz), 37.4 (br, $^1J_{\text{Pt-P}} = 1833$ Hz). $^{29}\text{Si}\{^1\text{H}\}$ -NMR (79.3 MHz, $\text{THF-}d_8$, 223 K) $\delta = -43.9$ (d, $^2J_{\text{Si-P}(\text{trans})} = 151$ Hz). IR (KBr, cm^{-1}) $\nu = 2029$ (Pt–H), 2054 (Si–H). Anal. Calcd for $\text{C}_{41}\text{H}_{40}\text{P}_2\text{PtSi}$: C, 60.21; H, 4.93. Found: C, 60.57; H, 5.00. Melting point: 115 °C (dec.).

3.2. X-ray Crystallographic Studies of 2, 3, and 5

Colorless single crystals of **2** were grown by the slow evaporation of its saturated toluene solution, and single crystals of **3** and **5** were grown by the slow evaporation of its saturated CH_2Cl_2 and hexane solution. The intensity data were collected at 103 K on a Bruker AXS SMART diffractometer (Karlsruhe, Germany) employing graphite-monochromatized Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELX-97) [50]. Hydrogen atoms, except for the PtH and SiH hydrogens of **2**, **3**, and **5**, were located by assuming ideal geometry, and were included in the structure calculations without further refinement of the parameters. Full details of the crystallographic analysis and accompanying cif files (see Supplementary Materials) may be obtained free of charge from the Cambridge Crystallographic Data Centre (CCDC numbers 1577277, 1577278, and 1577279) via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk).

3.2.1. [*cis*-PtH(SiH₂Trip)(PPh₃)₂] (**2**)

$\text{C}_{56}\text{H}_{46}\text{P}_2\text{PtSi}$, C_7H_8 , $M_W = 1096.18$, triclinic, space group $P-1$, $a = 12.7971(6)$ Å, $b = 13.4847(6)$ Å, $c = 14.8861(7)$ Å, $\alpha = 99.2791(10)^\circ$, $\beta = 99.2791(10)^\circ$, $\gamma = 90.3020(10)^\circ$, $V = 2472.4(2)$ Å³, $Z = 2$, $D_{\text{calc.}} = 1.472$ g·cm⁻³, R_1 ($I > 2\sigma I$) = 0.0310, wR_2 (all data) = 0.0718 for 11639 reflections and 617 parameters, $GOF = 1.025$.

3.2.2. [PtH(SiH₂Trip)(dppf)] (**3**)

$\text{C}_{54}\text{H}_{44}\text{FeP}_2\text{PtSi}$, CH_2Cl_2 , $MW = 1118.79$, monoclinic, space group $P2_1$, $a = 12.2585(6)$ Å, $b = 15.5003(7)$ Å, $c = 12.9367(6)$ Å, $\beta = 110.8060(10)^\circ$, $V = 2297.81(19)$ Å³, $Z = 2$, $D_{\text{calc.}} = 1.617$ g·cm⁻³, R_1 ($I > 2\sigma I$) = 0.0484, wR_2 (all data) = 0.1171 for 8350 reflections, 571 parameters, and 2 restraints, $GOF = 1.018$.

3.2.3. [PtH(SiH₂Trip)(PMe₃)(PPh₃)] (**5**)

$\text{C}_{41}\text{H}_{40}\text{P}_2\text{PtSi}$, CH_2Cl_2 , $M_W = 902.78$, orthorhombic, space group $Pbca$, $a = 15.9074(6)$ Å, $b = 20.9224(8)$ Å, $c = 22.6113(9)$ Å, $V = 7525.5(5)$ Å³, $Z = 8$, $D_{\text{calc.}} = 1.594$ g·cm⁻³, R_1 ($I > 2\sigma I$) = 0.0325, wR_2 (all data) = 0.0706 for 7011 reflections and 448 parameters, $GOF = 1.026$.

4. Conclusions

We have demonstrated that the oxidative addition of the sterically bulky primary silane, TripSiH₃ **1** with $[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)(\text{PPh}_3)_2]$ in toluene, resulted in the formation of the mononuclear (hydrido)(dihydrosilyl) complex [*cis*-PtH(SiH₂Trip)(PPh₃)₂] **2**. The ligand-exchange reactions of **2** with free chelating bis(phosphine)s such as DPPF or DCPE resulted in the formations of a series of (hydrido)(dihydrosilyl) complexes [PtH(SiH₂Trip)(L)] (**3**: L = dppf, **4**: L = dcpe). In contrast, the reaction of **2** with an excess amount of PMe_3 in toluene quantitatively produced [PtH(SiH₂Trip)(PMe₃)(PPh₃)] **5**. The latter is of particular interest, as it represents the first platinum

complex having different simple phosphine ligands such as a weakly electron-donating PPh₃ and a strongly electron-donating PMe₃. Further investigations on the reactivity of these complexes are currently in progress.

Supplementary Materials: The following are available online at www.mdpi.com/2304-6740/5/4/72/s1, cif and cif-checked files.

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