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PAPER

Reaction of bis(*o*-phosphinophenyl)silane with M(PPh₃)₄ (M = Ni, Pd, Pt): synthesis and structural analysis of η^2 -(Si–H) metal(0) and pentacoordinate silyl metal(II) hydride complexes of the Ni triad bearing a *PSiP*-pincer ligand⁺

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Reactions of bis(*o*-(diphenylphosphino)phenyl)methylsilane with M(PPh₃)₄ (M = Ni, Pd, Pt) were investigated. When M = Ni or Pd, synthesis and isolation of η^2 -(Si-H) complexes of mononuclear Ni(0) and Pd(0) were achieved for the first time as frozen intermediates for oxidative addition of the Si–H bond. Structural analysis by X-ray and NMR spectroscopy disclosed that their η^2 -(Si–H) structures were maintained in both solid and solution states and coordination of the Si–H bond to the metal center was relatively weak. On the other hand, reaction with a platinum(0) complex afforded two kinds of pentacoordinate silyl platinum(II) hydride complexes having a *PSiP*-pincer ligand, which underwent unique thermal isomerization from a square-pyramidal *cis*-H–Pt–Si to a trigonal-bipyramidal *trans*-H–Pt–Si isomer. Mechanistic investigations revealed that this isomerization proceeded *via* an intramolecular rearrangement process probably through a turnstile rotation.

1. Introduction

The oxidative addition of Si–H bonds to late transition-metal complexes is an important, fundamental reaction involved in metal catalyzed-hydrosilylation of unsaturated hydrocarbons. This elementary step is proposed to include coordination of the Si–H σ -bond to the metal center followed by cleavage of the σ -bond to give silyl metal hydride complexes (Si–M–H), and investigation on the structure and reactivity of these intermediates, η^2 -(Si–H)M (A) and Si–M–H (B) complexes, is highly desirable to provide deeper mechanistic insights into the hydrosilylation reactions (Fig. 1).¹ However, synthesis and structural characterization of mononuclear η^2 -(Si–H) metal complexes of late transition metals are rather rare, and in particular, those of the Ni triad remain mostly unexplored because of their high reactivity toward oxidative addition.²⁻⁵ Indeed, only few η^2 -(Si–H) complexes of



Fig. 1 η^2 -(Si–H) metal and silvl metal hydride complexes.

mononuclear Ni(II)⁶ and Pt(0),⁷ along with several dinuclear Pd and Pt complexes,⁸ have been reported although these group 10 metals are well recognized as practical catalysts for various hydrosilylation reactions.

There has been growing interest in the synthesis, reaction and catalysis of PSiP-pincer complexes with a phenylene backbone developed by several groups including ours.9-11 These PSiP-pincer complexes of group 10 metals are usually prepared by the reaction of (o-phosphinophenyl)silanes with metal precursors (such as MCl_2 , MClMe, $MCl(\eta^3-C_3H_5)$, etc.) via cleavage of the Si-H bond and loss of H–Y (Y = Cl, CH₃, C₃H₅, etc.), and the reactivity of the resulting PSiP-pincer complexes has been mainly investigated. In this context, the reaction of the Si-H bond of such silanes with zero-valent group 10 metals has scarcely been investigated in detail.¹² We expected that the pincer-type square-planar geometry of the d⁸ H-M^{II}-Si complexes generated by oxidative addition of the Si-H bond would be destabilized due to the strain of the bicyclo[3.3.0]octane core with the rigid phenylene backbone, and therefore observation of $d^{10} \eta^2$ -(Si-H)M(0) complexes might become possible as a frozen intermediate for oxidative addition of the Si-H bond.

In this paper we describe systematic investigations on the reaction of bis(*o*-(diphenylphosphino)phenyl)methylsilane with $M(PPh_3)_4$ complexes of the Ni triad (M = Ni, Pd, Pt). These reactions lead to formation of unique η^2 -(Si–H) complexes of mononuclear M(0) or pentacoordinate silyl metal(II) hydride complexes having a *PSiP*-pincer ligand depending on the kind of the metal. Structural analyses by X-ray and NMR spectroscopy and some interesting reactivities are also discussed in detail.¹³

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2. Results and discussion

2.1. Reaction with Pd(PPh₃)₄ and Ni(PPh₃)₄: synthesis, isolation and structural analysis of η^2 -(Si-H) complexes of Ni(0) and Pd(0)

First, we investigated the reaction of Pd(PPh₃)₄ with bis(o-(diphenylphosphino)phenyl)methylsilane 1. When 1 was treated with an equimolar amount of Pd(PPh₃)₄ in THF at room temperature, the starting materials disappeared immediately and a new phosphine-palladium complex was generated as a sole product as monitored by ³¹P NMR spectroscopy. Removal of the solvent followed by washing with diethyl ether afforded pale vellow solids, which were characterized to be an unprecedented η^2 -(Si-H)Pd(0) complex 2 bearing the Si-H σ -bond coordinated to Pd(0) along with one PPh₃ and two phosphorus atoms of 1 (Table 1, entry 1). This 18-electron complex was moderately stable and the solids could be handled even in the air over a short period of time. The same complex 2 was also synthesized by the reaction of 1 with another Pd(0)-precursor, CpPd(η^3 -C₃H₅), in the presence of 1 equiv. of PPh₃ to give 2 in 86% yield (entry 2). It should be noted that any PSiP-pincer palladium(II) hydride complexes, which could be formed via ligand exchange between Pd(PPh₃)₄ and 1 followed by oxidative addition of the Si-H bond to Pd(0), were not observed. Furthermore, the corresponding η^2 -(Si-H)Ni(0) complex 3 was obtained in 73% yield by using Ni(PPh₃)₄ (entry 3).

Crystals of 2 and 3 suitable for X-ray crystallography were obtained by recrystallization from THF-pentane for 2 and from THF-Et₂O for 3, and the ORTEP diagrams are shown in Fig. 2 and 3, respectively. The geometry around the metal centers seem to be distorted tetrahedral in both cases. The Si-H, Pd-H and Pd–Si distances are 1.60(3), 1.67(3) and 2.4283(8) Å for 2. The Pd– Si distance is relatively long among those of previously reported silyl palladium(II) complexes (2.26–2.43 Å),¹⁴ reflecting the η^2 -(Si-H)Pd(0) character. The Si-H, Ni-H and Ni-Si distances are 1.62(3), 1.44(2) and 2.2782(4) Å for 3. The Ni-Si distance is relatively long among known Ni(II)-SiR₃ bonds (2.14-2.30 Å), but shorter than the value of η^2 -(Si–H)Ni(II) complex (2.348 Å) reported by Shimada and Tanaka.6 Both of the Si-H distances are obviously longer than that of the parent silane (~1.5 Å), supporting the η^2 -(Si–H) structures, but relatively shorter compared to typical values of previously reported η^2 -(Si–H) complexes of other transition metals (~1.6–1.9 Å).^{1a,d,15} These are the first example of the synthesis, isolation and X-ray analysis of zero-valent Ni and Pd complexes with an η^2 -(Si–H) ligand, which could be regarded as intermediates in the early stage of a Si-H bond activation process.



Fig. 2 ORTEP plot of 2 (disorder of one of the Ph ring on P2 was observed) at 50% probability level (hydrogen atoms except Si–H are omitted for clarity). Selected bond lengths (Å) and angles (°): Si–H 1.60(3), Pd–H 1.67(3), Pd–Si 2.4283(8), Pd–P1 2.4425(8), Pd–P2 2.3776(8), Pd–P3 2.4140(8); Si–H–Pd 95.8(15), H–Pd–Si 40.9(10), Pd–Si–H 43.3(10), P1–Pd–P2 109.63(3), P2–Pd–P3 120.49(3), P3–Pd–P1 104.59(3).



Fig. 3 ORTEP plot of 3 at 50% probability level (hydrogen atoms except Si–H are omitted for clarity). Selected bond lengths (Å) and angles (°) of 3: Si–H 1.62(3), Ni–H 1.44(2), Ni–Si 2.2782(4), Ni–P1 2.1932(4), Ni–P2 2.2003(4), Ni–P3 2.2007(4); Si–H–Ni 96.4(11), H–Ni–Si 44.8(8), Ni–Si–H 38.8(7), P1–Ni–P2 111.011(16), P2–Ni–P3 110.634(15), P1–Ni–P3 112.320(15).

It is often reported that the structures of η^2 -(Si–H)M and H–M– Si complexes in the solid state are not necessarily the same as those in solution.¹⁶ For example, Shimada and Tanaka reported that the isolated η^2 -(Si–H)Ni(II) complex underwent oxidative addition of the Si–H bond to Ni(II) to give a silyl nickel(IV) hydride complex as the most stable form in solution at low temperature.⁶ Therefore, the structures of η^2 -(Si–H)M(0) complexes **2** and **3** in solution were investigated by measurement of various NMR spectra between 300 and 193 K.

The ³¹P NMR of **2** showed two types of phosphine ligands on the palladium as a pair of a doublet and a triplet at $\delta = 36.3$ (2P, d, J = 8.1 Hz) and $\delta = 32.4$ (1P, t, J = 8.1 Hz), supporting both PPh₃ and two phosphorus atoms of **1** were on the palladium. The ¹H NMR in benzene-d₆ at 300 K exhibited an upfield shift of the hydrogen atom on Si at $\delta = 0.25$, which was coupled not only with three phosphorus atoms (td, $J_{HP} = 34.9$, 7.6 Hz) but

also with methyl protons (q, $J_{HH} = 2.3$ Hz, cf. $J_{HH} = 3.8$ Hz in 1), suggesting that the Si-H bond was maintained but was weakened through interaction with the palladium center. The Si resonance of **2** appeared at $\delta = -1.1$ (br d, $J_{PSi} = 77$ Hz) in THF-d₈ at 300 K by ²⁹Si{¹H} NMR, which was shifted to a lower field than that of the ligand 1 ($\delta = -23.1$, t, $J_{PSi} = 20$ Hz). The ${}^{1}J_{HSi}$ coupling constant was observed to be 110 Hz by non-1H-decoupled ²⁹Si NMR, which was much larger than typical values found for H-M-Si complexes (<~20 Hz) but significantly decreased from that of 1 itself (J_{HSi} = 204 Hz), supporting the elongated Si–H bond by the η^2 -(Si–H) coordination to the metal. Since ${}^{1}J_{HSi}$ coupling constants of previously reported η^2 -(Si–H) metal complexes are usually in the range of 40–70 Hz,¹⁷ this relatively larger ${}^{1}J_{HSi}$ coupling constant of 2 suggests that back-donation from the metal center to the σ^* orbital of the Si–H bond in this complex is relatively weak. Furthermore, a similar ²⁹Si-¹H coupling for 2 was observed at 193 K in THF-d₈ (J_{HSi} = 97 Hz at 193 K). Thus, these spectroscopic data clearly support the η^2 -(Si-H)Pd(0) structure as the major component in solution between 193 and 300 K. Concerning the Ni complex 3, similar characteristic spectra were obtained by ¹H and ²⁹Si NMR spectroscopy. Thus, the ¹H NMR exhibited the resonance for the hydrogen atom on Si at $\delta = -2.90$ with both ${}^{31}P^{-1}H$ coupling (td, $J_{HP} = 29.9$, 15.8 Hz) and ${}^{1}H^{-1}H$ coupling with SiCH₃ (q, $J_{\rm HH}$ = 1.3 Hz).¹⁸ The ²⁹Si–¹H coupling constant was observed to be 89 Hz at 300 K and 77 Hz at 193 K, supporting the n²-(Si-H)Ni(0) structure in solution. It should be noted that these observations are in sharp contrast to the case of the η^2 -(Si-H)Ni(II) complex reported by Shimada and Tanaka,6 which afforded H-Ni(IV)-Si complex as the most stable form at 193 K in solution. Although intermediacy of η^2 -(Si–H)nickel(0) and palladium(0) complexes has been proposed in the fluxional process of H-M-Si complexes,^{3b,4b} direct observation of such structures of Ni(0) and Pd(0) complexes in solution has not been reported, and these results would provide a useful insight into the Si-H bond cleavage process by these group 10 metals.

2.2. Reaction with Pt(PPh₃)₄: formation and structural analysis of two types of pentacoordinate platinum hydride complexes with a *PSiP*-pincer ligand and their thermal isomerization reaction

With the successful synthesis of η^2 -(Si–H)Pd(0) and -Ni(0) complexes, we next examined the reaction of Pt(PPh₃)₄ with the silane 1. In contrast to the reactions of Pd and Ni complexes, treatment of 1 with a stoichiometric amount of Pt(PPh₃)₄ in benzene-d₆ at room temperature initially afforded a mixture of two different types of

Table 2 Selected NMR data (J/Hz) of η^2 -(Si-H)Pd(0) 2 and -Ni(0) 3

	$^{1}\mathrm{H}^{a}$	²⁹ Si ^b at 300 K	²⁹ Si ^b at 193 K
2	$\delta = 0.25$ ${}^{2}J(H,PPh_{3}) = 7.6$ ${}^{2}J(H,PSiP) = 34.9$ ${}^{3}J(H,SiCH_{3}) = 2.3$	$\delta = -1.1$ ² J(Si,PPh ₃) = 77 ¹ J(Si,H) = 110	$\delta = 3.0$ ² J(Si,PPh ₃) = 81 ¹ J(Si,H) = 97
3	$\delta = -2.90$ ${}^{2}J(H,PPh_{3}) = 15.8$ ${}^{2}J(H,PSiP) = 29.9$ ${}^{3}J(H,SiCH_{3}) = 1.3$	$\delta = 5.6$ ² J(Si,PPh ₃) = 72 ¹ J(Si,H) = 89	$\delta = 6.8$ ² <i>J</i> (Si,PPh ₃) = 69 ¹ <i>J</i> (Si,H) = 77

" In benzene-d₆ at room at 300 K. ^b In THF-d₈



Scheme 1 Reaction of Pt(PPh₃)₄ with 1 at room temperature.



Fig. 4 ORTEP plot of 4 at 50% probability level (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°) of 4: Pt–Si 2.370(2), Pt–P1 2.317(2), Pt–P2 2.301(2), Pt–P3 2.280(2); Si–Pt–P1 100.45(8), Si–Pt–P2 84.15(8), Si–Pt–P3 82.62(8), P1–Pt–P2 116.41(8), P2–Pt–P3 120.65(8), P1–Pt–P3 122.85(8).

phosphine-platinum complexes, but after 4 h the intermediate complex had converted to the product complex 4. The complex 4 was isolated as a pale yellow solid in 69% yield after 16 h from a preparative scale reaction. Recrystallization of this product from THF-pentane afforded single crystals suitable for X-ray crystallography and the ORTEP diagram is depicted in Fig. 4.

As seen from Fig. 4, the platinum center in 4 adopts a trigonalbipyramidal geometry with the hydride and the silyl ligand of the PSiP-pincer ligand at the apical positions. The three phosphorus centers are located in the equatorial plane and P-Pt-P angles are P1-Pt-P2 = 116.4°, P2-Pt-P3 = 120.7° and P3-Pt-P1 = 122.9°, supporting the trigonal-bipyramidal structure around the platinum. The structure is very similar to the pentacoordinate SiP₃Pt-H complex having a tris(phosphino)silyl ligand reported by Peters.^{10f} Although the position of the hydrogen atom on the platinum was not determined by X-ray diffraction, ¹H NMR spectra in THF-d₈ clearly showed the existence of the Pt-H bond observed at $\delta = -7.92$ as a quartet with a set of ¹⁹⁵Pt satellites (q, $J_{PH} = 18.9$ Hz with $J_{PtH} = 650$ Hz). The J_{PtH} was rather small compared to those of previously reported cis-H-Pt(II)-Si complexes (890–1010 Hz),⁵ supporting that the hydride was located trans to the Si atom having strong trans influence.19 Other NMR data were also consistent with the tbp-platinum hydride structure in solution. The ³¹P NMR spectrum of **4** in THF-d₈ showed two resonances at $\delta = 38.3$ and 16.4 as a doublet and a triplet with $J_{PP} = 160$ Hz. The Si resonance of 4 appeared at δ = 42.8 as a broad singlet with ¹⁹⁵Pt satellites (J_{SiPt} = 665 Hz), in which all ²⁹Si-³¹P coupling constants were less than 20 Hz, indicating all the three phosphorus–platinum bonds were nearly perpendicular to the silicon–platinum bond. These results clearly support the pentacoordinate, trigonal-bipyramidal structure of **4** having hydrogen and silicon atoms at the apical position in both crystalline and solution states. Although there have been numerous reports on the synthesis of platinum(II) hydride complexes, synthesis of pentacoordinate, trigonal-bipyramidal platinum(II) hydride complexes is rather rare.²⁰ It should also be noted that Turculet's group reported formation of a η^2 -(Si–H)Pt(0) complex instead of the H–Pt(II)–Si complex by the reaction of a similar *PSiP*-pincer platinum(II) chloride complex bearing cyclohexyl on the phosphorus with LiEt₃BH in the absence of an additional ligand.^{7,21}

As already mentioned, the reaction of **1** with $Pt(PPh_3)_4$ first afforded an intermediate phosphine–platinum complex, which was gradually converted to tbp-**4** at room temperature. However, it was found that the reaction of **1** with $Pt(PPh_3)_4$ in THF-d₈ at -20 °C afforded the intermediate complex as a sole product without further transformation to tbp-**4**. Therefore, structural characterization was carried out by NMR spectroscopy at -20 °C with the aid of theoretical calculations, and the molecular structure was assigned to be a square-pyramidal (spy) *PSiP*-pincer platinum hydride complex **5** with *cis*-oriented hydrogen and silicon atoms (Scheme 2).



Scheme 2 Reaction of $Pt(PPh_3)_4$ with 1 at low temperature.

Fig. 5 depicts other possible isomers of silvl platinum hydride complexes C-E that might be formed in this reaction. All NMR data reasonably supported the structure of 5 to be the spy-platinum hydride complex, where the PPh₃ ligand is *trans* to Si and the two phosphorus atoms on the PSiP-pincer linkage are rapidly exchanging with each other but are equivalent at -20 °C. Thus, the ³¹P NMR spectrum showed two resonances at $\delta = 24.4$ and 15.6 as a doublet and a triplet with J_{PP} (J_{PP} = 14.2 Hz) and an upfield shifted proton resonance was observed at $\delta = -7.88$ as a triplet of doublets with a set of ¹⁹⁵Pt satellites (td, $J_{HP} = 62.7$, 16.6 Hz with J_{PtH} = 1230 Hz) by ¹H NMR spectroscopy, indicative of a complex containing hydride, PSiP and PPh3 ligands. At the beginning, we assumed that η^2 -(Si-H)Pt(0) complex E, formed as in the case of Pd and Ni metals, would be the intermediate complex 5 and the coordinating Si-H bond underwent oxidative addition to platinum to give the tbp-platinum hydride 4. However, the non-1H-



Fig. 5 Possible isomers of silyl platinum hydride complexes other than tbp-4 and spy-5.

Table 3 Selected NMR data (J/Hz) of spy-5 (at 253 K) and tbp-4 (at 300 K) in THF-d₈

	¹ H	²⁹ Si	³¹ P
5	$\delta = -7.88$ ² J(H,PPh ₃) = 16.6 ² J(H,PSiP) = 62.7 ¹ J(H,Pt) = 1230	$\delta = 32.7$ ² J(Si,PPh ₃) = 135 ² J(Si,PSiP) = 7.2 ¹ J(Si,Pt) = 680 ² J(Si,H) = < 20	$\delta = 24.4 (d, 2P)$ ² J(P,P) = 14.2 ¹ J(P,Pt) = 2519 $\delta = 15.6 (t, 1P)$ ¹ J(P,Pt) = 2174
4	$\delta = -7.92$ ${}^{2}J(H,PPh_{3}) = 18.9$ ${}^{2}J(H,PSiP) = 18.9$ ${}^{1}J(H,Pt) = 650$	$\delta = 42.8$ ${}^{2}J(Si,PPh_{3}) = < 20$ ${}^{2}J(Si,PSiP) = < 20$ ${}^{1}J(Si,Pt) = 665$	$\delta = 38.3 (d, 2P)$ ² J(P,P) = 160 ¹ J(P,Pt) = 3100 $\delta = 16.4 (t, 1P)$ ¹ J(P,Pt) = 3060

decoupled ²⁹Si NMR spectrum of **5** showed its Si resonance at δ = 32.7 with a small $J_{\rm HSi}$ value less than 20 Hz, demonstrating **5** was not a η^2 -(Si–H)Pt(0) complex but a silyl metal hydride complex (H–M–Si).

Analysis of the observed coupling constants provide support for the geometry of spy-5 (Table 3). The smaller ³¹P–³¹P coupling constant of spy-5 ($J_{PP} = 14.2 \text{ Hz}$) than that of tbp-4 ($J_{PP} = 160 \text{ Hz}$) supported that PPh3 and PSiP-phosphorus atoms were located nearly *cis*. The resonance at $\delta = 24.4$ broadened at -80 °C, suggesting there existed fluxional behavior of two phosphorus atoms of the PSiP-pincer ligand and their exchanging process was going to be frozen at this temperature. In the ¹H NMR spectrum, the ¹H-³¹P coupling with the phosphorus atoms of the PSiP-pincer ligand became larger than that of tbp-4 (62.7 Hz for spy-5; 18.9 Hz for tbp-4) due to their nearly trans-orientation, and the ¹H-¹⁹⁵Pt coupling of spy-5 (${}^{1}J_{HPt}$ = 1230 Hz) was in the range of the values of cis-(bisphosphine)Pt(H)(Si) complexes.5 A similar tendency was also observed in ²⁹Si-³¹P coupling, and the Si resonance of spy-5 appeared as a doublet of triplets ($J_{siP} = 135, 7.2$ Hz) having a larger coupling constant with PPh₃ than that with the PSiP-pincer ligand, indicating PPh₃ was located *trans* to the silicon atom.

To gain more information on the structures and relative stability of these complexes, theoretical calculations were carried out using DFT with the mPW1PW91 functional, and the optimized structure of spy- 5_{DFT} and tbp- 4_{DFT} are shown in Fig. 6. The X-ray structure of tbp-4 was well reproduced in tbp-4_{DFT}. The optimized structure of spy-5_{DFT} showed a longer Pt-P(2) distance than that of Pt-P(1) and a wider angle of H-Pt-P(1) than that of H–Pt–P(2), clearly supporting the square-pyramidal geometry having P(2) at the apical position. The tbp-4_{DFT} turned out to be more stable by 2.8 kcal mol⁻¹, which was consistent with the experimental result. It should be noted that spy-C, tbp-D and η^2 -(Si-H)Pt(0) complex E, which were other possible isomers listed in Fig. 5, were not found as stationary points, and their geometry optimization resulted in tbp-4 from spy-C and spy-5 from tbp-D and $\eta^2\mbox{-}(Si\mbox{-}H)\mbox{-}E.^{22}$ These spectroscopic data and DFT calculations well supported the structures of pentacoordinate, square-pyramidal silyl platinum hydride complex 5 and trigonalbipyramidal platinum hydride 4.23 Thus, it was confirmed that the reaction of 1 with Pt(PPh₃)₄ initially proceeded with the formation of spy-5, followed by isomerization to tbp-4 at room temperature involving cis to trans isomerization of the silyl platinum hydride moiety (Scheme 3).



Fig. 6 Optimized structures of spy-5 (a) and tbp-4 (b) using DFT with the mPW1PW91 [6-31G**/LANL2DZ].



Scheme 3 Overall reaction of $Pt(PPh_3)_4$ with 1 involving *cis* to *trans* isomerization of silyl platinum hydride.

There have been several reports on the reaction of phosphine– Pt(0) complexes with silanes to give silyl platinum hydride complexes, and in most cases *cis*-Pt(H)(Si) complexes are thermodynamically more stable and formation of *trans*-isomer is relatively rare.²⁴ For example, Osakada and Yamamoto reported that *cis*-(PEt₃)₂Pt(H)SiPh₃ underwent isomerization to its *trans*-isomer to less than 3% conversion even at 70 °C for 6 h, indicating high thermodynamic stability of the *cis*-isomer.²⁵ With a rare example of *cis* to *trans* isomerization of the silyl platinum hydride complex at room temperature in hand, we investigated the mechanism of this isomerization in more detail.

Several kinetic experiments were carried out on the isomerization reaction of spy-5 to tbp-4 (Table 4). The spy-5, which was prepared in situ by mixing Pt(PPh₃)₄ and 1 in THF-d₈ at -78 °C, underwent isomerization to tbp-4 in THF-d₈ at 30 °C with a pseudo-first-order k_{obs} of 0.23×10^{-3} s⁻¹ as monitored by ¹H NMR (entry 1). The rate of the reaction was not affected by further addition of 7 equiv. of PPh₃ (total amount of PPh₃ was 10 equiv. to spy-5, entry 2) or by carrying out the reaction in a less polar solvent such as benzene- d_6 (entry 5). The entropy of activation in the presence of an excess amount of PPh₃ was estimated to be $-0.9 \text{ J} \text{ mol}^{-1} \text{ K}^{-1}$ ($T = 30-50 \degree \text{C}$). These observations suggest that this isomerization proceeds via an intramolecular rearrangement process without dissociation of the PPh₃ ligand. We assume a turnstile rotation mechanism may be operative due to the tridentate PSiP-pincer ligand, which inhibits usually favorable pseudorotation mechanism (Scheme 4).26 The mechanism of the thermal cis to trans isomerization of tetracoordinate silvl platinum hydride complexes (P₂Pt(H)Si) have been scarcely investigated,

 Table 4
 Isomerization of spy-5 to tbp-4



silyl platinum hydride (turnstile rotation)

Scheme 4 Proposed mechanism for the isomerization of spy-5 to tbp-4.

and the present results provide a useful mechanistic insight into such isomerization reactions since the isomerization of spy-5 to tbp-4 can be regarded as a partial process of associative isomerization of *cis-trans*- $P_2Pt(H)Si.^{27}$

Conclusions

conclusion, we investigated the reaction of bis(o-In (diphenylphosphino)phenyl)methylsilane 1 with M(PPh₃)₄ of Ni triad (M = Ni, Pd, Pt). When M = Ni or Pd, synthesis and isolation of η^2 -(Si–H) complexes of mononuclear Ni(0) and Pd(0) were achieved for the first time, as frozen intermediates for oxidative addition of the Si-H bond.28 Structural analysis by X-ray and NMR spectroscopy disclosed that their η^2 -(Si–H) structures were maintained in both solid and solution states, and the coordination of the Si-H bond to the metal center is relatively weak. On the other hand, reaction with a platinum complex afforded two kinds of pentacoordinate silvl platinum(II) hydride complexes having the PSiP-pincer ligand, which underwent thermal isomerization from the square-pyramidal cis-Pt(H)(Si) to the trigonal-bipyramidal trans-Pt(H)(Si) isomer. Such thermal cis to trans isomerization of silyl platinum hydride complexes is rare and mechanistic investigation revealed that this isomerization proceeded via an intramolecular rearrangement process.

Experimental

General procedure

All operations were performed under an argon atmosphere by using standard Schlenk and glovebox techniques. ¹H, ¹³C, ²⁹Si and ³¹P NMR spectra were recorded on a Bruker DRX-500 (500 MHz for H¹, 125 MHz for ¹³C, 99.4 MHz for ²⁹Si and 202 MHz

for ³¹P) or a JEOL ECX-400 (400 MHz for H¹, 100 MHz for ¹³C and 160 MHz for ³¹P) spectrometer in CDCl₃, C₄D₈O or C₆D₆ (99.8% atom enriched, Acros Co., Ltd.). Chemical shifts in ¹H and ¹³C NMR spectra are expressed in parts per million (ppm) downfield from tetramethylsilane and are referenced to residual solvents ($\delta_{\rm H}$ 7.26 and $\delta_{\rm C}$ 77.0 for chloroform, $\delta_{\rm H}$ 3.58 (OCH₂) and $\delta_{\rm C}$ 67.4 (OCH₂) for tetrahydrofuran, $\delta_{\rm H}$ 7.15 and $\delta_{\rm C}$ 128.6 for benzene).³¹P NMR spectra are referenced relative to an 85% H₃PO₄ external standard. ²⁹Si NMR spectra are referenced relative to a tetramethylsilane standard. IR spectra were recorded on an FT/IR-460 plus (JASCO Co., Ltd.). Elemental analyses were performed on a Perkin-Elmer 2400 instrument or on an elementar vario MICRO. THF, Et₂O, pentane and toluene were purified by a solvent purification system of Glass-Contour. Benzene-d₆ and THF-d₈ were purchased from ACROS chemicals, and degassed by freeze-dry technique for benzene-d₆ or dried and degassed by benzophenone ketyl for THF-d₈. Bis(o-(diphenylphosphino)phenyl)methylsilane 1 and CpPd(η^3 -C₃H₅) were prepared according to literature procedures.9,29

Procedure for the preparation of η^2 -(Si-H)M(0)

 η^2 -(Si-H)Pd(0) 2. From $Pd(PPh_3)_4$: Bis(o-(diphenylphosphino)phenyl)methylsilane 1 (113 mg, 0.199 mmol) and Pd(PPh_3)_4 (230 mg, 0.199 mmol) were mixed in THF (10 mL) and the mixture was stirred for 30 min at room temperature. After removal of the solvent under reduced pressure, the resulting solid was washed with ether twice and recrystalized from THF–pentane at $-30 \,^{\circ}$ C to give η^2 -(Si–H)Pd(0) complex 2 (131 mg, 0.140 mmol) as a pale yellow crystalline solid in 70% yield.

From $CpPd(\eta^3 - C_3H_5)$: To a stirred solution of 1 (283 mg, 0.50 mmol) and PPh₃ (132 mg, 0.50 mmol) in Et₂O-THF (4:1, 25 mL) was added CpPd(η^3 -C₃H₅) (107 mg, 0.50 mmol) at room temperature. After 20 min, the solvent was removed under reduced pressure and the resulting solid was washed with Et₂O. Crystalization from THF-pentane at -30 °C afforded n²-(Si-H)Pd(0) complex 2 (402 mg, 0.43 mmol) in 86% yield. Crystals suitable for X-ray analysis were obtained by recrystallization from THFpentane. IR (KBr) 3051, 1584, 1478, 1433, 1102, 1090 cm⁻¹; ¹H NMR (benzene-d₆, 500 MHz, 300 K) δ 0.25 (1H, tdq, J = 34.9, 7.6, 2.3 Hz), 1.33 (3H, d, J = 2.3 Hz), 6.70–7.00 (27H, m), 7.10 (2H, t, J = 7.8 Hz), 7.28–7.33 (2H, m), 7.35–7.51 (10H, m), 7.94 $(2H, d, J = 7.4 \text{ Hz}); {}^{13}\text{C}{}^{1}\text{H}$ NMR (THF-d₈, 125 MHz, 300 K) δ 5.8 (t, J = 7.6 Hz), 127.9, 128.2 (t, J = 8.6 Hz), 128.30 (t, J = 4.4 Hz), 128.33, 128.4 (t, J = 3.8 Hz), 128.5, 128.9, 129.1, 132.5, 132.9 (t, J = 7.0 Hz), 133.3 (t, J = 8.4 Hz), 133.7 (t, J = 12.1 Hz), 134.9 (d, J = 16.3 Hz), 139.0 (t, J = 3.8 Hz), 139.2 (t, J = 6.8 Hz), 140.6 (t, J = 13.3 Hz), 146.5 (td, J = 15.9, 8.6 Hz), 155.8 (td, J = 38.9, 8.4 Hz; ${}^{31}\text{P}$ { ^{1}H } NMR (benzene-d₆, 202 MHz, 300 K) δ 32.4 $(1P, t, J = 8.1 \text{ Hz}), 36.3 (2P, d, J = 8.1 \text{ Hz}); {}^{29}\text{Si NMR} (THF-d_8, 1)$ 100 MHz) 300 K: δ –1.11 (br d, J = 77 Hz (¹H-decoupled); br dd, J = 110, 77 Hz (non ¹H-decoupled)); 193 K: δ 3.01 (br d, J =81 Hz (¹H-decoupled); br dd, J = 97, 81 Hz (non ¹H-decoupled)); Anal. Calc. for C₅₅H₄₇P₃PdSi: C, 70.62; H, 5.06. Found: C, 70.84; H, 5.32%.

Crystal data for **2**: The hydrogen bound to Si was located in the final difference map and refined isotropically. $C_{55}H_{47}P_3PdSi$, $M_r = 935.33$, monoclinic, space group $P2_1/c$, a = 16.617(6), b = 10.690(4), c = 25.340(8) Å, $\beta = 93.252(12)^\circ$, V = 4494(3) Å³, Z = 4,

 $D_c = 1.382 \text{ g cm}^{-3}$, T - -123 °C, $\mu(\text{Mo-K}\alpha) = 5.84 \text{ cm}^{-1}$, $R_1 = 0.0326$ (for 8418 reflections with $I > 2\sigma(I)$), w $R_2 = 0.0744$ (all data).

 η^2 -(Si-H)Ni(0) 3. Prepared according to the procedure described for the preparation of 2 using Ni(PPh₃)₄ instead of Pd(PPh₃)₄. Yield: 32.5 mg (0.037 mmol) from 55.4 mg (0.050 mmol) of Ni(PPh₃)₄.

IR (ATR) 2757, 1478, 1432, 1088 cm⁻¹; ¹H NMR (benzene-d₆, 500 MHz, 300 K) δ –2.90 (1H, tdq, J = 29.9, 15.8, 1.3 Hz), 1.36 (3H, d, J = 1.3 Hz), 6.69 (4H, t, J = 7.5 Hz), 6.74–6.91 (23H, m), 6.92-6.98 (2H, m), 7.10-7.13 (2H, m), 7.20-7.24 (2H, m), 7.29-7.34 (4H, m), 7.37 (4H, t, *J* = 7.5 Hz), 7.92 (2H, d, *J* = 7.3 Hz); ¹³C{¹H} NMR (THF-d₈, 125 MHz, 300 K) δ 3.8 (t, J = 5.8 Hz), 127.9-128.2 (m), 128.7, 128.9, 131.5, 132.6 (t, J = 13 Hz), 133.1 (t, J = 6.6 Hz), 133.5 (t, J = 5.9 Hz), 134.7 (d, J = 13 Hz), 138.5 (t, J = 12 Hz), 138.9 (t, J = 6.0 Hz), 139.1 (t, J = 5.3 Hz), 140.3 (td, J = 17, 3.6 Hz), 148.7 (td, J = 20, 12 Hz), 155.4–156.1 (m); ³¹P{¹H} NMR (THF, 202 MHz, 300 K) δ 44.1 (d, J = 6.2 Hz, 2P), 43.9 (t, J = 6.2 Hz, 1P); ²⁹Si NMR (THF-d₈, 100 MHz) 300 K: δ 5.6 (br d, J = 72 Hz (¹H-decoupled); br dd, J = 89, 72 Hz (non-¹H-decoupled)); 193 K: δ 6.8 (br d, J = 69 Hz (¹H-decoupled); br dd, J = 77, 69 Hz (non-¹H-decoupled)); Anal. Calc. for C₅₅H₄₇P₃NiSi: C, 74.42 H, 5.34. Found: C, 74.35; H, 5.41%.

Crystal data for **3**: The hydrogen bound to Si was located in the final difference map and refined isotropically. $C_{55}H_{47}P_3NiSi$, $M_r = 887.66$, triclinic, space group $P\bar{1}$, a = 12.2584(4), b = 18.3081(8), c = 19.6284(8) Å, $\alpha = 91.3972(13)$, $\beta = 90.1161(12)$, $\gamma = 90.9045(12)^\circ$, V = 4403.3(3) Å³, Z = 4, $D_c = 1.339$ g cm⁻³, T = -100 °C, μ (Mo-K α) = 6.15 cm⁻¹, $R_1 = 0.0340$ (for 17720 reflections with $I > 2\sigma(I)$), $wR_2 = 0.1229$ (all data).

Synthesis of tbp-4

Complex 1 (56.7 mg, 0.100 mmol) and Pt(PPh₃)₄ (124 mg, 0.100 mmol) were mixed in benzene (5.0 mL) and the mixture was stirred for 16 h at room temperature. After removal of the solvent under reduced pressure, the resulting solid was washed with ether and recrystallized from THF-pentane at -30 °C to give tbp-4 (70.9 mg, 0.0692 mmol) as a pale yellow crystalline solid in 69% yield. IR (ATR) 2757, 1906, 1585, 1479, 1433 cm⁻¹; ¹H NMR (benzene-d₆, 500 MHz, 300 K) δ –7.36 (1H, q, J = 18.1 Hz, ${}^{1}J(H, Pt) = 650 Hz$, 0.63 (3H, s), 6.77–6.99 (20H, m), 7.12 (2H, t, J = 7.4 Hz), 7.25–7.34 (13H, m), 7.60–7.64 (2H, m), 7.68–7.73 (4H, m), 8.21 (2H, d, J = 7.4 Hz); ¹³C{¹H} NMR (benzene-d₆, 125 MHz, 300 K) δ 1.43 (t, J = 13 Hz), 127.5 (t, J = 4.6 Hz), 128.1, 128.3, 129.3, 132.3 (t, J = 12 Hz), 132.9 (t, J = 6.4 Hz), 133.1 (t, J = 7.2 Hz), 133.4 (t, J = 12 Hz), 133.6 (d, J = 14 Hz), 138.9 (d, J = 35 Hz), 139.8 (t, J = 26 Hz), 141.8–142.3 (m), 145.7 (t, J = 25 Hz), 158.6 (t, J = 31 Hz); ³¹P{¹H} NMR (THF-d₈, 202 MHz, 300 K) δ 16.4 (t, J = 160 Hz, ${}^{1}J(P,Pt) = 3060$ Hz, 1P), 38.3 (d, J = 160 Hz, ${}^{1}J(P,Pt) = 3100 \text{ Hz}, 2P$; ${}^{29}Si \text{ NMR} (THF-d_8, 100 \text{ MHz}, 300 \text{ K})$ δ 42.8 (br q, $J = \langle 20 \text{ Hz}, {}^{1}J(\text{Si,Pt}) = 665 \text{ Hz}, {}^{1}\text{H-decoupled}$); Anal. Calc. for C₅₅H₄₇P₃PtSi: C, 64.51 H, 4.63. Found: C, 64.53; H, 4.60%.

Crystal data for tbp-4: $C_{55}H_{47}P_3PtSi$, $M_r = 1024.05$, monoclinic, space group $P2_1/a$, a = 19.567(3), b = 12.9268(14), c = 19.692(3)Å, $\beta = 116.36(2)^\circ$, V = 4463.1(9) Å³, Z = 4, $D_c = 1.524$ g cm⁻³, T = -150 °C, μ (Mo-K α) 33.16 cm⁻¹, $R_1 = 0.0832$ (for 7292 reflections with $I > 2\sigma(I)$), $wR_2 = 0.2017$ (all data).

Synthesis of spy-5

To a solution of Pt(PPh₃)₄ (37.3 mg, 0.030 mmol) in THF-d₈ (0.5 mL) was added 1 (17.0 mg, 0.030 mmol) at -60 °C, and then the mixture was warmed to -20 °C. Complex spy-**4** was observed as a sole product by ¹H, ³¹P and ²⁹Si NMR spectroscopy and was confirmed to be stable at -20 °C overnight. Characteristic resonances of spy-**5**: ¹H NMR (THF-d₈, 500 MHz, 253 K) δ -7.88 (1H, td, J = 62.7, 16.6 Hz, ¹J(H, Pt) = 1230 Hz), 1.20 (3H, s), 6.12–6.18 (4H, m), 6.86 (6H, t, J = 7.2 Hz), 6.92–7.05 (16H, m), 7.05–7.14 (8H, m), 7.50–7.58 (2H, m), 7.68–7.74 (3H, m), 7.93 (2H, d, J = 7.3 Hz); ³¹P{¹H} NMR (THF-d₈, 202 MHz, 253 K) δ 15.6 (t, J = 14.2 Hz, ¹J(P,Pt) = 2174 Hz, 1P), 24.4 (d, J = 14.2 Hz, ¹J(P,Pt) = 2519 Hz, 2P); ²⁹Si NMR (THF-d₈, 100 MHz, 253 K) δ 32.7 (dt, J = 135, 7.2 Hz, ¹J(Si,Pt) = 680 Hz, ¹J(Si,H) was estimated to be less than 20 Hz by non¹H-decoupled ²⁹Si NMR).

General procedure for the kinetic experiments (Table 4)

To a solution of $Pt(PPh_{3})_{4}$ (37.3 mg, 0.030 mmol) in THF-d₈ (0.5 mL) was added 1 (17.0 mg, 0.030 mmol) at -60 °C, and then the mixture was warmed to -20 °C. After the formation of spy-4 was confirmed by ¹H and ³¹P NMR spectroscopy, the NMR sample was warmed to 303 K and the decay of spy-4 and the formation of tbp-5 was monitored by ³¹P NMR spectroscopy (entry 1). Other experiments in entries 2–5 were carried out according to this procedure under corresponding conditions.

Crystal structure determination

Single crystals were obtained by slow diffusion of pentane into a solution of the complexes in THF for **2** and **4** and by slow diffusion of Et₂O into a solution of the complex in THF for **3**. Diffraction data were collected on Bruker SMART 1000 system for **2**, on Rigaku RAXIS-RAPID system for **3** and on Rigaku Mercury CCD system for **4** using graphite-monochromated Mo-Ka radiation ($\lambda = 0.7107$ Å). Structures were solved by direct methods using SHELX program package. Hydrogen atoms on Si in **2** and **3** were located in the final electron density map and refined isotropically. Disorder of one of the Ph ring on P was observed in **2**.

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- 22 These geometrical optimizations of spy-C, tbp-D and η^2 -(Si-H)-E were carried out using model structures, in which all Ph groups on phosphorus were replaced by Me. Additionally, geometry optimization of tbp-D with the real structure (phenyls on phosphorus) was confirmed to give spy-platinum as in the case of model system, although more detailed investigation on the conformation of phenyl groups was necessary.
- 23 Concerning fluxional behavior of two phosphorus atoms of the *PSiP*-pincer ligand of spy-**5**, it was disclosed that there existed an isomerization pathway from spy-**5** to its enantiomer, spy-**5**', *via* **TS**_{iso} with activation energy of 0.1 kcal mol⁻¹ by DFT calculations using model compound $\mathbf{5}_{model}$, in which all Ph groups were replaced by Me.



Exchange reaction of two phosphorus atoms on the *PSiP*-pincer ligand via TS_{iso} .

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- 27 There have been many reports on *cis-trans* isomerization of square-planar platinum(II) complexes, and a dissociative pathway *via* tricoordinate platinum intermediates or an associative pathway by the formation of pentacoordinate platinum intermediate followed by pseudorotation, are often postulated. See: (a) G. K. Anderson and R. J. Cross, *Chem. Soc. Rev.*, 1980, **9**, 185–215; (b) F. Ozawa, T. Ito, Y. Nakamura and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 1868–1880; (c) D. Minniti, *Inorg. Chem.*, 1994, **33**, 2631–2634.
- 28 We have already reported that the η^2 -(Si–H) Pd(0) complex 2 underwent oxidative addition of the Si–H bond in solution and acted as an equivalent to *PSiP*-pincer palladium hydride (see ref. 9g). The nickel complex 3 was also found to act as a nickel hydride complex during preliminary investigation, and these results will be reported in due course.
- 29 F. Ozawa, in Synthesis of Organometallic Compounds, ed. S. Komiya, Wiley, New York, 1997, p. 290.