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Bis(*o*-phosphinophenyl)silane as a Scaffold for Dynamic Behavior of H−Si and C−Si Bonds with Palladium(0)

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Summary: Synthesis and structural analysis of an unprecedented η^2-Si−H complex of mononuclear Pd(0) was achieved utilizing bis(o-phosphinophenyl)silane as a PSiP pincer-type scaffold for the first time. This complex showed dynamic behavior in its reaction with an allene, involving a reversible oxidative addition/reductive elimination sequence of a C(sp^3)−Si bond at room temperature. This system will be useful as a synthetic equivalent of highly reactive hydrido- and (σ-allyl)palladium species.

The studies of η^2-Si−H complexes have been attracting much attention, since they can provide deeper mechanistic insight into transition-metal-catalyzed silylation reactions involving oxidative addition of the Si−H bond, in which such σ complexes can be considered as "frozen intermediates".[1] However, the synthesis and structural characterization of such η^2-Si−H metal complexes of the Ni triad remains mostly unexplored because of their high reactivity toward oxidative addition to give silyl metal hydride complexes (H−M−Si),[2] and no structural analysis of zerovalent, mononuclear η^2-Si−H Pd(0) complexes has been reported, even though these low-valent metals are well recognized as practical catalysts for various hydrosilylation reactions.[3−5] Herein we report the first synthesis and structural analysis of a η^2-Si−H complex of mononuclear Pd(0) and its dynamic behavior with an allene through an oxidative addition/insertion/reductive elimination sequence utilizing a *PSiP* pincer-type structure.

Our recent finding of the *PSiP* pincer-type palladium complex catalyzed hydrocarboxylation of allenes under 1 atm of CO_2 prompted us to synthesize a possible key intermediate, the silyl pincer-type palladium hydride **A**, for detailed mechanistic studies.[6] When bis(*o*-(diphenylphosphino)phenyl)methylsilane (**1**)[7] was treated with an equimolar amount of $Pd(PPh_3)_4$ in THF at room temperature, the complex obtained was not the expected palladium hydride **A** but the (η^2-Si−H)Pd^0 species **2** with a Si−H σ-bond coordinated to Pd(0) along with one PPh_3 and the two phosphorus atoms of **1** (Scheme 1, conditions a). Complex **2** was also obtained in 86% yield by the reaction of **1** with $CpPd(C_3H_5)$ in the presence of PPh_3 (conditions b).

The ORTEP diagram of **2** is shown in Figure 1. The structure around Pd is distorted tetrahedral, and the Si−H, Pd−H, and Pd−Si distances are 1.60(3), 1.67(3), and 2.4283(8) Å, respectively.[8] The Si−H distance is obviously longer than that of the parent silane (~1.5 Å) but relatively shorter compared to typical

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(1) (a) Schubert, U. *Adv. Organomet. Chem.* **1990**, *30*, 151. (b) Crabtree, R. H. *Angew. Chem., Int. Ed.* **1993**, *32*, 789. (c) Schneider, J. J. *Angew. Chem., Int. Ed.* **1996**, *35*, 1068. (d) Kubas, G. J. *J. Organomet. Chem.* **2001**, *635*, 37. (e) Lin, Z. *Chem. Soc. Rev.* **2002**, *31*, 239.

(2) For examples of oxidative addition of the H−Si bond to group 10 metals to give silyl metal complexes, see: (a) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175 and references therein. (b) Shimada, S.; Tanaka, M. *Coord. Chem. Rev.* **2006**, *250*, 991. (c) Iluc, V. M.; Hillhouse, G. L. *Tetrahedron* **2006**, *62*, 7577. (d) Steinke, T.; Gemel, C.; Cokoja, M.; Winter, M.; Fischer, R. A. *Angew. Chem., Int. Ed.* **2004**, *43*, 2299. (e) Boyle, R. C.; Pool, D.; Jacobsen, H.; Fink, M. J. *J. Am. Chem. Soc.* **2006**, *128*, 9054.

(3) Syntheses of η^2-Si−H complexes stabilized by dinuclear structures involving Pt−Pt, Pt−Pd, and Pd−Pd have been reported: (a) Auburn, M.; Ciriano, M.; Howard, J. A. K.; Murray, M.; Pugh, N. J.; Spencer, J. L.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1980**, 659. (b) Kim, Y.-J.; Lee, S.-C.; Park, J.-I.; Osakada, K.; Choi, J.-C.; Yamamoto, T. *Organometallics* **1998**, *17*, 4929. (c) Tanabe, M.; Yamada, T.; Osakada, K. *Organometallics* **2003**, *22*, 2190. (d) Nakajima, S.; Sumimoto, M.; Nakao, Y.; Sato, H.; Sakaki, S.; Osakada, K. *Organometallics* **2005**, *24*, 4029. (e) White, C. P.; Braddock-Wilking, J.; Corey, J. Y.; Xu, H.; Redekop, E.; Sedinkin, S.; Rath, N. P. *Organometallics* **2007**, *26*, 1996 and references therein. (f) Tanabe, M.; Ito, D.; Osakada, K. *Organometallics* **2008**, *27*, 2258 and references therein.

(4) The synthesis and X-ray analysis of a mononuclear η^2-Si−H complex of Ni(II) have been reported: (a) Chen, W.; Shimada, S.; Tanaka, M.; Kobayashi, Y.; Saigo, K. *J. Am. Chem. Soc.* **2004**, *126*, 8072. Recently, Turculet and co-workers reported the synthesis of a η^2-Si−H coordinated Pt(0) complex, which was structurally identified by NMR, IR, and low-resolution X-ray analysis; however, an exact X-ray structure analysis was not reported: (b) Mitton, S. J.; McDonald, R.; Turculet, L. *Organometallics* **2009**, *28*, 5122.

(5) (a) Ball, Z. T. In *Comprehensive Organometallic Chemistry III*; Ojima, I., Ed.; Elsevier: Oxford, U.K., 2007; Vol. *10*, p 789. (c) Makabe, H.; Negishi, E.; In *Organopalladium Chemistry*; Negishi, E., Ed.; Wiley: New York, 2002; Vol. *2*, p 2789.

(6) Takaya, J.; Iwasawa, N. *J. Am. Chem. Soc.* **2008**, *130*, 15254.

(7) For the synthesis of **1** and **3**, see: MacInnis, M. C.; MacLean, D. F.; Lundgren, R. J.; McDonald, R.; Turculet, L. *Organometallics* **2007**, *26*, 6522.

(8) Synthesis of **2** by the reaction of **1** with $Pd(PPh_3)_4$: 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 solvent under reduced pressure, the resulting solid was washed with ether twice and recrystallized from THF−pentane at −30 °C to give the (η^2-Si−H)Pd^0 complex **2** (131 mg, 0.140 mmol) as a pale yellow crystalline solid in 70% yield. IR (KBr): 3051, 1584, 1478, 1433, 1102, 1090 cm^{-1}. ^1H NMR (benzene-d_6, 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 Hz). ^{13}C NMR (THF-d_8, 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); $^{31}P\{^1H\}$ NMR (benzene-d_6, 202 MHz, 300 K): δ 32.4 (1P, t, J = 8.1 Hz), 36.3 (2P, d, J = 8.1 Hz). ^{29}Si NMR (THF-d_8, 100 MHz): 300 K, δ −1.11 (br d, J = 77 Hz (^1H decoupled); brdd, 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. Calcd for $C_{55}H_{47}P_3PdSi$: 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, $C_{55}H_{47}P_3PdSi$, fw = 935.33, monoclinic, space group $P2_1/c$, a = 16.617(6) Å, b = 10.690(4) Å, c = 25.340(8) Å, β = 93.252(12)°, V = 4494(3) Å^3, Z = 4, D_{calcd} = 1.382 g/cm^3, temperature −123 °C, μ(Mo Kα) = 5.84 cm^{-1}, R1 = 0.0326, wR2 = 0.0744 for 8418 reflections with $I > 2\sigma(I)$.

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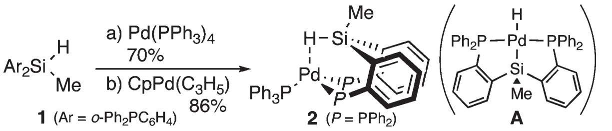
Scheme 1. Synthesis of (η^2-Si$-$H)Pd^0 Complex 2[a]



[a] Conditions: (a) 1.0 equiv of Pd(PPh$_3$)$_4$, THF, room temperature, 30 min; (b) 1.0 equiv of PPh$_3$, 1.0 equiv of CpPd(C$_3$H$_5$), Et$_2$O$-$THF, room temperature, 20 min.

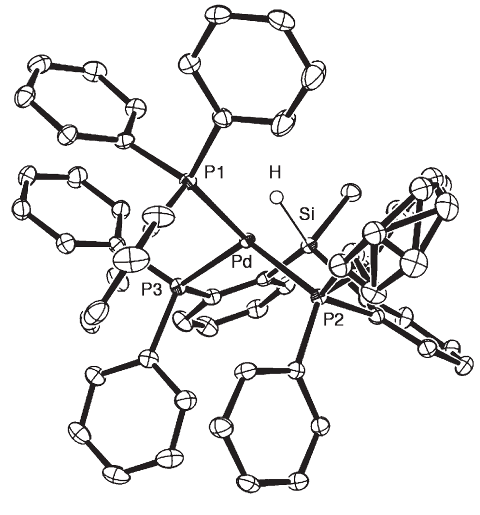
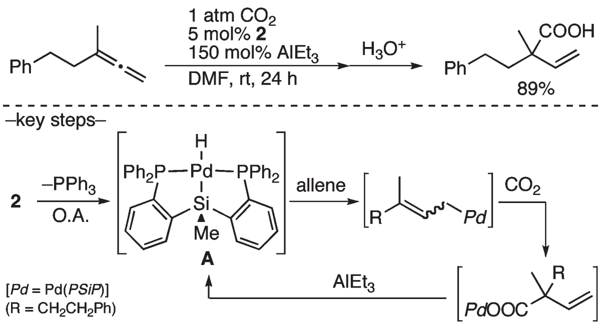
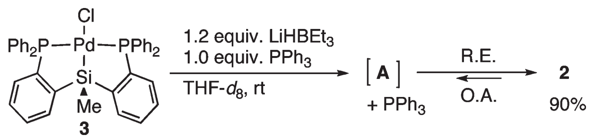


Figure 1. ORTEP plot of **2** (disorder of one of the Ph rings on P2 was observed) at the 50% probability level (hydrogen atoms except Si$-$*H* are omitted for clarity). Selected bond lengths (Å) and angles (deg): Si$-$H, 1.60(3); Pd$-$H, 1.67(3); Pd$-$Si, 2.4283(8); Pd$-$P1, 2.4425(8); Pd$-$P2, 2.3776(8); 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).

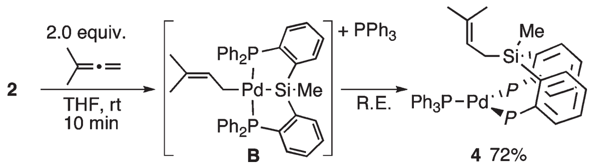
Scheme 2. Catalytic Hydrocarboxylation of an Allene using 2



Scheme 3. Formation of 2 from *PSiP* Pincer-Type Pd(II)



Scheme 4. Reaction of (η^2-Si$-$H)Pd^0 2 with an Allene



values of previously reported η^2-Si$-$H complexes ($\sim$1.6$-$1.9 Å),[1a,e] suggesting weak back-donation from the metal center to the σ^* orbital of the Si$-$H bond. The structure in solution was confirmed to be the same (η^2-Si$-$H)Pd^0 by measurement of various NMR spectra of **2** between 300 and 193 K. The ^{1}H NMR spectrum in benzene-d_6 at 300 K exhibited an upfield shift of the hydrogen atom on Si at 0.16 ppm, which is coupled with three phosphorus atoms (td, J_{HP} = 34.9, 7.6 Hz) and with the methyl protons (q, J_{HH} = 2.3 Hz, cf. J_{HH} = 3.8 Hz in **1**). The $^1J_{HSi}$ coupling constant (J_{HSi} = 110 Hz at 300 K, 97 Hz at 193 K) which was observed by non ^{1}H-decoupled ^{29}Si NMR was larger than typical values found for H$-$M$-$Si complexes ($<\sim$20 Hz) but significantly decreased from that of **1** itself (J_{HSi} = 204 Hz), clearly supporting the η^2-Si$-$H structure.[9] This relatively larger $^1J_{HSi}$ coupling constant suggests a weak interaction between the Pd(0) and Si$-$H bond in solution, as was observed in the crystalline state. This observation is in sharp contrast to the (η^2-Si$-$H)Ni^{II} complex reported by Shimada and Tanaka, which afforded a H$-$Ni^{IV}$-$Si structure as the most stable form at 193 K in solution.[4]

This (η^2-Si$-$H)Pd^0 complex **2** was found to be an active catalyst in the hydrocarboxylation of an allene under the reported conditions as shown in Scheme 2,[6] suggesting that **2** can function as a synthetic equivalent of reactive palladium hydride intermediate **A** through dissociation of PPh$_3$ and oxidative addition (OA) of the Si$-$H bond in solution. Moreover, reduction of the *PSiP* pincer palladium chloride **3** with LiBHEt$_3$ in the presence of 1.0 equiv of PPh$_3$ afforded **2** in 90% yield (Scheme 3). Thus, **2** and **A** appear to interconvert at room temperature, and the significant point is that the reductive elimination (RE) of the Si$-$H bond to give η^2-Si$-$H complex **2** is more favorable than its reverse pathway, even with the weak and easily cleaved Si$-$H bond. It is likely that the *PSiP* linkage of **A** constrained by benzene rings makes the pincer-type square planar structure rather strained, thus facilitating reductive elimination and relatively stabilizing the (η^2-Si$-$H)Pd^0 structure.

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(9) The $^1J_{HSi}$ coupling constants of (η^2-Si$-$H)metal complexes are usually in the range of 40$-$70 Hz.[1,2a] See also: Schubert, U.; Gilges, H. *Organometallics* **1996**, *15*, 2373and references therein.

(10) Synthesis of **4**: to a stirred solution of the (η^2-Si$-$H)Pd^0 complex **2** (94 mg, 0.10 mmol) in THF (1.0 mL) was added 3-methyl-1,2-butadiene (20 μL, 0.20 mmol) at room temperature. The solution turned red immediately and then yellow within 1 min. After 10 min, the solution was layered with pentane and allowed to stand at $-$30 °C to give the triphosphine Pd(0) complex **4** (72 mg, 0.072 mmol) in 72% yield, which was suitable for X-ray analysis. The complex **4** exists as a mixture of two conformational isomers in solution. IR (KBr): 3048, 1583, 1476, 1432, 847, 830 cm^{-1}. ^{1}H NMR (THF-d_8, 500 MHz, 253 K): δ 0.30 (2.1H, s), 1.00 (0.9H, s), 1.02 (2.1H, s), 1.33 (0.9H, s), 1.49 (0.9H, s), 1.53 (2.1H, s), 1.97 (0.6H, d, J = 7.8 Hz), 2.69 (1.4H, d, J = 8.0 Hz), 4.74 (0.7H, t, J = 8.0 Hz), 4.87 (0.3H, t, J = 7.8 Hz), 6.52$-$6.56 (1.4H, m), 6.60$-$6.65 (0.6H, m), 6.82$-$7.22 (39H, m), 7.44 (1.4H, d, J = 7.4 Hz), 7.62 (0.6H, d, J = 7.4 Hz). ^{13}C NMR (THF-d_8, 125 MHz, 253 K): δ 0.45, 3.44 (t, J = 10.3 Hz), 18.0, 18.1, 21.4, 22.2 (t, J = 10.6 Hz), 26.1, 26.6, 121.2, 121.9, 127.6, 127.8, 128.2 (t, J = 4.0 Hz), 128.3 (t, J = 4.0 Hz), 128.5$-$129.0 (m), 129.6, 130.0, 133.9, 134.0, 136.3$-$134.8 (m), 136.9 (t, J = 7.8 Hz), 137.4 (t, J = 7.8 Hz), 138.5 (t, J = 11.3 Hz), 138.9 (t, J = 11.3 Hz), 140.3 (t, J = 4.1 Hz), 140.5 (t, J = 4.0 Hz), 142.2 (t, J = 13.1 Hz), 142.9 (t, J = 12.8 Hz), 144.9 (t, J = 18.9 Hz), 145.1 (t, J = 18.9 Hz), 146.7$-$147.0 (m), 147.1$-$147.4 (m). ^{31}P NMR (THF-d_8, 102 MHz, 253 K): δ 17.0 (1.4P, d, J = 82 Hz), 17.5 (0.6P, d, J = 82 Hz), 23.9 (0.7P, t, J = 82 Hz), 24.3 (0.3P, t, J = 82 Hz). ^{29}Si{^{1}H} NMR (THF-d_8, 100 MHz, 253 K): δ $-$8.51 (t, J = 7.5 Hz). Anal. Calcd for $C_{60}H_{55}P_3PdSi$: C, 71.81; H, 5.52. Found: C, 71.80; H, 5.81. Crystal data for **4**: $C_{60}H_{55}P_3PdSi$, fw = 1003.44, triclinic, space group $P\bar{1}$, a = 12.462(3) Å, b = 12.602(3) Å, c = 16.283(3) Å, α = 78.139(9)°, β = 84.032(11)°, γ = 79.523(9)°, V = 2455.0(9) Å^3, Z = 2, D_{calcd} = 1.357 g/cm^3, temperature $-$123 °C, μ(Mo Kα) = 5.40 cm^{-1}, R1 = 0.0743, wR2 = 0.0712 for 2643 reflections with $I > 2\sigma(I)$.

We next carried out the detailed investigation of each step of the hydrocarboxylation of an allene using the (η^2-Si−H)Pd^0 complex **2** and found a facile dynamic behavior involving the C(sp^3)−Si bond, which is more robust and less reactive toward oxidative addition with Pd(0) than the H−Si bond. Thus, reaction of **2** with a stoichiometric amount of 3-methyl-1,2-butadiene in benzene at room temperature immediately afforded the tris(phosphine) Pd(0) complex **4**, bearing an allylsilane moiety, in 72% yield (Scheme 4). The structure of **4** was determined by X-ray analysis, as depicted in Figure 2.[10] The reaction was thought to proceed through hydropalladation of the allene with palladium hydride **A** generated in situ from **2** to afford the *PSiP* pincer-type prenylpalladium complex **B**, followed by reductive elimination of the C(sp^3)−Si bond and coordination of PPh$_3$ to give **4**. The prenylpalladium complex **B** was prepared in situ by an independent route, including the reaction of palladium chloride **3** with prenylmagnesium chloride. Addition of PPh$_3$ to an equimolar amount of complex **B** resulted in immediate reductive elimination to give complex **4**.[11,12]

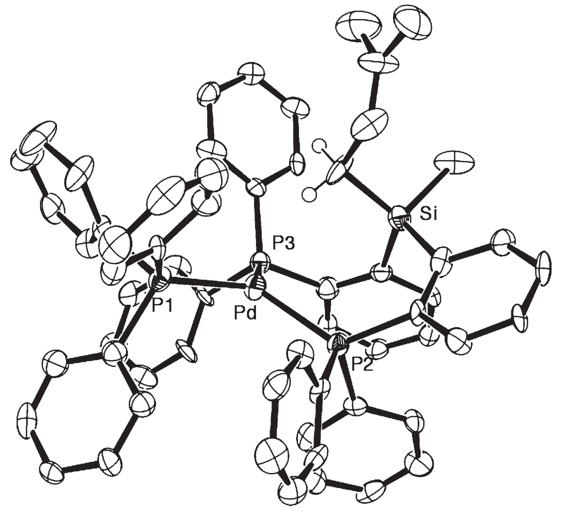
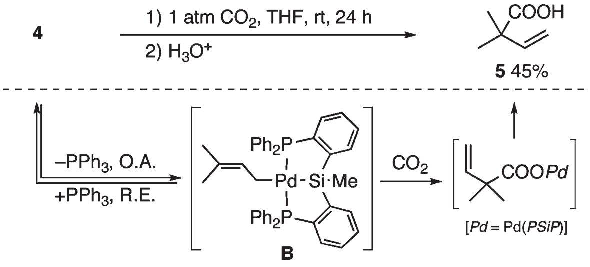


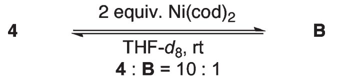
Figure 2. ORTEP plot of **4** at the 50% probability level (hydrogen atoms except allylic protons are omitted for clarity). Selected bond lengths (Å) and angles (deg): Pd−P1, 2.288(3); Pd−P2, 2.303(2); Pd−P3, 2.325(3); P1−Pd−P2, 123.02(10); P2−Pd−P3, 115.68(10); P3−Pd−P1, 119.09(9).

More interestingly, when complex **4** was stirred under 1 atm of CO$_2$ in THF at room temperature for 24 h, allylation of CO$_2$ proceeded to give 2,2-dimethyl-3-butenoic acid (**5**) in 45% yield after acidic hydrolysis (Scheme 5). Regeneration of **B** from **4** was actually observed in the ratio **4**:**B** = ca. 10:1 by ^{1}H and ^{31}P NMR when 2 equiv of Ni(cod)$_2$ was added to a THF-d_8 solution of **4** as a phosphine scavenger (Scheme 6). Thus, facile, reversible oxidative addition and reductive elimination of an C(sp^3)−Si bond with Pd(0) was obviously realized at room temperature. As oxidative addition of a C(sp^3)−Si bond has been recognized to be rather difficult and very few examples are known,[13−16] this system demonstrates the high utility of *PSiP* pincer structures based on the bis(*o*-phosphinophenyl)silyl ligand for efficient activation of the C−Si bond.

Scheme 5. Carboxylation of 4 via Oxidative Addition of a C−Si Bond



Scheme 6. Equilibrium between 4 and B in the Presence of Ni(cod)$_2$



In conclusion, the synthesis of a (η^2-Si−H)Pd^0 complex and its dynamic behavior through the reaction with an allene was disclosed, utilizing a bis(*o*-phosphinophenyl)silyl ligand as a *PSiP* pincer-type scaffold. Facile, reversible oxidative addition/reductive elimination of H−Si and C(sp^3)−Si bonds with Pd(0) was achieved in this system, leading to useful synthetic equivalents of highly reactive hydrido- and (σ-allyl)palladium species. Studies on the detailed mechanism of the dynamic behavior are in progress.

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Supporting Information Available: Text and CIF files giving preparative methods, spectral and analytical data, and crystallographic data for **2** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) The preparation of **B** and its structural analysis by ^{1}H, ^{31}P, and ^{29}Si NMR are described in the Supporting Information.

(12) The formation of **4** from **B** apparently involves coupling of the two ligands at the trans position of the square-planar complex. This type of reaction is not common, and further computational studies on the mechanism are in progress. For examples of coupling reactions involving sp^3 carbon ligands at the central atom of tridentate pincer ligands in Ni triad metal complexes, see: (a) Albrecht, M.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **2001**, *123*, 7233. (b) Madison, B. L.; Thyme, S. B.; Keene, S.; Williams, B. S. *J. Am. Chem. Soc.* **2007**, *129*, 9538. (c) Steinke, T.; Shaw, B. K.; Jong, H.; Patrick, B. O.; Fryzuk, M. D.; Green, J. C. *J. Am. Chem. Soc.* **2009**, *131*, 10461. See also ref 4b.

(13) Oxidative addition of the C(sp^3)−Si bond has been mostly limited to those in strained small rings, in dinuclear metal complexes, and in systems that could be regarded as α- or β-carbon elimination: (a) Tanaka, Y.; Yamashita, H.; Shimada, S.; Tanaka, M. *Organometallics* **1997**, *16*, 3246. (b) Hendriksen, D. E.; Oswald, A. A.; Ansell, G. B.; Leta, S.; Kastrup, R. V. *Organometallics* **1989**, *8*, 1153. (c) Thomson, S. K.; Young, G. B. *Organometallics* **1989**, *8*, 2068. (d) Hofmann, P.; Heiss, H.; Neiteler, P.; Müller, G.; Lachmann, J. *Angew. Chem., Int. Ed.* **1990**, *29*, 880. (e) Koloski, T. S.; Carroll, P. J.; Berry, D. H. *J. Am. Chem. Soc.* **1990**, *112*, 6405. (f) Shelby, Q. D.; Lin, W.; Girolami, G. S. *Organometallics* **1999**, *18*, 1904 and references therein. (g) Akita, M.; Hua, R.; Oku, T.; Tanaka, M.; Moro-oka, Y. *Organometallics* **1996**, *15*, 4162. (h) Ong, C. M.; Burchell, T. J.; Puddephatt, R. J. *Organometallics* **2004**, *23*, 1493.

(14) For examples of allyl transfer to Pd(II) via transmetalation, see: Denmark, S. E.; Werner, N. S. *J. Am. Chem. Soc.* **2008**, *130*, 16382 and references therein.

(15) For catalytic reactions via oxidative addition of a C(sp^3)−Si bond, see: (a) Takeyama, Y.; Nozaki, K.; Matsumoto, K.; Oshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1461. (b) Hirano, K.; Yorimitsu, H.; Oshima, K. *Org. Lett.* **2008**, *10*, 2199. (c) Hirano, K.; Yorimitsu, H.; Oshima, K. *Chem. Commun.* **2008**, 3234. (d) Yamashita, H.; Tanaka, M.; Honda, K. *J. Am. Chem. Soc.* **1995**, *117*, 8873. (e) Palmer, W. S.; Woerpel, K. A. *Organometallics* **1997**, *16*, 4824.

(16) During the preparation of this paper, structural rearrangement of Ni and Pd silyl pincer complexes that involves C(sp^3)−Si and C(sp^2)−Si bond activation was reported by Turculet and co-workers: Milton, S. J.; McDonald, R.; Turculet, L. *Angew. Chem., Int. Ed.* **2009**, *48*, 8568.