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Reaction Mechanisms

Silyl Ligand Mediated Reversible β-Hydrogen Elimination and Hydrometalation at Palladium

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Abstract: The mechanism and origin of the facile β-hydrogen elimination and hydrometalation of a palladium complex bearing a phenylene-bridged PSiP pincer ligand are clarified. Experimental and theoretical studies demonstrate a new mechanism for β-hydrogen elimination and hydrometalation mediated by a silyl ligand at palladium, which enables direct interconversion between an ethylpalladium(II) complex and an η^2-(Si-H)palladium(0) complex without formation of a square-planar palladium(II) hydride intermediate. The flexibility of the PSiP pincer ligand enables it to act as an efficient scaffold to deliver the hydrogen atom as a hydride ligand.

Introduction

Group 10 metal complexes bearing an EXE-type pincer ligand (X = anionic C, N; E = P, N, Se, S etc.) have been widely employed as useful catalysts in synthetic organic chemistry.[1] Characteristic features of these complexes are their high thermal stability and restricted oxidation state to +2, which are attributed to the rigid tridentate structure, which efficiently suppresses ligand dissociation and reductive elimination of the two anionic ligands located in a *trans* relationship (Figure 1). However, once dissociation of a side arm followed by reductive elimination of the two anionic ligands occurs, the catalyst decomposes irreversibly to give zero-valent metal species.[2,3] Recently, metal complexes bearing a phenylene-bridged PSiP pincer-type ligand have been attracting much attention as a new type of EXE-pincer ligand in organometallic chemistry.[4–6] One of unique properties of the PSiP ligand is the "flexibility", which contrasts with typical pincer ligands, allowing both *mer*- and *fac*-coordination to a metal center and reversible reductive elimination/oxidative addition of two anionic ligands (Me-Si, allyl-Si, H-Si) as reported by the group of Turculet and by us.[4e,5b]

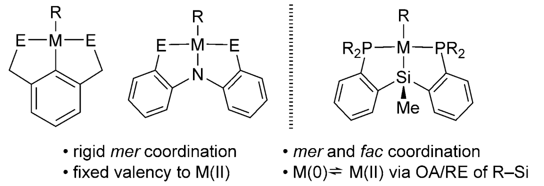

Figure 1. Group 10 metal complexes with a PXP pincer-type ligand.

In our continuing research on the synthetic utilization of the PSiP ligand,[5] we have developed a hydrocarboxylation reaction of allenes and 1,3-dienes with CO_2 catalyzed by a PSiP–palladium complex.[5a,c] This reaction is a synthetically useful CO_2-fixation reaction with simple unsaturated hydrocarbons that demonstrates the promising utility of the PSiP pincer-type ligand in synthetic chemistry. The reaction was proposed to proceed via palladium(II) hydride complex **A** as a key intermediate, which was thought to be generated by β-hydrogen elimination of ethylpalladium(II) complex (Figure 2, step 1), and

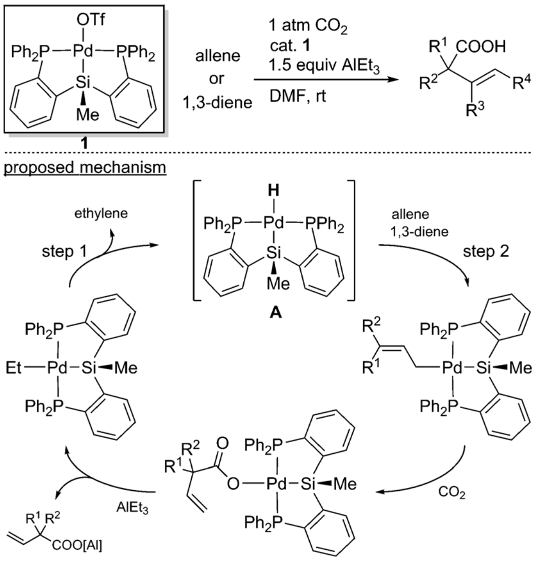

Figure 2. Proposed mechanism of the PSiP–palladium complex catalyzed hydrocarboxylation via palladium(II) hydride **A** as a key intermediate.

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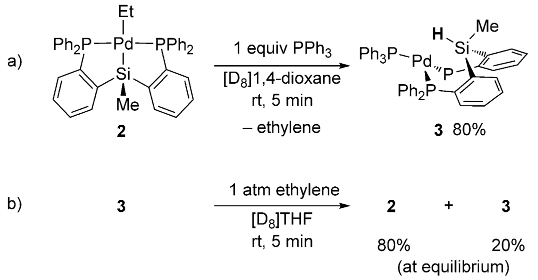
facile hydrometalation of allenes and dienes (step 2) even at room temperature. However, such a facile reaction proceeding through β-hydrogen elimination is quite surprising because there have been several examples in which pincer-type ligands efficiently stabilize alkylpalladium(II) and nickel(II) complexes having β-hydrogen atoms owing to the rigid tridentate structure, which prevents the generation of a *cis*-coordination site.[7,8] These findings suggest a key role for the flexibility of the PSiP ligand in the promotion of β-hydrogen elimination, thus prompting us to elucidate the mechanism and the origin of the facile β-hydrogen elimination for further synthetic application of the PSiP pincer-type metal complexes.

Herein, we report the results of our experimental and theoretical investigations on the mechanism of β-hydrogen elimination and its reverse reaction, hydrometalation, of the palladium complex with the PSiP pincer-type ligand. This study discloses a unique mechanism for β-hydrogen elimination and hydrometalation mediated by the silyl ligand, which proceeds directly (and reversibly) between an ethylpalladium(II) complex and an η^2-(Si-H)palladium(0) complex without formation of the palladium(II) hydride intermediate **A**. We demonstrate a new aspect of the silicon-based pincer ligand—its flexibility— that allows the ligand to act as an efficient scaffold to deliver the hydrogen atom.

Results and Discussion

Experimental studies: reaction between ethylpalladium(II) 2 and η^2-(Si-H)palladium(0) complex 3

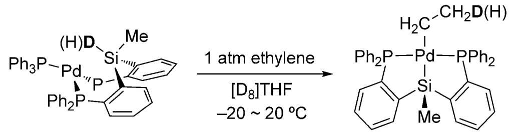
We first investigated the reactivity of ethylpalladium(II) **2**, bearing a PSiP pincer ligand, which was proposed to undergo facile β-hydrogen elimination to generate a palladium(II) hydride complex **A** in the hydrocarboxylation reaction. Ethylpalladium(II) **2** was prepared by treatment of palladium triflate complex **1** with EtMgCl in 1,4-dioxane. Although isolation of **2** was unsuccessful due to its instability under evaporation conditions during removal of solvent, it was moderately stable in 1,4-dioxane solution and was used as such for the next investigation.[9] When 1 equiv of PPh_3 was added to a solution of **2** at room temperature, most **2** disappeared immediately to afford a PPh_3-coordinated η^2-(Si-H)palladium(0) complex **3**, along with the formation of ethylene (Scheme 1a). The structure of **3** was confirmed by comparison of its ^1H and ^{31}P NMR spectra with those of an authentic sample.[5b] This result clearly shows that β-hydrogen elimination of the ethylpalladium(II) **2** occurs quickly, in spite of its pincer structure. Furthermore, this reaction was found to be reversible. The reaction of **3** with an atmospheric pressure of ethylene in $[D_8]$tetrahydrofuran proceeded at around −20 °C and gave an equilibrium mixture of **2**/**3** in a ratio of 80:20 at room temperature (Scheme 1b). The ratio was nearly unchanged at −78 or 50 °C, whereas the equilibrium shifted to the left producing more **3** when ethylene was roughly removed by evacuation for a short time (see the Supporting Information). Therefore, an ethylene-mediated interconversion between the ethylpalladium(II) **2** and η^2-(Si-H)palladium(0) **3** takes place in the presence of PPh_3. In these experiments, generation of palladium(II) hydride species was not observed.



Scheme 1. Reversible interconversion between ethylpalladium(II) complex **2** and η^2-(Si-H)palladium(0) complex **3**. **2** was prepared in situ from **1** and EtMgCl. For the top reaction, ethylene was observed by ^1H NMR spectroscopy. The yields were determined by ^1H NMR spectroscopy.

A deuterium labeling experiment using η^2-(Si-D)palladium(0) **3**, prepared by the reaction of PSiP-palladium(II) chloride complex with $LiBDEt_3$ and PPh_3, provided further evidence of the equilibrium between **2** and **3**. The reaction of **3** (90 %D) with ethylene in $[D_8]$THF afforded deuterated ethylpalladium(II) **2** in ca. 40 % at 253 K after 20 min (Table 1, entry 1). Deuterium incorporation was observed at the CH_3 position of the ethyl moiety of **2** in 82 %, and not at the methylene position. This result clearly supports the conclusion that hydropalladation of ethylene occurs with the hydrogen on silicon. Moreover, the reaction proceeded smoothly above 0 °C to give a mixture of **3** and **2** in a ratio of 7:93 (entries 2–4). Importantly, decrease of deuterium incorporation of **2** was observed as the reaction temperature was raised (58 %D at 0 °C after 30 min, 5 %D at 20 °C after 10 min, and 0 %D at 20 °C after 60 min), although the ratio of **3** and **2** remained unchanged. This facile H/D exchange can be explained by β-hydrogen elimination of deuterated **2** to release $[D_1]$ethylene followed by reinsertion of

Table 1. Time course analysis of the reaction of η^2-(Si-D)palladium(0) **3** with ethylene.[a]



3
(90 %D)

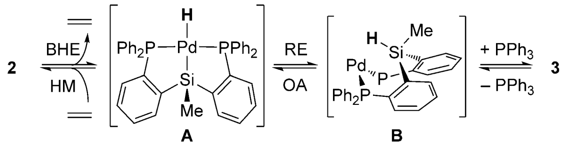
2

Entry	Temp. [°C]	Time [min]	**3**/**2**	D in **2** [%]
1	−20	20	60:40	82
2	0	30	7:93	58
3	20	10	7:93	5
4	20	60	7:93	0

[a] A solution of η^2-(Si-D)palladium(0) **3** in $[D_8]$THF under ethylene was prepared at −78 °C in a sealed NMR tube. The reaction proceeded very slowly below −40 °C. The reaction was monitored by ^1H NMR spectroscopic analysis after the time shown in the table at the indicated temperature.

[D$_0$]ethylene, thus clearly demonstrating the existence of facile equilibrium between **3**, **2**, and ethylene at around room temperature.

As a reaction mechanism, we initially proposed the intermediacy of palladium(II) hydride complex **A** in view of the fluxional behavior of the Si–H bond with palladium.[5b,g,10] Thus, ethylpalladium(II) complex **2** was thought to undergo facile β-hydrogen elimination to give a PSiP-pincer palladium hydride **A**, which was converted into η^2-(Si-H)palladium(0) intermediate **B** through reductive elimination of the Si–H bond (Scheme 2).

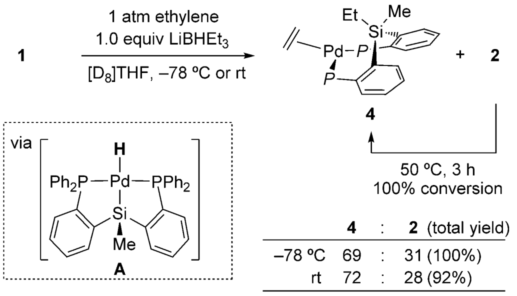


Scheme 2. Initially proposed mechanism for the interconversion between **2** and **3** via palladium(II) hydride intermediate **A**. BHE = β-hydrogen elimination, HM = hydrometalation, RE = reductive elimination, OA = oxidative addition.

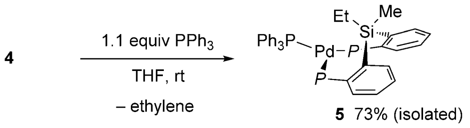
These reactions were reversible and the equilibrium favored ethylpalladium(II) **2** in solution. Addition of PPh$_3$ captured the transiently generated **B** to give η^2-(Si-H)palladium(0) **3**, whereas the presence of excess ethylene shifted the equilibrium to the ethylpalladium(II) side.

Reaction of palladium(II) hydride A with ethylene

To gain experimental support for the intermediacy of the palladium hydride complex **A**, we attempted the hydrometalation of ethylene with **A** to give **2**. Although preparation of a PSiP-palladium(II) hydride complex having dicyclohexylphosphine side arms using LiHBEt$_3$ was reported by Hazari and Kemp,[11] synthesis and isolation of diphenylphosphino derivative **A** by a similar procedure was unsuccessful, even at low temperature, due to its instability. Therefore, palladium triflate complex **1** was treated with LiBHEt$_3$ (1 equiv) under ethylene (1 atm) in [D$_8$]THF with the expectation that generated palladium(II) hydride **A** reacted with ethylene immediately to give **2**.[12] However, to our surprise, the reaction afforded an ethylene-coordinated bisphosphine-palladium(0) complex **4**, having an ethyl(methyl)silane moiety, as the major product (ca. 70%) along with a minor amount of **2** (ca. 30%) at −78 °C (Scheme 3). The ratio of **2** to **4** was not affected by carrying out the same reaction at room temperature. However, the formed **2** was fully converted into **4** by heating the mixture at 50 °C for 3 h. The structure of **4** was deduced by ^{1}H and ^{31}P NMR spectroscopic analysis (see the Supporting Information for details) and supported by derivatization of **4** as the corresponding triphenylphosphine–Pd complex **5** by addition of PPh$_3$ (Scheme 4), and characterization of **5** by X-ray analysis (Figure 3). Deuterium labeling experiments using LiBDEt$_3$ (ca. 95%D) instead of LiBHEt$_3$ in Scheme 4 gave deuterated **5**, having a deuterium at the Me position of the ethyl moiety (ca. 50%D) (Scheme 5). Thus, it is confirmed that the ethylsilane moiety is derived from hydride and ethylene, and not from BEt$_3$.[13]



Scheme 3. Reaction of palladium(II) hydride **A** with ethylene. The yields in parentheses are those determined by ^{1}H NMR spectroscopy.



Scheme 4. Trapping of **4** by PPh$_3$. Compound **4** was prepared by the reaction of **1** with LiBHEt$_3$ under ethylene (1 atm) in THF at room temperature followed by heating at 50 °C for 2 h. The yield of **5** was calculated based on **1**.

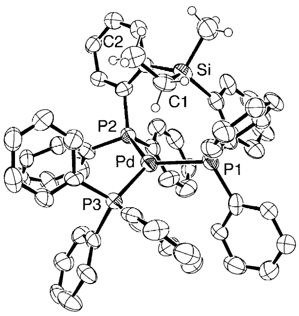
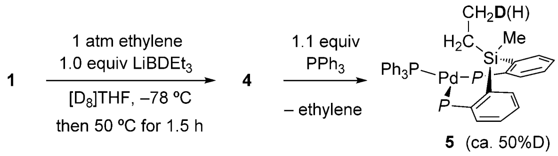


Figure 3. ORTEP drawing of **5** at 50% probability level. Hydrogen atoms except for those on Et and Me moieties are omitted for clarity.



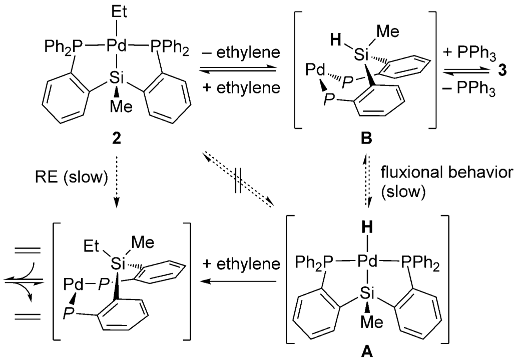
Scheme 5. Formation of deuterated **5** from **1**, LiBDEt$_3$, and ethylene.

Although the conversion of **2** into **4** through *trans*-coupling of the Et and the Si ligands was observed at 50 °C, this reaction was relatively slow and mostly negligible under the conditions employed for the generation of the palladium hydride species (−78 °C to ca. rt) shown in Scheme 3.[14,15] Thus, there should exist a direct, kinetically favored pathway leading to the "ethylsilane" product **4** through the reaction of palladium(II) hydride **A** with ethylene. A related coupling reaction of an ethyl ligand and the central atom of a pincer ligand has been reported by

Fryzuk and Green in the hydrometalation reaction of a PCP–nickel(II) hydride complex (C=N-heterocyclic carbene) with ethylene.[16] On the other hand, no formation of **4** or **5** was observed in the interconversion between **3** and **2** in Scheme 1b. If the palladium(II) hydride **A** exists during this interconversion, as we initially proposed in Scheme 2, the "ethylsilane" products **4** and **5** should also be formed considering the results presented in Scheme 3. Therefore, our initial proposal involving palladium(II) hydride **A** and fluxional behavior of the Si–H bond between **A** and **B** is not consistent with these results. It is clarified that 1) the reaction of the palladium(II) hydride **A** with ethylene does not afford ethylpalladium(II) **2** but, instead, delivers mainly the "ethylsilane" product **4**, and 2) the fluxional behavior of the Si–H bond between **A** and **B** is relatively slow compared with the reaction of **A** or **B** with ethylene. These results prompted us to consider a new possibility of ethylene-mediated *direct* interconversion between ethylpalladium(II) **2** and η²-(Si-H)palladium(0) **B** (Scheme 6).

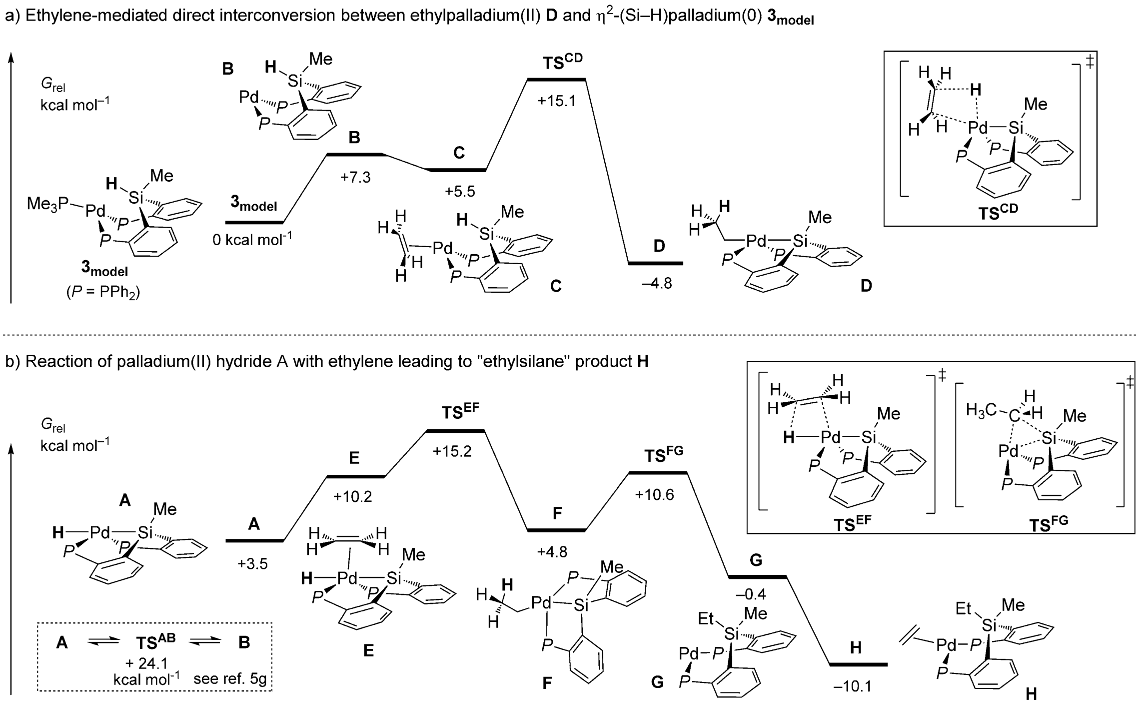
Theoretical studies

The experimental studies revealed that two distinct ethylene-mediated reactions exist among ethylpalladium(II) **2**, η²-(Si-H)palladium(0) **3**, "ethylsilane" product **4**, and palladium(II) hydride **A** as follows: 1) Ethylene-mediated direct interconversion between ethylpalladium(II) **2** and η²-(Si-H)palladium(0) **3** without intermediacy of palladium(II) hydride **A**. 2) Reaction of palladium(II) hydride **A** with ethylene leading to "ethylsilane" product **4**.



Scheme 6. Revised mechanism: ethylene-mediated direct interconversion between ethylpalladium(II) **2** and η²-(Si-H)palladium(0) **B** without formation of palladium(II) hydride **A**.

We carried out DFT calculations to clarify the mechanisms of these reactions (see the Supporting Information for details of theoretical calculations). Concerning the ethylene-mediated direct interconversion between **2** and **3** (type 1, above), it is clarified that η²-(Si-H)palladium(0) **B** itself undergoes hydrometalation of ethylene via five-coordinate transition state **TS**$^{\mathbf{CD}}$, leading to square-planar ethylpalladium(II) **D**, directly without formation of any palladium(II) hydride intermediates (Figure 4a).[17] This reaction is energetically feasible from both sides (ΔG[**TS**$^{\mathbf{CD}}$–**D**] = +19.9, ΔG[**TS**$^{\mathbf{CD}}$–**3**$_{\mathbf{model}}$] = +15.1 kcal mol^{-1}), which reasonably accounts for the facile H/D exchange of deuterated **2** at 20 °C reported in Table 1.[18] In contrast, the initially proposed hydrometalation pathway from palladium(II) hydride


a) Ethylene-mediated direct interconversion between ethylpalladium(II) **D** and η²-(Si–H)palladium(0) **3**$_{\mathbf{model}}$

b) Reaction of palladium(II) hydride A with ethylene leading to "ethylsilane" product **H**

Figure 4. Energy profiles. a) Ethylene-mediated direct interconversion between ethylpalladium(II) **2** and η²-(Si-H)palladium(0) **3**. b) Reaction of palladium(II) hydride **A** with ethylene leading to "ethylsilane" product **4**. DFT calculation by PW91PW91 [6-31G(d,p)/LANL2DZ] in THF(PCM). G_{rel} refer to Gibbs' free energies relative to the sum of **3**$_{\mathbf{model}}$ and two molecules of ethylene in kcal mol^{-1}.

A (type 2, above) is found to proceed via trigonal bipyramidal transition state **TS^{EF}**, consisting of an ethylene group in the equatorial position and a hydride and a silicon in apical positions (Figure 4b). However, this reaction affords *cis*-ethylpalladium(II) complex **F**, which easily undergoes reductive elimination of an Et–Si bond to give bisphosphine-palladium(0) **G**, having an ethyl(methyl)silane moiety. Coordination of an ethylene to **G** forms **H** as the most stable compound. Once the reductive elimination product **H** is formed, the back reaction to palladium(II) hydride complex **A** at room temperature is difficult (ΔG[**TS^{EF}**–**H**] $= +25.3$ kcal mol^{-1}). This is in good agreement with the results of the deuterium labeling experiments shown in Scheme 5, in which a certain amount of deuterium was retained in the "ethylsilane" product **4** after heating at 50 °C for 1.5 h. The small energetic barrier for the reductive elimination step (ΔG[**TS^{FG}**–**F**] $= +5.8$ kcal mol^{-1}) supports the facile formation of **4** without any detectable intermediates at −78 °C reported in Scheme 3. The direct interconversion between **A** and **B** requires higher activation energy (**TS^{AB}** $= +24.1$ kcal mol^{-1})[5g] than for hydrometalation with **A** or **B** (**TS^{CD}** $= +15.1$, **TS^{EF}** $= +15.2$ kcal mol^{-1}), supporting the conclusion that the fluxional behavior of the Si–H bond between palladium(II) hydride and η^2-(Si-H)Pd(^{0}) is negligible in these reactions. These experimental and theoretical investigations demonstrate that two distinct hydrometalation pathways from η^2-(Si-H)palladium(0) **B** and palladium(II) hydride **A** exist. The former affords ethylpalladium(II) complex **2** in equilibrium as shown in Scheme 1, whereas the latter results in the irreversible formation of reductive elimination product **4** as shown in Scheme 3.

The most important finding in this theoretical study is the feasible interconversion between **D** and **3$_{model}$** via **TS^{CD}**. This is a relatively rare example of reversible β-hydrogen elimination and hydrometalation mediated by the silyl ligand accompanying a change of the oxidation state of palladium between II and 0.[19] The geometry around the palladium in **TS^{CD}** is trigonal bipyramidal, consisting of a hydride and two phosphorous ligands in an equatorial plane (Figure 5). This reaction can be regarded as a hydrometalation reaction by a transiently generated trigonal pyramidal palladium hydride and also as an associative β-hydrogen elimination reaction of an ethylpalladium(II) complex bearing a PSiP pincer ligand. Yamamoto reported a rare example of associative β-hydrogen elimination in thermolysis of *trans*-[PdEt$_2$(PR$_3$)$_2$], resulting in the formation of ethylene, ethane, and a bisphosphine–palladium(0) complex.[20] The authors pointed out the importance of the steric environment of the tertiary phosphine ligand to distort the original square-planar geometry to trigonal bipyramidal. Our system clearly possesses two advantages that facilitate this reaction as follows. 1) The phenylene-bridged PSi(sp^3)P pincer ligand facilitates formation of trigonal bipyramidal geometry in which the P1-Pd-P2 angles bend significantly (116.8°) due to its distortion in square planar geometry. 2) The PSiP ligand works as an efficient scaffold for keeping the hydride ligand after β-hydrogen elimination as a silane. The Si–H bond is a weak bond and is easily cleaved by palladium(0) again, enabling the system to work as an efficient catalyst in hydrometalation (Figure 6). This is in contrast to carbon ligand systems such as those described in Yamamoto's report and the PCP pincer ligand, in which the hydride ligand is lost by reductive elimination of a C–H bond and does not return to the metal as a hydride ligand. Therefore, the PSiP pincer ligand enables facile, reversible β-hydrogen elimination and hydrometalation despite its tridentate structure. This unique mechanism, based on the characteristic features of the phenylene-bridged PSiP pincer ligand, is highly promising for the development of new catalytic synthetic reactions that are difficult to achieve by common EXE pincer ligands.[21] Further utilization of the PSiP pincer-type metal complexes in synthetic chemistry is in progress in our group.

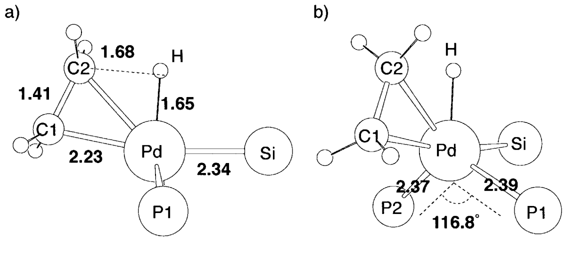
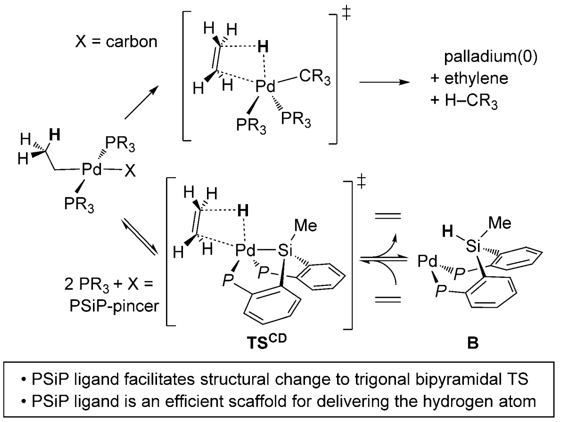


Figure 5. Selected bond lengths (Å) and angles (deg) for **TS^{CD}**. a) Side view. b) Front view.



- PSiP ligand facilitates structural change to trigonal bipyramidal TS
- PSiP ligand is an efficient scaffold for delivering the hydrogen atom

Figure 6. The key roles of the PSiP-pincer ligand in β-hydrogen elimination and hydrometalation between **2** and **B**.

Conclusion

We have clarified the mechanism and the origin of a facile β-hydrogen elimination and hydrometalation of the palladium complex bearing a phenylene-bridged PSiP pincer ligand. Experimental and theoretical studies demonstrated a unique mechanism for β-hydrogen elimination and hydrometalation mediated by the silyl ligand, which enables facile interconversion between ethylpalladium(II) and η^2-(Si-H)palladium(0). The PSiP pincer ligand acts as an efficient scaffold for delivering the hydrogen atom as a hydride ligand and facilitating structural change in the transition state by utilizing its flexibility. We envision that these characteristic features of the silicon-based pincer ligand will open up new possibilities for the development of new catalytic synthetic reactions.

Experimental Section

General

All operations were performed under an argon atmosphere. NMR spectra were recorded with a Bruker DRX-500 spectrometer (500 MHz for ^{1}H, 125 MHz for ^{13}C, 202 MHz for ^{31}P, and 99.4 MHz for ^{29}Si) in [D$_8$]THF, [D$_8$]1,4-dioxane, or [D$_6$]benzene (99.8% atom enriched, Acros Co., Ltd.). Chemical shifts are expressed in parts per million (ppm) downfield from tetramethylsilane and are referenced to residual solvents ($\delta_H = 3.58$ (OCH$_2$) and $\delta_C = 67.4$ ppm (OCH$_2$) for THF, $\delta_H = 3.53$ and $\delta_C = 66.5$ ppm for 1,4-dioxane, $\delta_H = 7.15$ and $\delta_C = 128.6$ ppm for benzene). ^{31}P NMR spectra are referenced relative to an 85% H_3PO_4 external standard. ^{29}Si NMR spectra are referenced relative to tetramethylsilane external standard. IR spectra were recorded with an FTIR-460 plus (JASCO Co., Ltd.). High-resolution mass analyses (FAB$^+$) were performed with a JEOL JMS-700 mass spectrometer. THF, Et_2O, pentane, and toluene were purified with a solvent purification system from Glass-Contour. [D$_6$]Benzene, [D$_8$]1,4-dioxane, and [D$_8$]THF were purchased from ACROS chemicals, and dried and degassed by benzophenone ketyl. Crystal data were collected with a Rigaku Saturn CCD system equipped with a Rigaku GNNP low-temperature device. PSiP–palladium triflate complex **1** and η^2-(Si-H)palladium(0) complex **3** bearing PPh_3 were prepared according to previously reported procedures.[5a,b] See the Supporting Information for details and spectra of each reaction.

Preparation of ethylpalladium(II) complex 2

EtMgCl (1.0 м in THF, 7.0 μL, 0.0070 mmol) was added to a solution of PSiP–palladium triflate **1** (4.1 mg, 0.0050 mmol) in [D$_8$]1,4-dioxane (0.5 mL) at RT in a sealed NMR tube. The solution became yellow immediately, and the ethylpalladium complex **2** was formed as a major product. The yield is estimated to be ca. 70% by using mesitylene (0.022 mmol) as an internal standard. The choice of [D$_8$]1,4-dioxane as solvent was crucial for the major formation of **2**; performing the reaction in other solvents such as [D$_8$]THF or [D$_6$]benzene caused partial decomposition of the complex. Several attempts to isolate **2** were unsuccessful due to its decomposition during removal of solvent under reduced pressure. The solution was therefore used for subsequent investigation. ^{1}H NMR (500 MHz, [D$_8$]1,4-dioxane): $\delta = -0.14$ (s, 3H), 0.52–0.61 (m, 2H), 0.91 (t, $J = 8.3$ Hz, 3H), 7.30–7.46 (m, 22H), 7.57–7.64 (m, 4H), 8.15 ppm (d, $J = 7.3$ Hz, 2H); ^{31}P NMR (202 MHz, [D$_8$]1,4-dioxane): $\delta = 58.1$ ppm (s); ^{29}Si NMR (99.4 MHz, [D$_8$]1,4-dioxane): $\delta = 59.3$ ppm; ^{13}C NMR (125 MHz, [D$_8$]1,4-dioxane): $\delta = 5.6$ (s; SiCH$_3$), 13.3 (t, $J = 9$ Hz; PdCH$_2$CH$_3$), 17.8 ppm (s, PdCH$_2$CH$_3$).

Reaction of ethylpalladium(II) complex 2 with PPh_3 (Scheme 1a)

PPh_3 (1.4 mg, 0.0053 mmol, ca. 1 equiv to originally used palladium triflate **1**) was added to the solution of ethylpalladium complex **2** in [D$_8$]1,4-dioxane prepared as described above at RT in a sealed NMR tube. After 5 min, ^{31}P NMR spectroscopic analysis showed that η^2-(Si-H)palladium(0) complex **3** was formed as the major product (80% yield calculated from **2**). A small amount of free PSiP-ligand (ca. 15%) and **2** (ca. 8%) were also observed. The yield was determined by using H_3PO_4 as an external standard. Generation of ethylene was observed by ^{1}H NMR spectroscopic analysis.

Reaction of η^2-(Si-H)palladium(0) complex 3 with ethylene (Scheme 1b)

A solution of η^2-(Si-H)palladium(0) complex **3** (4.7 mg, 0.0050 mmol) in [D$_8$]THF (0.5 mL) was placed in a sealed NMR tube and the atmosphere was replaced by ethylene (1 atm) by using standard Schlenk techniques at RT. After 5 min, an equilibrium mixture of ethylpalladium **2** and **3** was observed by ^{1}H and ^{31}P NMR spectroscopic analysis in a ratio of 80:20. The yields were determined by using H_3PO_4 as an external standard. The ratio was nearly unchanged at −78 or 50 °C. The equilibrium shifted to the left, producing more **3** in the ratio of **2**/**3** = 55:45 when ethylene was roughly removed three-times by quick evacuation.

Reaction of palladium(II) hydride A with ethylene (Scheme 3)

A solution of palladium triflate complex **1** (4.1 mg, 0.0050 mmol) in [D$_8$]THF (0.50 mL) was placed in a sealed NMR tube and the atmosphere was replaced by ethylene (1 atm) by using standard Schlenk techniques at RT. To the solution was added LiBHEt$_3$ (1.0 м in THF, 5.0 μL, 0.0050 mmol) at −78 °C, then ^{1}H and ^{31}P NMR spectra were recorded at −80 °C after 20 min. The formation of "ethylsilane" product **4** (η^2-(ethylene)(P)$_2$palladium(0)) and ethylpalladium(II) complex **2** was observed in ca. 70 and 30% yield, respectively, by using H_3PO_4 as an external standard. The same reaction at RT also led to the formation of **4** and **2** in almost the same ratio. Furthermore, ethylpalladium(II) **2** was fully converted into "ethylsilane" **4** when the mixture obtained above was heated at 50 °C for 3 h. Structural analyses of **4** are described in the Supporting Information in detail. Selected spectroscopic data of **4**: ^{1}H NMR (500 MHz, [D$_8$]THF, 300 K): $\delta = 0$–2 (8H, aliphatic protons (CH$_3$ and CH$_2$CH$_3$) cannot be identified.), 2.4–3.2 (br, 4H), 6.58–6.64 (br, 2H), 6.83 (t, $J = 7.5$ Hz, 2H), 7.01 (t, $J = 7.5$ Hz, 2H), 7.04–7.26 (m, 20H), 7.48 ppm (d, $J = 7.5$ Hz, 2H); ^{1}H NMR (500 MHz, [D$_8$]THF, 213 K): δ (75:25 mixture of two diastereoisomers) = 0–2 (8H, aliphatic protons (CH$_3$ and CH$_2$CH$_3$) cannot be identified.), 2.50–2.70 (br, 2H), 2.98 (d, $J = 13.1$ Hz, 0.5H), 3.04 (d, $J = 13.1$ Hz, 1.5H), 6.47–6.53 (br, 0.5H), 6.54–6.59 (br, 1.5H), 6.82–6.90 (br, 2H), 7.10–7.32 (m, 22H), 7.47 ppm (br d, 2H). ^{31}P NMR ([D$_8$]THF, 202 MHz, 300 K): $\delta = 23.8$ ppm (s); ^{31}P NMR ([D$_8$]THF, 213 K): $\delta = 24.0$ (s, 1.5P), 23.5 ppm (s, 0.5P); ^{29}Si NMR ([D$_8$]THF, 99.4 MHz, 213 K): $\delta = -7.9$ (t, $J = 8.5$ Hz, 0.75Si), −4.0 ppm (t, $J = 8.3$ Hz, 0.25Si); ^{13}C NMR ([D$_8$]THF, 125 MHz, 213 K): $\delta = 54.1$–54.4 ppm (m, η^2-(ethylene)Pd(^{0})).

Derivatization of 4 to a PPh_3-coordinated palladium(0) complex having an ethylsilane moiety (Scheme 4)

LiBHEt$_3$ (1.0 м in THF, 110 μL, 0.11 mmol) was added to a solution of the palladium triflate complex **1** (82.2 mg, 0.10 mmol) in THF (5.0 mL) at −78 °C under an ethylene atmosphere. The cooling bath was removed and the mixture was allowed to stand at RT, then the mixture was heated at 50 °C for 2 h to convert the ethylpalladium(II) **2** into **4**. PPh_3 (28.8 mg, 0.11 mmol) was added to the solution at RT and the mixture was stirred for 1 h. After the solvent was removed under reduced pressure, the crude product was purified by reprecipitation from THF–Et_2O to give **5** (70.0 mg, 0.073 mmol, 73%) as a yellow solid. The structure of **5** was determined by X-ray analysis; single crystals suitable for X-ray analysis were obtained by recrystallization from THF–Et_2O. In solution, **5** exists as an equilibrium mixture of two diastereoisomers (ca. 1:1), one of which contains the Et moiety inside and the second contains the Me inside (see the Supporting Information). The ^{31}P NMR spectrum of **5** in [D$_8$]THF shows two broad signals around $\delta = 15$ and 22 ppm, whereas the signals split into two pairs of doublets (for PSiP) and triplets (for PPh$_3$) at $\delta = 14.7$ (d), 15.1 (d), 22.1 (t), and 22.5 ppm (t) at $-20\,^{\circ}$C. Similar temperature-dependent behavior was also observed in the ^{1}H NMR spectra. The interconversion of two diastereoisomers in solution was confirmed by saturation transfer experiment in ^{1}H NMR spectra at $-40\,^{\circ}$C. Crystallographic data are given in the Supporting Information (CCDC-969321). Spectroscopic data of **5** (as a 1:1 mixture of **5a** and **5b**): ^{1}H NMR (500 MHz, [D$_8$]THF, 300 K): $\delta = 0.3$–1.8 (br, 8H), 6.54–6.65 (br, 2H), 6.85 (t, $J = 7.3$ Hz, 2H), 6.88–7.21 (m, 37H), 7.53 (d, $J = 7.3$ Hz, 2H); ^{1}H NMR (500 MHz, [D$_8$]THF, 233 K): $\delta = 0.39$ (s, 1.5H), 0.52 (t, $J = 7.4$ Hz, 1.5H), 0.69 (t, $J = 7.4$ Hz, 1.5H), 0.97 (s, 1.5H), 1.02–1.08 (m, 1H), 1.63–1.70 (m, 1H), 6.51–6.55 (m, 1H), 6.57–6.64 (m, 1H), 6.84–7.25 (m, 39H), 7.50–7.56 ppm (m, 2H); ^{31}P NMR ([D$_8$]THF, 202 MHz, 300 K): $\delta = 14.5$–15.6 (m, 2P), 21.5–23.1 ppm (m, 1P); ^{31}P NMR ([D$_8$]THF, 202 MHz, 253 K): $\delta = 14.7$ (d, $J = 85$ Hz, 1P), 15.1 (d, $J = 85$ Hz, 1P), 22.1 (t, $J = 85$ Hz, 0.5P), 22.5 ppm (t, $J = 85$ Hz, 0.5P); IR (ATR): $\tilde{\nu} = 3051$, 2923, 1584, 1476, 1433, 1255, 1179, 1089, 1030 cm^{-1}; HRMS (FAB$^+$): m/z calcd for C$_{38}$H$_{33}$P$_2$PdSi [M-PPh$_3$-CH$_3$] 685.0862; found 685.0848.

General procedure for computational studies

All calculations were performed with the Gaussian 09 program package (revision B.01).[22] Equilibrium and transition-state structures were optimized by density functional theory (DFT) using the PW91PW91 hybrid functional with tight SCF convergence and ultrafine integration grids. The LANL2DZ basis set, including a double-z valence basis set with the Hay and Wadt effective core potential (ECP), was used for palladium and the 6–31G(d,p) basis set was used for carbon, hydrogen, phosphorous, and silicon. Each of the stationary points was adequately characterized by normal coordinate analysis (no imaginary frequency for an equilibrium structure and one imaginary frequency for a transition-state structure). Intrinsic reaction coordinates (IRC) were calculated to verify the relevance of transition-state structures. The bulk effects of the THF solvent were taken into account by performing geometry optimizations with the polarizable continuum model (PCM). In all the calculations, the temperature was set to 298.15 K.

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Keywords: hydride ligands · ligand effects · palladium · reaction mechanisms · silicon

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[9] The structure of **2** was supported by ^{1}H and ^{31}P NMR spectroscopic analysis. The ^{31}P NMR spectra show a singlet peak at $\delta = 58.1$ ppm and the ^{1}H NMR spectra exhibited methylene protons of the Et moiety at $\delta = 0.52$–0.61 ppm (m, 2H) and terminal methyl protons at $\delta = 0.91$ ppm (t, $J = 8.3$ Hz, 3H). See the Supporting Information for more details.

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[12] The reaction of an isolated PSiP–palladium(II) hydride complex having dicyclohexylphosphine side arms with ethylene afforded a new complex, which was thought to be the corresponding “ethylsilane” product

by ^{31}P NMR analysis ($\delta = 22–24$ (br) at 233 K), below −40 °C. However, neither isolation nor characterization by its conversion into a phosphine-coordinated complex were successful due to facile formation of an aryl(silyl)palladium(II) complex through oxidative addition of an aryl–silyl bond, as reported by Turculet in ref. [4e].

[13] Considering the result in Scheme 3, it is conceivable that ca. 30% of **4** (Scheme 5) is derived from ethylpalladium(II) **2**, which is capable of undergoing rapid H/D exchange above room temperature as shown in Table 1 (see also ref. [14] and [15]). Additionally, a part of **4** might undergo H/D exchange through reverse reaction at 50 °C, as described in the theoretical studies section. Therefore, the 50% deuterium incorporation of **5** seems reasonable and supports the conclusion. The determination of the deuterium content of **4** at low temperature was difficult because of its complex ^{1}H NMR spectrum (see the Supporting Information).

[14] Detailed investigations on the mechanism for the formation of **4** from **2** through *trans* coupling of the Et and Si ligands are in progress. The results will be reported in due course.

[15] The mechanism for the formation of **2** (Scheme 3) is unclear at present. We confirmed that ethylpalladium(II) **2** was not formed by the reaction of **1** and $LiBHEt_3$ under Ar atmosphere, thus ruling out the possibility that BEt_3 worked as an ethyl source. There might be a pathway for direct formation of η^2-(Si-H)palladium(0) **B** by reaction of **1** with $LiBHEt_3$.

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[18] One might consider the possibility of generating of a square-planar *cis*-palladium(II) hydride complex, in which the hydride and the silicon ligands are located *cis*, with one phosphine ligand liberated, followed by hydrometalation of ethylene to give the ethylpalladium(II) **D** directly. However, dissociation of one of the phosphine ligands is energetically unfavorable, and attempts to optimize a reaction pathway with such a complex resulted in the same reaction with η^2-(Si-H)palladium(0) **B**.

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