ORGANOMETALLICS

Dipalladium Complexes with Bridging Monoalkyl or Monophenyl Silyl Ligands in the Solid State and in Solution

Makoto Tanabe, Atsushi Takahashi, Tetsuyuki Yamada, and Kohtaro Osakada*

Chemical Resources Laboratory, Tokyo Institute of Technology, 4259-R1-3 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

Supporting Information

ABSTRACT: HexSiH₃, PhSiH₃, and PhSiClH₂ reacted with $[Pd(PCy_3)_2]$ to yield dipalladium complexes with bridging silyl ligands: $[\{Pd(PCy_3)\}_2(\mu-HSiXR)_2]$ (1, R = Hex, X = H; 2, R = Ph, X = H; 3, R = Ph, X = Cl). The X-ray crystallographic results displayed a typical bis(silyl)-bridged dinuclear structure with an anti conformation of the substituents on the Si atom in the solid state. Temperature-dependent NMR spectroscopic analyses of 1 and 2 revealed a dynamic *syn-anti* isomerization



of the complex via exchange of the bridging and nonbridging Si-H hydrogens in solution. Complex 3 with bridging chloro(phenyl)silyl ligands did not show such a dynamic behavior.

INTRODUCTION

Transition-metal multinuclear complexes with bridging primary $(\mu$ -SiH₂R) and secondary $(\mu$ -SiHR₂) silvl ligands have been investigated by many research groups because of their unique bonding structures and chemical properties.¹ Stone reported such complexes containing group 10 metals, $[{Pt(PCy_3)}_2(\mu SiHR_2$] (R = Me, Ph), in 1980.² The studies on related diplatinum,³ dipalladium,⁴ dinickel,⁵ and Pt-Pd heterobimetallic⁶ complexes revealed the detailed structures of the fourmembered M_2Si_2 ring composed of M-Si σ bonds and M-Si(H) three-center-two-electron (3c-2e) bonds. Late-transition-metal complexes with primary and secondary silyl ligands undergo 1,2-migration of the hydrido ligand from the silyl groups to form monometallic silylene-coordinated complexes.⁷ The secondary silvlene ligands are much more stable than the primary silylene ligands in these complexes because of low electrophilicity and significant steric hindrance of the Si atom. Less bulky primary silylene ligands are converted easily to form dinuclear structures with bridging Si ligands.⁸ Diplatinum complexes with bridging arylsilylene (μ -SiHAr) ligands are proposed as potential intermediates for the Si-Si bond-forming coupling reactions of arylsilanes.⁹

Reactions of primary silanes having bulky 9-triptycyl and 2,6dimesitylphenyl substituents with low-valent complexes of Pd and Pt did not cause Si–Si coupling reactions but led to the formation of mononuclear silyl(hydrido)palladium¹⁰ and -platinum¹¹ complexes. Si ligands with a less bulky substituent bridge two to four metal centers in multinuclear complexes of group 10 metals. Mochida synthesized tri- and tetraplatinum complexes with triply or quadruply bridging silylyne or germylyne ligands.¹² Tessier reported that the nonbridging Si–H bonds of the silylene-bridged diplatinum complex [$\{Pt(PR_3)_2\}_{2}\{\mu$ -SiHHex}] (R = Et, 'Pr) reacted with [$PtH_2(PR_3)_2$] to form tetraplatinum complexes, [$\{Pt-(PR_3)\}_{2}\{\mu$ -SiHHex{PtH(PR₃)_2}], which were composed of a silyl-bridged diplatinum structure and two {PtH(PR₃)₂} fragments connected by bridging Si atoms.¹³ Braddock-Wilking prepared a series of diplatinum complexes with arylsilyl ligands, [{Pt(PPh₃)}₂(μ -SiH₂Ar)₂] (Ar = 2,4,6-trimethylphenyl, 2,4,6trimethoxyphenyl, etc.).¹⁴ Thus, bridging monoalkyl (or monoaryl) silyl ligands bonded to Pd and Pt are less common than bridging disubstituted silyl ligands of the multinuclear complexes, and there have been only a few reports of multinuclear palladium complexes with chelating primary silyl or silylene ligands.¹⁵ In this paper, we report the isolation of dipalladium complexes with bridging primary silyl ligands and their structures in the solid state and in solution.

RESULTS AND DISCUSSION

Reactions of $[Pd(PCy_3)_2]$ with HexSiH₃, PhSiH₃, and PhSiClH₂ at ambient temperature produced dipalladium complexes with bridging silyl ligands, $[{Pd(PCy_3)}_2(\mu-HSiXR)_2]$ (1, R = Hex, X = H; 2, R = Ph, X = H; 3, R = Ph, X = Cl), in 88–96% yields, as shown in eq 1. Secondary

$$Pd(PCy_{3})_{2} + RSiXH_{2} \xrightarrow{rt, toluene} \begin{array}{c} R & X \\ Si-H \\ Cy_{3}P - Pd - Pd \\ H - Si \\ X \\ R \end{array}$$
(1)
$$H - Si \\ X \\ R \\ 1: R = Hex, X = H, 88\% \\ 2: R = Ph, X = H, 96\% \\ 3: R = Ph, X = CL 96\% \end{array}$$

silanes were reported to react with the zerovalent complexes $[M(PCy_3)_2]$ (M = Pt,^{3f,g} Pd,^{6a} Ni^{5b,c}) to produce the

Received: December 22, 2012 Published: March 11, 2013 corresponding dinuclear complexes, but the dipalladium complexes with bridging monoalkyl (or monoaryl) silyl ligands have not yet been reported.

Figure 1 shows the molecular structures of 1-*anti*, 2-*anti*, and 3-*anti*, which were determined by X-ray crystallography.



Figure 1. Thermal ellipsoids (50% probability) of (a) 1-*anti*, (b) 2-*anti*, and (c) 3-*anti*. Hydrogen atoms, except for Si-H hydrogens, are omitted for simplicity. The molecule of 1-*anti* has a crystallographic symmetry at the midpoint of the two Pd atoms. The *n*-hexyl group of 1-*anti* was disordered and refined anisotropically.

Selected bond parameters for these compounds and dipalladium analogues with bridging diphenylsilyl ligands, [{Pd-(PR₃)}₂(μ -SiHPh₂)₂] (R = Cy,^{6a} Me^{4a}), are summarized in Table 1. The molecule of 1-*anti* has a crystallographic C₂ symmetry around the midpoint of the Pd(I)–Pd(I) bond. The molecules of 1–3 contain a typical bis(silyl)-bridged dinuclear structure with a Pd–Si(H) 3c-2e bond and adopt an *anti* conformation of the organic substituents relative to the Si–Si vector. The crystal structures of 1 and 2 contain short SiH…HC distances (2.418 and 2.450 Å) between an nonbridging Si-H bond of the Pd₂Si₂ ring and a HC group of the PCy₃ ligand, which are attributed to a weak dihydrogen bonding interaction (ca. 2.4 Å) assisted by the electropositive Si atom.¹⁶ The SiCl···HC hydrogen bonds of 3 (2.805 and 2.833 Å) are also found within the sum of van der Waals radius of Si and Cl (2.95 Å). The Pd-Pd distances of 1-anti and 2-anti (2.7036(8) and 2.7110(6) Å) are slightly longer than those of dipalladium complexes with diphenylsilyl ligands, $[{Pd(PR_3)}_2(\mu-\bar{SiHPh}_2)_2]$ (R = Cy, 2.691(1) Å; R = Me, 2.691(1) Å). Introduction of an electron-withdrawing chloro substituent to the bridging silyl ligand strengthens and shortens the Pd-Pd bond of 3-anti (2.6952(9) Å) in comparison to the dipalladium complexes with primary silyl ligands (1-anti, 2.7036(8) Å; 2-anti, 2.7110(6) Å). These bond distances are shorter than the sum of the atomic radii of Pd (1.38 Å) and Pt (1.38 Å), indicating the formation of a strong bond between the two metals.¹⁷

The Pd–Si σ bonds lengthen in the order 3-anti (2.300(2), 2.305(2) Å) < 1-anti (2.309(1) Å) < 2-anti (2.318(1), 2.324(1) Å) < $[{Pd(PR_3)}_2(\mu$ -SiHPh₂)₂] (R = Cy, 2.326(2) Å; R = Me, 2.328(2) Å), whereas the Pd–Si(H) bonds are shortened in the order 1-anti (2.410(2) Å) > 2-anti (2.381(1), 2.391(1) Å) ≈ $[{Pd(PR_3)}_2(\mu-SiHPh_2)_2]$ (R = Cy, 2.384(2) Å; R = Me, 2.386(2) Å) > 3-anti (2.371(2), 2.380(2) Å). The electronwithdrawing chloro substituent of 3-anti shortens both Pd–Si σ bonds and Pd-Si(H) bonds and stabilizes the σ bond significantly. 1-anti has a Pd-Si(H) bond which is much longer than those in other complexes with Si-Ph groups in Table 1. Less effective coordination of the Si-H group without Ph groups to Pd may cause elongation of the Pd-Si(H) bond and consequent shortening of the Pd–Si σ bond. These bond parameters of complexes 1-anti and 3-anti obtained in this study differ from those of analogous complexes. The dipalladium complexes with two bridging silyl ligands prepared so far, $[{Pd(PR_3)}_2(\mu$ -SiHPh₂)₂] (R = Me, Et, Cy), and their optimized structures by theoretical calculations have ratios of the Pd–Si(H) bond length to the Pd–Si σ bond length (d(Pd– Si(H)/d(Pd-Si) close to 1.025–1.027.^{4,6a} The ratios of the bond lengths of 1-anti and 3-anti are larger (1.044 and 1.032), and the unique structural parameters of the new complexes are attributed to electronic effects of hexyl and chloro groups on the Si atom. Diplatinum complexes with bridging dialkylsilyl groups, $[{Pt(PR'_3)}_2(\mu-SiHR_2)_2]$ (R' = Cy, R = Me, Et, Hex; R' = Ph, R = Me, ^{2,3e,g} have bond length ratios (1.041–1.043) that are larger than those with diphenylsilyl ligands ([{Pt- $(PCy_3)_2(\mu-SiHPh_2)_2$, 1.025).^{3g}

NMR spectra of the complexes provided detailed information of the structures in solution. Complexes 1-3 display a single ³¹P NMR signal at δ 44.8–46.7 at room temperature. As shown in Figure 2, the ³¹P{¹H} NMR signal of 1 at 25 °C (δ 46.2 in toluene- d_8) is broadened on cooling to -20 °C and is split into two signals at δ 46.0 and 46.7 in an approximate 2:1 intensity ratio at -50 °C. The signals are assigned to the two isomers 1-anti and 1-syn, and the former is assigned to the more stable anti structure. Two ³¹P NMR signals of 2-anti and 2-syn (δ 45.2 and 44.9) at -60 °C also coalesce into a single signal (δ 45.4) at -30 °C. The ¹H NMR spectrum of 1 at -50 °C showed a signal for the nonbridging Si–H hydrogen signal at δ 7.18, while the corresponding signal of 2 (-60 °C) was observed as two signals at δ 6.59 and 6.69 in an 81:19 ratio, and they are assigned to 2-anti and 2-syn, respectively (Figure 3). As the temperature of the solution of 2 is increased, the two Si-H

Article

	1-anti	2-anti	3-anti	$[{\rm Pd}({\rm PCy}_3)]_2(\mu-{\rm HSiPh}_2)_2]^a$	$[{Pd(PMe_3)}_2(\mu-HSiPh_2)_2]^b$
Pd-Pd	2.7036(8)	2.7110(6)	2.6952(9)	2.691(1)	2.691(1)
Pd-Si	2.309(1)	2.318(1), 2.324(1)	2.305(2), 2.300(2)	2.326(2)	2.328(2)
Pd-Si(H)	2.410(2)	2.381(1), 2.391(1)	2.371(2), 2.380(2)	2.384(2)	2.386(2)
Pd-P	2.306(2)	2.319(1), 2.319(1)	2.326(2), 2.325(2)	2.316(2)	2.294(2)
Si-H(Pd)	1.659(2)	1.38(8), 1.63(6)	1.52(8), 1.48(7)	1.63	1.75
Si-H	1.401	1.39(6), 1.41(6)			
Pd-H	1.9045(5)	1.90(7), 1.82(5)	1.55(8), 1.74(7)	1.61	1.91
Pd-Si-Pd	69.87(4)	70.27(3), 70.36(3)	70.46(5), 70.22(5)	69.68(7)	69.61(5)
^{<i>a</i>} Reference 6a. ^{<i>b</i>} I	Reference 4a.				

Table 1. Selected Bond Distances (Å) and Angles (deg) of 1-anti, 2-anti, 3-anti, and $[{Pd(PR_3)}_2(\mu-HSiPh_2)_2]$ (R = Cy, Me)



signals coalesce into one broad signal (δ 6.62) at -30 °C and then the combined signal does not appear in any region at 0 $^{\circ}$ C. The chemical shifts of nonbridging Si-H hydrogens are at low magnetic field positions, similarly to the reported diplatinum complexes $[{Pt(PPh_3)}_2(\mu-H_2SiAr)_2]$ (Ar = 2,4,6-trimethylphenyl, δ 8.95; Ar = pentaphenylphenyl, δ 7.48).¹⁴ The bridging Si-H hydrogen signals of 1 and 2 are overlapped with PCy₃ hydrogen signals. The ²H{¹H} NMR spectrum of $[{Pd(PCy_3)}_2(\mu-D_2SiHex)_2]$ (1-d₄), obtained from an analogous reaction of $[Pd(PCy_3)_2]$ with HexSiD₃, shows two deuterated resonances at δ 7.08 and 1.00 at -50 °C, while the spectrum of $[{Pd(PCy_3)}_2(\mu-D_2SiPh)_2]$ (2-d₄) at -60 °C shows broadened nonbridging and bridging Si–D signals at δ 6.72 and 1.03. Warming the latter solution to 30 °C causes coalescence of the deuterium signals to a broadened peak around δ 4.0. Mononuclear Ru complexes with silvlene and hydride ligands, $[Cp^{*}(^{i}Pr_{2}MeP)(H)Ru=SiHAr]$ (Cp^{*} = pentamethylcyclopentadienyl; Ar = 2,4,6-triisopropylphenyl, δ 9.41; Ar = 2,6-dimesitylphenyl, δ 8.00), also exhibited the Si–H hydrogen peak at low magnetic field.^{7e} The bridging organosilyl ligands of the group 10 metal dinuclear structures were



Figure 3. ¹H NMR spectra of 2 in CD_2Cl_2 at -90, -60, -30, 0, and 25 °C.

reported to involve the silylene character with sp² hybridization, as supported by theoretical calculations.¹⁸ The chemical shifts of Si–H hydrogens of 1 and 2 may be influenced by the above bonding situation.

Scheme 1 displays a plausible pathway for the fluxional behavior of the bridging silyl ligands of 1 and 2. Activation of the Pd–Si(H_A) 3c-2e bond of A-anti generates the intermediate





B, in which the Si-H_A bond interacts with Pd to form a σ complex. Further activation of the interaction and rotation of the Pd–Si bond leads to formation of a new Pd–Si($H_{\rm B}$) bond to give A-syn, with the two organic substituents on the same side of the Pd₂Si₂ plane. This dynamic motion of the bridging silvl group at -30 °C is slow enough to allow the H_A and H_B signals to be distinguished in the ¹H NMR spectrum. The anti conformation of the dinuclear structures is more stable than the syn form and exists as the major structure in solution and as the exclusive structure in the solid state.¹⁹ Braddock-Wilking reported on the fluxional NMR behavior of diplatinum analogues and estimated the ΔG^{\ddagger} values (15–17 kcal mol⁻¹) with coalescence of the two 31 P NMR signals at 69–83 °C.¹⁴ The activation free energy of 1 was estimated as 6.4 kcal mol⁻¹ $(T_c = -20 \text{ °C})$ from the line-shape analysis of the ³¹P NMR signals.²⁰ A smaller ΔG^{\ddagger} value and lower coalescence temperature of 1 in comparison to those of the diplatinum complexes suggest that the rotation of the Pd–Si σ bond occurs more easily than rotation of the Pt–Si σ bond. In contrast, the 1H and $^{3\dot{1}}P\{^1H\}$ NMR spectra of 3 do not change with temperature.

In summary, we prepared dipalladium complexes 1-3 with bridging monoalkyl and monophenyl silyl ligands and characterized the molecular structures by X-ray crystallography. Although the organic substituents on the Si atom of 1-3 are located on opposite sides of the Pd₂Si₂ rings in the solid state, the dynamic *syn-anti* exchange behavior of 1 and 2 in solution suggests dissociation/coordination of the Si-H bonds to the Pd center or formation of a σ complex coordinated by the Si-H bond to Pd.

EXPERIMENTAL SECTION

General Procedures. All manipulations were carried out using standard Schlenk techniques under an argon or nitrogen atmosphere or in a nitrogen-filled glovebox (Miwa MFG). Hexane and toluene were purified by using a Grubbs-type solvent purification system (Glass Contour).²¹ The ¹H, ¹³C{¹H}, ²⁹Si{¹H}, and ³¹P{¹H} NMR spectra were recorded on JEOL EX-400 MHz, Bruker Biospin Avance III 400 MHz, and JEOL JNM-500 MHz NMR spectra were referenced to the residual peaks of the solvents used.²² The ²⁹Si and ³¹P chemical shifts were referenced to external SiMe₄ (δ 0) and 85% H₃PO₄ (δ 0) in C₆D₆, toluene-d₈, or CD₂Cl₂. IR spectra were recorded on a JASCO FTIR-4100 spectrometer. Elemental analyses were performed using a LECO CHNS-932 or Yanaco MT-5 CHN autorecorder. The compounds [Pd(PCy₃)₂]²³ and HexSiH₃²⁴ were prepared according to the reported procedures. PhSiH₃ and PhClSiH₂ (Sigma-Aldrich) were used as received.

Preparation of $[{Pd(PCy_3)}_2(\mu-H_2SiHex)_2]$ (1). To a hexane solution (3 mL) of [Pd(PCy₃)₂] (500 mg, 0.75 mmol) was added HexSiH₃ (152 μ L, 0.94 mmol), and the reaction mixture was stirred at room temperature for 15 h to give a white precipitate. The white solid was collected by filtration, washed with hexane $(1 \text{ mL} \times 4)$, and dried in vacuo to afford 1 (331 mg, 88%). Single crystals suitable for X-ray crystallography were obtained by recrystallization from hexane at -20°C. All signals of 1 in the ¹H and ¹³C{¹H} NMR spectra were assigned by using 2D NMR experiments. Anal. Calcd for C48H96P2Pd2Si2: C, 57.41; H, 9.64. Found: C, 57.25; H, 9.76. ¹H NMR (400 MHz, C₆D₆) room temperature): δ 2.01-1.90 (18H, PCH, PCHCH₂), 1.73 (12H, PCHCH₂CH₂), 1.66-1.50 (30H, PCHCH₂, PCHCH₂CH₂CH₂) SiCH₂, SiCH₂CH₂, Si(CH₂)₄CH₂), 1.44 (8H, Si(CH₂)₂CH₂, Si- $(CH_2)_3CH_2$, 1.30–1.18 (m, 18H, PCHCH₂CH₂CH₂, PCHCH₂CH₂CH₂CH₂), 0.96 (t, 6H, Si(CH₂)₅CH₃, $J_{H-H} = 7.0$ Hz). Si-H signals were not observed, due to the fluxional behavior. ¹H NMR (400 MHz, toluene d_{87} – 50 °C): δ 7.18 (nonbridging SiH), 1.91–1.02 (PC₆H₁₁, SiC₆H₁₃, bridging SiH). ¹³C{¹H} NMR (101 MHz, C₆D₆, room temperature): δ

36.3 (br, PCH), 33.8 (Si(CH₂)₄CH₂), 32.6 (Si(CH₂)₂CH₂ or Si(CH₂)₃CH₂), 31.1 (PCHCH₂), 30.9 (SiCH₂CH₂), 28.0 (PCHCH₂CH₂), 26.7 (PCHCH₂CH₂CH₂), 23.2 (Si(CH₂)₂CH₂ or Si(CH₂)₃CH₂), 21.1 (SiCH₂), 14.5 (Si(CH₂)₅CH₃). ²⁹Si{¹H} NMR (79 MHz, C₆D₆, room temperature): δ 132 (m, J_{P-Si} = 46 Hz). ³¹P{¹H} NMR (162 MHz, C₆D₆, room temperature): δ 46.1 (J_{Si-P} = 46 Hz). ³¹P{¹H} NMR (162 MHz, toluene-d₈, -50 °C): δ 46.7 (1syn), 46.0 (1-anti), The ratio of 1-anti and 1-syn was estimated to be 67:33. IR (KBr): 2034 (s, ν _{Si-H}), 1114 (w, ν _{Si-H-Pd}) cm⁻¹.

Preparation of [{Pd(PCy₃)}₂(μ-D₂SiHex)₂] (1-d₄). The procedure to synthesize 1-d₄ was similar to the preparation of 1. The reaction of [Pd(PCy₃)₂] (300 mg, 0.45 mmol) with D₃SiHex (53.6 mg, 0.45 mmol) gave the deuterated dipalladium complex 1-d₄ (128 mg, 56%) as a white solid. ²H{¹H} NMR (77 MHz, toluene, -50 °C): δ 7.08 (br, 1D, SiD), 1.00 (br, 1D, SiDPd). ³¹P{¹H} NMR (162 MHz, C₆D₆, room temperature): δ 46.2.

Preparation of $[{Pd(PCy_3)}_2(\mu-H_2SiPh)_2]$ (2). To a toluene solution (10 mL) of $[Pd(PCy_3)_2]$ (1.60 g, 2.40 mmol) was added H₃SiPh (355 μ L, 2.88 mmol), and the solution was stirred for 1 h at room temperature. The solvent was removed under reduced pressure to give a residue, which was washed with hexane $(5 \text{ mL} \times 2)$ and dried in vacuo to afford 2 as a white solid (1.14 g, 96%). Single colorless crystals suitable for X-ray crystallography were obtained by diffusion of hexane into the toluene solution at room temperature. Anal. Calcd for C₄₈H₈₀P₂Pd₂Si₂: C, 58.35; H, 8.16. Found: C, 58.68; H, 7.97. ¹H NMR (500 MHz, C_6D_6 , room temperature): δ 8.02 (dd, 4H, C_6H_5 ortho, $J_{\rm H-H}$ = 7.5 Hz), 7.29 (t, 4H, C₆H₅ meta, $J_{\rm H-H}$ = 7.5 Hz), 1.84 (br, 18H, PC₆H₁₁), 1.59–1.52 (m, 18H, PC₆H₁₁), 1.38 (m, 12H, PC₆H₁₁), 1.10–0.88 (m, 18H, PC_6H_{11}), The C_6H_5 para proton signal was overlapped. ¹H NMR (400 MHz, CD₂Cl₂, -60 °C): δ 7.50 (C₆H₅ ortho; 2-anti), 7.46 (C₆H₅ ortho; 2-syn), 7.26-7.19 (C₆H₅ meta and para), 6.69 (nonbridging SiH; 2-syn), 6.59 (nonbridging SiH; 2-anti), 1.80–0.86 (PC_6H_{11} , PdHSi). The ratio of 2-anti and 2-syn was estimated to be 81:19. ¹³C{¹H} NMR (126 MHz, CD₂Cl₂, room temperature): δ 144.0 (C₆H₅ ipso), 136.3 (C₆H₅ ortho), 128.0 (C₆H₅ *para*), 127.6 (C_6H_5 *meta*), 35.9 (apparent triplet, PCH, $J_{P-C} = 8.3$ Hz), 31.0 (s, PCHCH₂), 27.8 (apparent triplet, PCHCH₂CH₂, $J_{P-C} = 6.2$ Hz), 26.7 (s, PCHCH₂CH₂CH₂). ²⁹Si^{{1}H} NMR (79 MHz, CD₂Cl₂, room temperature): δ 126 (J_{P-Si} was not determined). ³¹P{¹H} NMR (202 MHz, C_6D_{67} room temperature): δ 46.7 ($J_{Si-P} = 67$ Hz). ${}^{31}P{}^{1}H{}$ NMR (162 MHz, CD_2Cl_2 , -60 °C): δ 45.2 (2-anti, $J_{Si-P} = 70$ Hz), 44.9 (2-syn). IR (KBr): 2051 (s, ν_{Si-H}), 1093 (w, $\nu_{Si-H-Pd}$) cm⁻¹.

Preparation of [{**Pd**(**PCy**₃)}₂(μ -**D**_2**SiPh**)₂] (2- d_4). The procedure to synthesize 2- d_4 was similar to the preparation of 2. The reaction of [Pd(PCy₃)₂] (300 mg, 0.45 mmol) with D₃SiPh (105 mg, 0.94 mmol) gave the deuterated dipalladium complex 2- d_4 (97 mg, 44%) as a white solid. ²H{¹H} NMR (77 MHz, CH₂Cl₂, -60 °C): δ 6.72 (br, 1D, SiD), 1.03 (br, 1D, SiDPd).

Preparation of $[{Pd(PCy_3)}_2(\mu-HSiClPh)_2]$ (3). To a toluene solution (3 mL) of [Pd(PCy₃)₂] (400 mg, 0.60 mmol) was added PhClSiH₂ (240 μ L, 1.80 mmol), and then the reaction mixture was stirred at room temperature for 60 h. The solvent was removed under reduced pressure to give a residue, which was washed with hexane (1 mL \times 10) and dried in vacuo to give 3 (303 mg, 96%) as a white powder. Single colorless crystals suitable for X-ray crystallography were obtained by slow diffusion of hexane into a THF solution at room temperature. Anal. Calcd for C48H78Cl2P2Pd2Si2: C, 54.54; H, 7.44. Found: C, 54.82; H, 6.45. It was difficult to obtain satisfactory data for the elemental analysis due to severe air sensitivity. ¹H NMR (400 MHz, C_6D_6 , room temperature): δ 8.09 (d, 4H, C_6H_5 ortho), 7.26 (d, 4H, C₆H₅ meta), 2.30 (apparent triplet, 2H, SiHPd, J_{H-P} = 4.8 Hz), 1.90 (m, 12H, PCH, PCHCH₂), 1.69 (m, 6H, PCHCH₂), 1.59 (m, 6H, PCHCH₂CH₂), 1.49 (m, 12H, PCHCH₂CH₂, PCHCH₂CH₂CH₂), 1.37-1.29 (m, 12H, PCHCH₂), 1.13 (m, 6H, PCHCH₂CH₂), 0.98 (m, 12H, PCHCH₂CH₂, PCHCH₂CH₂CH₂). The C_6H_5 para proton signal was overlapped. ¹³C{¹H} NMR (101 MHz, C_6D_6 , room temperature): δ 144.7 (C_6H_5 ipso), 134.3 (C_6H_5 *ortho*), 129.2 (C_6H_5 *para*), 35.9 (apparent triplet, PCH, $J_{P-C} = 8.1$ Hz), 31.0 (PCHCH₂), 30.7 (PCHCH₂), 27.7 (m, PCHCH₂CH₂), 26.4 (PCHCH₂CH₂CH₂). The C_6H_5 meta carbon signal was overlapped.

³¹P{¹H} NMR (162 MHz, C₆D₆, room temperature): δ 44.8 (J_{Si-P} = 71, 27 Hz). IR (KBr): 1508 ($\nu_{Si-H-Pd}$) cm⁻¹. The ²⁹Si{¹H} NMR spectrum was not obtained due to decomposition of 3 during the measurement overnight.

X-ray Crystal Structure Analysis. Single crystals of 1–3 suitable for an X-ray diffraction study were mounted on MicroMounts (MiTeGen). The crystallographic data of 1–3 were collected on a Rigaku Saturn CCD area detector equipped with monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 113 K. Calculations were carried out using the program package Crystal Structure, version 4.0, for Windows. The positional and thermal parameters of non-hydrogen atoms were refined anisotropically on F^2 by full-matrix least-squares methods using SHELXL-97.²⁵ Hydrogen atoms, except for the Si–H hydrogens, were placed at calculated positions and refined with a riding mode on their corresponding carbon atoms. All SiH hydrogens were located from difference Fourier maps. Disordered hexyl groups were refined as two sets of positions, one with an occupancy of 0.64 and with anisotropic displacement parameters and the other with an occupancy of 0.36. Crystallographic data of 1–3 are given in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

A CIF file and a table giving crystallographic data for 1-3 and figures giving NMR and IR spectroscopic data for 1-3 and an Eyring plot of 1. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail for K.O.: kosakada@res.titech.ac.jp.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was financially supported by Grants-in-Aid for Scientific Research (B) (No. 24350027) for Young Chemists (No. 23750059) from the Ministry of Education, Culture, Sport, Science, and Technology of Japan. We thank our colleagues in the Center for Advanced Materials Analysis, Technical Department, Tokyo Institute of Technology, for elemental analysis.

REFERENCES

(1) For recent reviews on dinuclear complexes with bridging silyl ligands, see: (a) Ogino, H.; Tobita, H. Adv. Organomet. Chem. 1998, 42, 223–290. (b) Corey, J. Y.; Braddock-Wilking, J. Chem. Rev. 1999, 99, 175–292. (c) Osakada, K.; Tanabe, M. Bull. Chem. Soc. Jpn. 2005, 78, 1887–1898. (d) Shimada, S.; Tanaka, M. Coord. Chem. Rev. 2006, 250, 991–1011. (e) Corey, J. Y. Chem. Rev. 2011, 111, 863–1071.

(2) 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**, 659–666.

(3) (a) Braddock-Wilking, J.; Levchinsky, Y.; Rath, N. P. Inorg. Chim. Acta 2002, 330, 82–88. (b) Braddock-Wilking, J.; Corey, J. Y.; Trankler, K. A.; Dill, K. M.; French, L. M.; Rath, N. P. Organometallics 2004, 23, 4576–4584. (c) Braddock-Wilking, J.; Corey, J. Y.; Trankler, K. A.; Xu, H.; French, L. M.; Praingam, N.; White, C.; Rath, N. P. Organometallics 2006, 25, 2859–2871. (d) Braddock-Wilking, J.; Corey, J. Y.; French, L. M.; Choi, E.; Speedie, V. J.; Rutherford, M. F.; Yao, S.; Xu, H.; Rath, N. P. Organometallics 2006, 25, 3974–3988. (e) Arii, H.; Takahashi, M.; Noda, A.; Nanjo, M.; Mochida, K. Organometallics 2008, 27, 1929–1935. (f) Tanabe, M.; Ito, D.; Osakada, K. Organometallics 2007, 26, 459–462. (g) Tanabe, M.; Ito, D.; Osakada, K. Organometallics 2008, 27, 2258–2267. (4) (a) Kim, Y.-J.; Lee, S.-C.; Park, J.-I.; Osakada, K.; Choi, J.-C.; Yamamoto, T. Organometallics **1998**, *17*, 4929–4931. (b) Kim, Y.-J.; Lee, S.-C.; Park, J.-I.; Osakada, K.; Choi, J.-C.; Yamamoto, T. J. Chem. Soc., Dalton Trans. **2000**, 417–421.

(5) (a) Beck, R.; Johnson, S. A. Organometallics **2012**, 31, 3599–3609. (b) Tanabe, M.; Yumoto, R.; Osakada, K. Chem. Commun. **2012**, 48, 2125–2127. (c) Tanabe, M.; Yumoto, R.; Osakada, K.; Sanji, T.; Tanaka, M. Organometallics **2012**, 31, 6787–6795.

(6) (a) Tanabe, M.; Yamada, T.; Osakada, K. Organometallics 2003, 22, 2190–2192. (b) Yamada, T.; Tanabe, M.; Osakada, K.; Kim, Y.-J. Organometallics 2004, 23, 4771–4777.

(7) (a) Mork, B. V.; Tilley, T. D. J. Am. Chem. Soc. 2004, 126, 4375–4385. (b) Mork, B. V.; Tilley, T. D.; Schultz, A. J.; Cowan, J. A. J. Am. Chem. Soc. 2004, 126, 10428–10440. (c) Hayes, P. G.; Beddie, C.; Hall, M. B.; Waterman, R.; Tilley, T. D. J. Am. Chem. Soc. 2006, 128, 428–429. (d) Ochiai, M.; Hashimoto, H.; Tobita, H. Angew. Chem., Int. Ed. 2007, 46, 8192–8194. (e) Hayes, P. G.; Waterman, R.; Glaser, P. B.; Tilley, T. D. Organometallics 2009, 28, 5082–5089. Review: (f) Waterman, R.; Hayes, P. G.; Tilley, T. D. Acc. Chem. Res. 2007, 40, 712–719.

(8) (a) Wang, W.-D.; Eisenberg, R. J. Am. Chem. Soc. **1990**, 112, 1833–1841. (b) McDonald, R.; Cowie, M. Organometallics **1990**, 9, 2468–2478. (c) Mobarok, M. H.; Ferguson, M. J.; Cowie, M. Organometallics **2012**, 31, 4722–4728. (d) Mobarok, M. H.; McDonald, R.; Ferguson, M. J.; Cowie, M. Inorg. Chem. **2012**, 51, 9249–9258.

(9) (a) Zarate, E. A.; Tessier-Youngs, C. A.; Youngs, W. J. J. Am. Chem. Soc. 1988, 110, 4068–4070. (b) Zarate, E. A.; Tessier-Youngs, C. A.; Youngs, W. J. J. Chem. Soc., Chem. Cmmun. 1989, 577–578.
(c) Heyn, R. H.; Tilley, T. D. J. Am. Chem. Soc. 1992, 114, 1917–1919.
(d) Shimada, S.; Tanaka, M.; Honda, K. J. Am. Chem. Soc. 1995, 117, 8289–8290.

(10) Nakata, N.; Fukazawa, S.; Kato, N.; Ishii, A. Organometallics **2011**, *30*, 4490–4493.

(11) (a) Simons, R. S.; Sanow, L. M.; Galat, K. J.; Tessier, C. A.; Youngs, W. J. Organometallics **2000**, *19*, 3994–3996. (b) Nakata, N.; Fukazawa, S.; Ishii, A. Organometallics **2009**, *28*, 534–538.

(12) (a) Arii, H.; Takahashi, M.; Nanjo, M.; Mochida, K. *Organometallics* 2009, 28, 4629–4631. (b) Arii, H.; Takahashi, M.; Nanjo, M.; Mochida, K. *Organometallics* 2011, 30, 917–920. (c) Arii, H.; Hashimoto, R.; Mochida, K.; Kawashima, T. *Organometallics* 2012, 31, 6635–6641.

(13) Sanow, L. M.; Chai, M.; McConnville, D. B.; Galat, K. J.; Simons, R. S.; Rinaldi, P. L.; Youngs, W. J.; Tessier, C. A. Organometallics **2000**, 19, 192–205.

(14) (a) Levchinsky, Y.; Rath, N. P.; Braddock-Wilking, J. Organometallics **1999**, *18*, 2583–2586. (b) Braddock-Wilking, J.; Levchinsky, Y.; Rath, N. P. Organometallics **2000**, *19*, 5500–5510.

(15) Multinuclear palladium complexes with chelating di- or trisilyl ligands: (a) Chen, W.; Shimada, S.; Hayashi, T.; Tanaka, M. *Chem. Lett.* **2001**, 1096–1097. (b) Chen, W.; Shimada, S.; Tanaka, M. *Science* **2002**, 295, 308–310. (c) Shimada, S.; Li, Y.-H.; Choe, Y.-K.; Tanaka, M.; Bao, M.; Uchimaru, T. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, 104, 7758–7763.

(16) (a) Crabtree, R. H. Science **1998**, 282, 2000–2001. (b) Juárez-Pérez, E. J.; Viñas, C.; Teixidor, F.; Núñez, R. J. Organomet. Chem. **2009**, 694, 1764–1770.

(17) Emsley, J. The Elements, 3rd ed.; Oxford University Press: Oxford, U.K., 1998.

(18) Nakajima, S.; Sumimoto, M.; Nakao, Y.; Sato, H.; Sakaki, S.; Osakada, K. Organometallics **2005**, *24*, 4029–4038.

(19) The *anti* isomer is considered to be more stable than the *syn* isomer. See also ref 14.

(20) An Eyring plot of 1 is given in the Supporting Information.

(21) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. Organometallics **1996**, *15*, 1518–1520.

(22) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. Organometallics **2010**, *29*, 2176–2179. (23) Tanabe, M.; Ishikawa, N.; Osakada, K. Organometallics 2006, 25, 796–798.

(24) Amin, S. B.; Marks, T. J. J. Am. Chem. Soc. 2007, 129, 2938–2953.

(25) Sheldrick, G. M. SHELXL-97: Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1997.