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

Norio Nakata *, Nanami Kato, Noriko Sekizawa and Akihiko Ishii *

Department of Chemistry, Graduate School of Science and Engineering, Saitama University, 255 Shimo-Okubo, Sakura-ku, Saitama 338-8570, Japan; rdhns681@yahoo.co.jp (N.K.); jjhs61ns@yahoo.co.jp (N.S.)
* Correspondence: nakata@chem.saitama-u.ac.jp (N.N.); ishiiaki@chem.saitama-u.ac.jp (A.I.);
Tel.: +81-48-858-3392 (N.N.); Fax: +81-48-858-3700 (N.N.)

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Abstract: A hydrido platinum(II) complex with a dihydrosilyl ligand, [\textit{cis}-PtH(SiH}_2\textit{Trip})(PPh}_3\textit{]}(2) was prepared by oxidative addition of an overcrowded primary silane, TripSiH}_3\textit{(1, Trip = 9-triptycyl) with [Pt(\eta}_2\textit{C}_2\textit{H}_4)(PPh}_3\textit{]} 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 PPh}_3\textit{ 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(SiH}_2\textit{Trip})(L-L)] (3: L-L = dppf, 4: L-L = dcpe). In contrast, the ligand-exchange reaction of 2 with an excess amount of PMe}_3\textit{ in toluene quantitatively produced [PtH(SiH}_2\textit{Trip})(PMe}_3\textit{)(PPh}_3\textit{]} (5), where the PMe}_3\textit{ 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 \textit{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 \textit{m}-terphenyl group with [Pt(PPPr}_3\textit{]} produced the first example of a stable hydrido(dihydrosilyl) complex [\textit{cis}-PtH(SiH}_2\textit{Ar})(PPPr}_3\textit{]} (\textit{Ar} = 2,6-MesC}_6\textit{H}_3) [35]. Quite recently, Lai et al. also
described the synthesis of a bis(phosphine) hydrido(dihydrosilyl) complex [PtH(SiH2Si′Bu2Me)(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(dihydrosilyl) platinum(II) complexes [PtH(GeH2Trip)(L)] (Trip = 9-triptycyl) using a bulky substituent, 9-triptycyl group [37]. In addition, we reported the first synthesis and structural characterizations of hydrido palladium(II) complexes with a dihydrosilyl- or dihydrosileryl 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(dcone))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 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–31H 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)(PPr2)] (Ar = 2,6-MesC6H3) (δ = -3.40) [35] and [cis-PtH(SiH2Si′Bu2Me)(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 (JPt-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 (JPt-P = 2317 Hz) and 31.6 (JPt-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 (JPt(trans)-Si = 161, JPt(cis)-Si = 15 Hz) and 195Pt satellites (JPt-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]](image_url)

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 Pt1–Pt1–P2 angle of 101.63(3)° and Pt1–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 $^{31}$P[$^1$H] NMR spectrum.

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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 DCPF (1,2-bis(diphenylphosphino)ferrocene) or DCPE gave the corresponding complexes [PtH(SiH$_2$Trip)(PPh$_3$)$_2$] or [PtH(SiH$_3$)$_2$L-L] in 87% and 80% yields, respectively (Scheme 2). In the $^1$H NMR spectra of 2 and 4, the hydride resonated as a doublet of doublets at $\delta$ = –1.62 ($^2$J$_{P-H}$ = 20, 164, $^1$J$_{Pt-H}$ = 995 Hz) for 2 and –0.46 ($^2$J$_{P-H}$ = 13, 166, $^1$J$_{Pt-H}$ = 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 2 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 $^{31}$P[$^1$H] NMR spectrum of 3 showed two doublets ($^2$J$_{P-P}$ = 21 Hz) with $^{195}$Pt satellites at $\delta$ = 30.5 ($^1$J$_{Pt-P}$ = 2247 Hz) and 34.5 ($^1$J$_{Pt-P}$ = 1837 Hz), which are close to those of 2 ($\delta$ = 33.8 ($^1$J$_{Pt-P}$ = 2183 Hz) and 34.5 ($^1$J$_{Pt-P}$ = 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 $^{31}$P[$^1$H] resonances for 4 were observed as two singlets at $\delta$ = 69.2 ($^1$J$_{Pt-P}$ = 1809 Hz) and 85.3 ($^1$J$_{Pt-P}$ = 1678 Hz), respectively, which are relatively shifted downfield relative to those of 2 and 3. The larger $^1$J$_{Pt-P}$ 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 $^{29}$Si[1H] NMR spectra of 3 and 4 showed a doublet of doublets signals at $\delta = -39.0$ ($^{2}$J$_{Si-P} = 167$, 12 Hz) for 3, and $-44.6$ ($^{2}$J$_{Si-P} = 173$, 11 Hz) for 4, which were accompanied by $^{195}$Pt satellites of 1207 Hz for 3 and 1253 Hz for 4, respectively.

![Scheme 2](image)

**Scheme 2.** Ligand-exchange reaction of [cis-PtH(SiH$_2$Trip)(PMe$_3$)$_2$] 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)°, and other angles around the platinum atom are less than 90°, except the P1–Pt1–Si1 angle [95.19(9)°]. The Pt–Si bond lengths [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 [PtH(SiH$_2$Ph$_2$)(dppf)] [2.3366(4), 2.2830(4), and 2.3192(4) Å, respectively] [40].

![Figure 2](image)

**Figure 2.** ORTEP of [PtH(SiH$_2$Trip)(dppf)] 3 50% thermal ellipsoids, a solvation CH$_2$Cl$_2$ molecule, and hydrogen atoms, except H1, H2, and H3 were omitted for clarity. Selected bond lengths (Å) and bond angles (°): 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–P1 = 162.10(9), P1–Pt1–H1 = 171(5).

It is well known that trimethylphosphine (PMe$_3$) is a strong $\sigma$-donating ligand for a wide variety of transition-metal complexes. Therefore, one can reasonably expect the formation of [PtH(SiH$_2$Trip)(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 [PtH(SiH$_2$Trip)(PMe$_3$)(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 $^1$H 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 $^{31}$P–$^1$H ($J_{Pt\text{trans}}^P$–H = 157 Hz) and $^{195}$Pt–$^1$H ($J_{Pt-H}$ = 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 ($\delta = 4.68$–5.50). The $^{31}$P[$^1$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-$^1$H-decoupled $^{31}$P NMR technique at 253 K. The $^{29}$Si[$^1$H] NMR spectrum of 5 at 223 K featured one $^{29}$Si resonance as a broad doublet signal at $\delta = -43.9$ ($J_{Si-P}$ = 151 Hz). The broadening of NMR signals possibly implies the existence of the Si–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 $^1$H 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 phosphate 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 [cis-PtH(SiH$_2$Trip)(PPh$_3)_2$] 2 with trimethylphosphine (PMe$_3$).](image)

**Figure 3.** ORTEP of [PtH(SiH$_2$Trip)(PMe$_3$)(PPh$_3$)] 5 50% thermal ellipsoids, a solvation CH$_2$Cl$_2$ molecule, and hydrogen atoms, except H1, H2, and H3 were omitted for clarity. Selected bond lengths (Å) and bond angles (°): 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.

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 or C₆D₆ 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(η⁵-C₅H₄)(PPh₃)₂] [49] were prepared according to the reported procedures.

3.1.1. [cis-PtH(SiH₂Trip)(PMe₃)(PPh₃)] (2)

A solution of TripSiH₃ 1 (50.9 mg, 0.179 mmol) and [Pt(η⁵-C₅H₄)(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, 2J₉–Pt(trans) = 157, 2J₉–Pt(cis) = 19, ¹H–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, 1H, TripCH), 7.81 (d, 3J = 7 Hz, 6H, Ar), 8.11 (d, 3J = 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)), 134.2 (Ar(CH)), 135.5 (d, 1J = 46.6 Hz, Ar(C)), 148.4 (Ar(C)), 149.5 (Ar(C)). ³¹P{¹H} NMR (162.0 MHz, CDCl₃): δ = 46.6, 34.5 (d, 2J₉–P = 15 Hz, 1J₉–C = 38 Hz, Ar(C)).
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^Pt[^1^H] NMR (162.0 MHz, CDCl$_3$): δ = 33.8 (d, 2J_Pt–P = 15, 1J_Pt–P = 2183 Hz), 34.5 (d, 2J_Pt–P = 15, 1J_Pt–P = 1963 Hz). ^29^Si[^1^H] NMR (79.3 MHz, CD$_2$Cl$_2$): δ = −40.6 (dd, 2J_Si–P$_{trans}$ = 161, 1J_Si–P$_{cis}$ = 15, 1J_Si–P$_{cis}$ = 1220 Hz). IR (KBr, cm$^{-1}$): ν = 2041 (Pt–H), 2080 (Si–H). Anal. Calcd. for C$_{56}$H$_{46}$P$_2$PtSi: C, 66.99; H, 4.62. Found: C, 66.55; H, 4.61. Melting point: 123 °C (dec.).

3.1.2. [PtH(SiH$_2$Trip)(dpff)] (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$_2$O and hexane to give [PtH(SiH$_2$Trip)(dpff)] (3) (37.1 mg, 0.035 mmol, 87%) as yellow crystals.

$^1$H NMR (400 MHz, CDCl$_3$): δ = −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, Cpp and SiH$_2$), 5.30 (s, 1H, TrippCH), 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[1^H] NMR (101 Hz, CDCl$_3$): δ = 46.5 (m, TrippC), 55.2 (TrippC), 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(CH)), 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)), 127.3 (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^Pt[1^H] NMR (202 MHz, CDCl$_3$): δ = 30.5 (d, 2J_Pt–P = 21 Hz, 1J_Pt–P = 2247 Hz), 34.5 (dd, 2J_Pt–P = 21, 1J_Pt–P = 1837 Hz). ^29^Si[^1^H] NMR (79.3 MHz, CDCl$_3$): δ = −39.0 (dd, 2J_Si–P$_{trans}$ = 167, 1J_Si–P$_{cis}$ = 12, 1J_Si–P$_{cis}$ = 1207 Hz). IR (KBr, cm$^{-1}$): ν = 2055 (Pt–H), 2081 (Si–H). Anal. Calcd. for C$_{54}$H$_{44}$Fe$_2$PtSi: C, 62.73; H, 4.29. Found: C, 62.70; H, 4.27. Melting point: 183 °C (dec.).

3.1.3. [PtH(SiH$_2$Trip)(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$_2$O and hexane to give [PtH(SiH$_2$Trip)(dcpe)] (4) (25.5 mg, 0.028 mmol, 80%) as colorless crystals.

$^1$H NMR (500 MHz, CDCl$_3$): δ = −0.45 (dd, 2J_H–P$_{trans}$ = 165, 2J_H–P$_{cis}$ = 13, 1J_H–Pt = 1004 Hz, 1H, PtH), 1.16–1.51 (m, 20H, Cpp), 1.65–1.86 (m, 24H, Cpp), 2.16–2.19 (m, 2H, Cpp), 2.30–2.37 (m, 2H, Cpp), 5.32 (s, 1H, TrippCH), 5.50 (dd, 2J_H–H$_{cis}$ = 15, 3J_H–H$_{cis}$ = 6, 2J_Pt–H$_{cis}$ = 31 Hz, 2H, SiH$_2$), 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[^1^H] NMR (101 Hz, CDCl$_3$): δ = 23.2 (dd, 3J_C–P = 21, 16 Hz, PCH$_2$), 26.2 (dd, 3J_C–P = 23, 21 Hz, PCH$_2$), 26.9 (d, 3J_C–P = 14 Hz, PCy(CH$_2$)), 26.4 (d, 3J_C–P = 13 Hz, PCy(CH$_2$)), 26.8 (d, 3J_C–P = 10 Hz, PCy(CH$_2$)), 27.0 (d, 3J_C–P = 12 Hz, PCy(CH$_2$)), 28.9 (m, PCy(CH$_2$) × 2), 29.7 (m, PCy(CH$_2$)), 35.3–35.8 (m, PCy(CH) × 2), 46.8 (TrippC), 55.4 (TrippC), 122.7 (Ar(CH)), 123.6 (Ar(CH)), 126.9 (Ar(CH)), 148.6 (Ar(C)), 159.2 (Ar(C)). ^31^Pt[^1^H] NMR (162 Hz, CDCl$_3$): δ = 69.2 (s, 1J_Pt–P = 1809 Hz), 85.3 (s, 1J_Pt–P = 1678 Hz). ^29^Si[^1^H] NMR (79.3 MHz, CD$_2$Cl$_2$): δ = −44.6 (dd, 2J_Si–P$_{trans}$ = 173, 1J_Si–P$_{cis}$ = 11, 1J_Si–P$_{cis}$ = 1253 Hz). IR (KBr, cm$^{-1}$): ν = 2057 (Pt–H), 2081 (Si–H). Anal. Calcd. for C$_{46}$H$_{34}$P$_2$PtSi: C, 61.24; H, 7.15. Found: C, 61.10; H, 7.10. Melting point: 134 °C (dec.).

3.1.4. [PtH(SiH$_2$Trip)(PMe$_3$)(PPh$_3$)] (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$_2$O and hexane to give [PtH(SiH$_2$Trip)(PMe$_3$)(PPh$_3$)] (5) (75.6 mg, 94%) as colorless crystals.
\(^1\text{H}\) NMR (400 MHz, C\textsubscript{6}D\textsubscript{6}): \(\delta = -1.91\) (d, \(\text{J}_{\text{H-P}}\text{trans} = 157\), \(\text{J}_{\text{H-P}}\text{cis} = 899\) Hz, 1H, Pt(H), 1.03–1.11 (m, 9H, PMe), 5.34 (s, 1H, TripCH), 5.95–5.97 (m, 2H, SiH\(_2\)).

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\(_2\)Cl\(_2\) and hexane solution. The intensity data were collected at 103 K on a Bruker AXS SMART diffractometer (Karlsruhe, Germany) employing graphite-monochromatized Mo K\(\alpha\) radiation (\(\lambda = 0.71073\) Å). The structures were solved by direct methods and refined by full-matrix least-squares 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(SiH\(_2\)Trip)(PPh\(_3\))\(_2\)] (2)

C\textsubscript{56}H\textsubscript{46}P\textsubscript{2}PtSi, C\textsubscript{7}H\textsubscript{6}P, MW = 1096.18, triclinic, space group P\textsubscript{1}, \(a = 12.7971(6)\) Å, \(b = 13.4847(6)\) Å, \(c = 14.8861(7)\) Å, \(\alpha = 99.2791(10)^\circ\), \(\beta = 99.2791(10)^\circ\), \(\gamma = 90.3020(10)^\circ\), \(V = 2472.42\) Å\(^3\), \(Z = 2\), \(D\text{calc} = 1.472\) 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(SiH\(_2\)Trip)(dppf)] (3)

C\textsubscript{54}H\textsubscript{44}FeP\textsubscript{2}PtSi, CH\(_2\)Cl\(_2\), MW = 1118.79, monoclinic, space group P\textsubscript{2}\textsubscript{1}, \(a = 12.2585(6)\) Å, \(b = 15.5003(7)\) Å, \(c = 12.9367(6)\) Å, \(\beta = 110.8060(10)^\circ\), \(V = 2297.81(19)\) Å\(^3\), \(Z = 2\), \(D\text{calc} = 1.617\) 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(SiH\(_2\)Trip)(PM\textsubscript{3})(PPh\(_3\))] (5)

C\textsubscript{41}H\textsubscript{48}P\textsubscript{2}PtSi, CH\(_2\)Cl\(_2\), MW = 902.78, orthorhombic, space group P\textsubscript{bca}, \(a = 15.9074(6)\) Å, \(b = 20.9224(8)\) Å, \(c = 22.6113(9)\) Å, \(V = 7525.5(5)\) Å\(^3\), \(Z = 8\), \(D\text{calc} = 1.594\) 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, TriPSiH\(_3\) 1 with [Pt\((\eta^2\text{-C}_2\text{H}_4)\)(PPh\(_3\))\(_2\)] in toluene, resulted in the formation of the mononuclear (hydrido)(dihydrosilyl) complex [cis-PtH(SiH\(_2\)Trip)(PPh\(_3\))\(_2\)] 2. The ligand-exchange reactions of 2 with free chelating bis(phosphines) such as DPPF or DCPE resulted in the formations of a series of (hydrido)(dihydrosilyl) complexes [PtH(SiH\(_2\)Trip)(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(SiH\(_2\)Trip)(PM\textsubscript{3})(PPh\(_3\))] 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 PPh$_3$ and a strongly electron-donating PMe$_3$. 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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**Conflicts of Interest:** The authors declare no conflicts of interest.

**References**


21. Levchinsky, Y.; Rath, N.P.; Braddock-Wilking, J. Reaction of a symmetrical diplatinum complex containing bridging μ-η²-H–SiH(IM) ligands (IM = 2-isopropyl-6-methylphenyl) with PMe₂Ph. Formation and characterization of [(PhMe₂P)₂Pt(μ-SiH(IM))₂]. *Organometallics* 1999, 18, 2583–2586. [CrossRef]


30. Mullica, D.F.; Sappenfield, E.L. Synthesis and X-ray structural investigation of cis-hydrido(triphenylsilyl)-1,4-butadienyl-bis(dicyclohexylphosphine)platinum(II). *Polyhedron* 1991, 10, 867–872. [CrossRef]


32. Koizumi, T.; Osakada, K.; Yamamoto, T. Intermolecular transfer of triarylsilane from RhCl(H)(SiAr₃)[P(i-Pr)₃]₂ to a platinum(0) complex, giving cis-PtH(SiAr₃)(PEt₃)₂ (Ar = C₆H₅, C₆H₆H₂-p, C₆H₄Cl-p). *Organometallics* 1997, 16, 6014–6016. [CrossRef]


