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Ligand Exchange of Diplatinum Complexes with Bridging Silyl Ligands Involving Si−H Bond Cleavage and Formation

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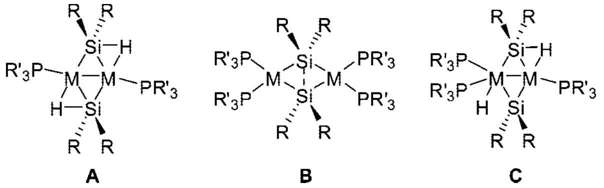
Reactions of excess H_2SiEt_2 and H_2SiHex_2 with $[Pt(PCy_3)_2]$ at room temperature form mononuclear *cis*-hydrido(silyl)platinum complexes, *cis*-$[Pt(H)(SiHR_2)(PCy_3)_2]$ (**1**: R = Et, **2**: R = Hex), which are converted into diplatinum complexes with bridging dialkylsilyl ligands, $[\{Pt(PCy_3)\}_2(\mu\text{-}\eta^2\text{-}HSiR_2)_2]$ (**3**: R = Et, **4**: R = Hex), upon heating at 80 °C. Complex **3** reacts with excess $H_2SiPhMe$ and H_2SiPh_2 to afford dinuclear complexes $[\{Pt(PCy_3)\}_2(\mu\text{-}\eta^2\text{-}HSiPhR)_2]$ (**5**: R = Me, **6**: R = Ph) via exchange of the bridging silyl ligands. An equimolar reaction of H_2SiPh_2 with **3** yields a mixture of diplatinum complexes $[\{Pt(PCy_3)\}_2(\mu\text{-}\eta^2\text{-}HSiEt_2)(\mu\text{-}\eta^2\text{-}HSiPh_2)]$ (**7**) and $[\{Pt(PCy_3)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}H_2SiEt_2)(\mu\text{-}SiPh_2)]$ (**8**). Use of D_2SiPh_2 in the reaction results in distribution of deuterium in the diethylsilyl and diphenylsilyl ligands of **7**, the diethylsilane ligand of **8**, and the diphenylsilyl ligand of **6**. Complex **6** undergoes exchange of the phosphine ligands with dmpe (1,2-bis(dimethylphosphino)ethane) and with dppe (1,2-bis(diphenylphosphino)ethane) to afford diplatinum complexes with bridging silylene ligands and the chelating diphosphine ligands, $[\{Pt(dmpe)\}_2(\mu\text{-}SiPh_2)_2]$ (**9**) and $[\{Pt(dppe)\}_2(\mu\text{-}SiPh_2)_2]$ (**10**). Short contact between the two Si atoms (2.718(2) and 2.646(2) Å) suggests a weak Si···Si interaction.

Introduction

Organosilyl and organosilylene groups coordinate to two transition metals as the bridging ligands and form stable dinuclear complexes of these metals.[1] Chart 1 summarizes structures of the dinuclear complexes containing group 10 metals reported so far. Complexes with structures **A** and **B** are common. Diplatinum,[2–4] dipalladium,[5] and Pd−Pt heterobimetallic complexes[6] with two bridging diorganosilyl ($SiHR_2$) ligands contain both M−Si σ-bonds and M−H−Si three-center two-electron (3c-2e) bonds, which stabilize the dinuclear structure (structure **A**). A bond between the d^9 metals also stabilizes the four-membered M_2Si_2 core. Bridging silylene (SiR_2) ligands form diplatinum[3,7–11] and dipalladium[12,13] complexes with two M−Si σ-bonds (structure **B**). Most of the complexes with structure **B** have a short Si···Si contact in the M_2Si_2 ring, whereas dipalladium complexes, $[\{Pd(PR_3)\}_2\{\mu\text{-}\overline{Si(^tBuNCH{=}CHN^tBu)}\}_2]$ (R = Ph,[14] ^{t}Bu[15]), have a structure with short contact between the Pd centers. Both the bridging silyl and silylene complexes of Pd and Pt atoms are obtained from the reaction of primary and secondary silanes with low-valent complexes of these metals. Oxidative addition of the silanes to Pd(0)

Chart 1



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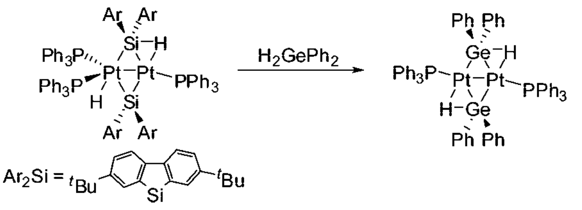
Scheme 1



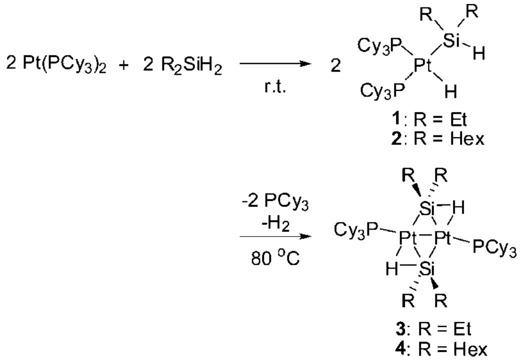
or Pt(0) complexes and dimerization of the resulting mononuclear silyl complexes produce the dinuclear silyl complexes **A**, while Si−H bond activation and elimination of H_2 during the reaction lead to the silylene-bridged dinuclear complexes **B**. Unsymmetrical structures having both silyl and silylene ligands (structure **C**) are observed in the variable-temperature NMR spectra of the dinuclear complexes with three phosphine ligands.[4c,d,6b]

Addition of organosilanes having Si−H bonds to mononuclear late-transition-metal complexes with silyl ligands causes facile exchange of the ligands and forms new metal−silicon bonds.[16–18] The primary organosilanes are more reactive than the secondary silanes toward the silyl ligand exchange probably due to steric reasons. The silyl ligand exchange reaction favors formation of the complex containing the silyl ligand with aryl substituents rather than the ligand with alkyl substituents. Formal exchange of the bridging silyl or silylene ligands of the dinuclear complexes caused by the added organosilane would produce the complexes having new coordination bonds of the bridging Si ligands to transition metals, but there have been only a few papers on such ligand exchange of the bridging Si ligands. Eisenberg and co-workers reported that dinuclear Rh complexes with bridging silylene ligands undergo exchange of the ligand on addition of organosilanes.[19] Recently, Braddock-Wilking and co-workers prepared a diplatinum complex with bridging diphenylgermyl ligands from the reaction of diphenylgermane with the dinuclear Pt complex with bridging diarylsilyl and diarylsilylene ligands (Scheme 1).[20]

In this article, we report exchange reaction of the two bridging dialkylsilyl groups of the diplatinum complexes with diarylsilyl groups and stepwise mechanism of the reaction. Part of this article was reported as a preliminary communication.[21]

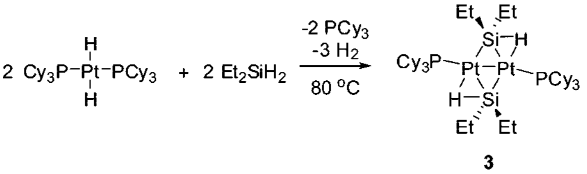
Results and Discussion

Reactions of excess H_2SiEt_2 and H_2SiHex_2 with $[Pt(PCy_3)_2]$, which is obtained *in situ* from the thermal reaction of *cis*-$[PtPh_2(PCy_3)_2]$,[22] yield hydrido(silyl)platinum complexes *cis*-$[PtH(SiHR_2)(PCy_3)_2]$ (**1**: R = Et, **2**: R = Hex) quantitatively. The ^1H and $^{31}P\{^1H\}$ NMR spectra of the reaction mixtures are identical with the data of the complexes reported by Duckett and Perutz et al.[23] Heating the solutions of **1** and **2**, thus obtained, produces diplatinum complexes with bridging bis(dialkyl)silyl ligands, $[\{Pt(PCy_3)\}_2(\mu\text{-}\eta^2\text{-}HSiR_2)_2]$ (**3**: R = Et, **4**: R = Hex), in 91% and 90% yields (eq 1).



(1)

Thermolysis of isolated **1** in a toluene solution at 70 °C was reported to form a platinum dihydride complex, *trans*-$[PtH_2(PCy_3)_2]$, as a major product.[23] Our attempted reaction of excess H_2SiEt_2 ([Si]:[Pt] = 5:1) with *trans*-$[PtH_2(PCy_3)_2]$ at 80 °C yields the diplatinum complex **3** in 34% yield (eq 2).



(2)

A platinum dihydride complex, $[PtH_2(PMe_3)_2]$, was reported to react with $HSiPh_3$ to produce *cis*-$[PtH(SiPh_3)(PMe_3)_2]$ with hydride and silyl ligands.[24] Formation of **1** and **2** is also ascribed to initial formation of $[PtH_2(PCy_3)_2]$ and its reaction with the dialkylsilanes. Oxidative addition of H_2SiEt_2 to a Pt(0) complex with PCy_3 ligands is expected to yield **1**, which may be further converted into **3** on heating. The reaction of H_2SiEt_2 with $[Pt(PCy_3)_2]$ in 2:1 ratio at 80 °C, however, gives **3** in a lower yield (28%), together with *trans*-$[PtH_2(PCy_3)_2]$. Thus, adding an excess amount of organosilanes to the reaction mixture increases the isolated yields of **3** and **4**.

Diplatinum complexes **3** and **4** were isolated and fully characterized by X-ray crystallography and NMR spectroscopy. Figure 1a,b shows the molecular structures of these complexes, and they are essentially similar to the reported dinuclear Pt(I) complexes with bridging silyl ligands, $[\{Pt(PCy_3)\}_2(\mu\text{-}\eta^2\text{-}HSiMe_2)_2]^2$ and $[\{Pt(PPh_3)\}_2\{\mu\text{-}\eta^2\text{-}HSiH(PPP)\}_2]^{4b}$ (PPP = pentaphenylphenyl). The $^{29}Si\{^1H\}$, $^{31}P\{^1H\}$, and $^{195}Pt\{^1H\}$ NMR spectra of **4** show the coupling patterns, which are consistent with an AA′MM′XX′ spin system.[25] The ^{29}Si NMR spectrum of **4** (Figure 2) contains three intense peaks centered at δ 183.2, which is assigned to the bridging Si nuclei of the complex that is coordinated to non-NMR-

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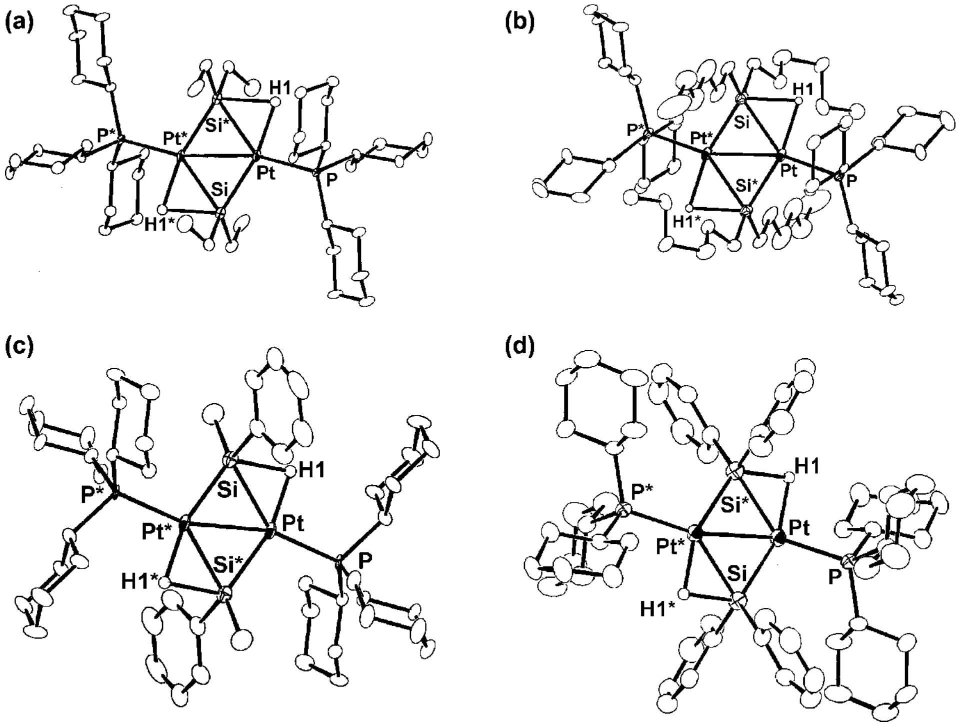


Figure 1. ORTEP drawings of (a) **3**, (b) **4**, (c) **5**-*trans*, and (d) **6** with thermal ellipsoids shown at the 50% probability level. All the molecules have a C_2 symmetry center at the midpoint of two Pt centers. Atoms with asterisks are crystallographically equivalent to those having the same number without asterisks. Hydrogen atoms except for bridging Si−H hydrogens are omitted for clarity. Four carbons of one hexyl group of **4** were disordered.

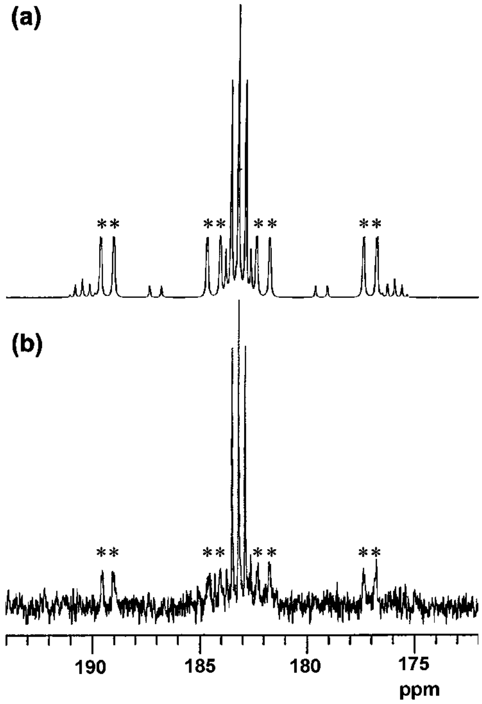


Figure 2. (a) Computer-simulated and (b) observed $^{29}Si\{^1H\}$ NMR spectra of **4** in C_6D_6 at 25 °C. The signals with asterisks correspond to the isotopomer containing one ^{195}Pt nucleus.

active Pt nuclei. A significant interaction between two magnetically equivalent ^{31}P nuclei results in an apparent triplet due to the virtual coupling. The isotopomer containing one ^{195}Pt nucleus exhibits a signal that is coupled with one ^{195}Pt nucleus ($^1J_{Pt-Si}$ = 1451 and 273 Hz) and with two ^{31}P nuclei ($^2J_{P-Si}$ = 73 and 7 Hz). The peaks assigned to the isotopomer having two ^{195}Pt nuclei were not observed due to a low proportion of ^{195}Pt nuclei (11.3%). The signal position is close to similar complexes having unsymmetrically bridging bis(silyl) ligands coordinated to two Pt centers, $[\{(Pt(PEt_3)\}_2\{\mu\text{-}\eta^2\text{-}HSi(Hex)(PtH(PEt_3)_2)\}_2]$ (δ_{Si} = 194.7)[3] and $[\{Pt(PPh_3)\}_2\{\mu\text{-}\eta^2\text{-}SiH_2(PPP)\}_2]$ (δ_{Si} = 174.5).[4b] Complexes with other monoarylsilyl ligands, $[\{Pt(PPh_3)\}_2(\mu\text{-}\eta^2\text{-}SiH_2Ar)_2]$ (Ar = $C_6H_2(OMe)_3$-2,4,6; $C_6H_2Me_3$-2,4,6; $C_6H_2(CF_3)_3$-2,4,6), show the corresponding signals at lower magnetic field position (δ_{Si} = 126–135).[4b] The $^{195}Pt\{^1H\}$ NMR signal of **4** is centered at δ −5835 with splitting due to ^{29}Si and ^{31}P nuclei (Figure 3). Computer-simulated $^{29}Si\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectra based on two Si−Pt and P−Pt coupling constants (J_{Pt-Si} = 1451, 273 Hz, J_{Pt-P} = 3969, 264 Hz) agree with all the above results. The J_{Pt-Pt} value is estimated to be 2995 Hz from the simulation and is close to the coupling constants of $[\{Pt(PR_3)\}_2(\mu\text{-}\eta^2\text{-}HSiMe_2)_2]$ (PR_3 = PCy_3: 2853 Hz, PR_3 = PMe^tBu_2: 3331 Hz).[2] The $^{13}C\{^1H\}$ NMR spectrum of **4** shows α- and β-carbon signals of the hexyl groups at δ 26.6 and 29.1, respectively. These signals are flanked with two satellite signals owing to the ^{195}Pt−Si σ-bond and ^{195}Pt−H−Si 3c-2e bond (α: $^2J_{Pt-C}$ = 69, 40 Hz, β: $^3J_{Pt-C}$ = 21, 10 Hz). The ^1H NMR signals due to the Pt−H−Si hydrogen of **4** should appear in the range δ 0.4−2.4,[2,3] but their positions are not determined due to overlapping with PCy_3 hydrogen peaks.

Treatment of **3** with $H_2SiMePh$ ([Pt]:[Si] = 1:3) at room temperature caused replacement of the bridging diethylsilyl ligands with methyl(phenyl)silyl groups to produce $[\{Pt(PCy_3)\}_2(\mu\text{-}\eta^2\text{-}HSiMePh)_2]$ (**5**) in 88% yield (Scheme 2). The ^1H and $^{31}P\{^1H\}$ NMR spectra of the product indicated the presence of two isomers with *trans* and *cis* structures in 98:2 ratio. The major isomer exhibits a ^1H NMR signal of the phenyl hydrogens at the *ortho* position at δ 7.99 and a $^{31}P\{^1H\}$ NMR signal at δ

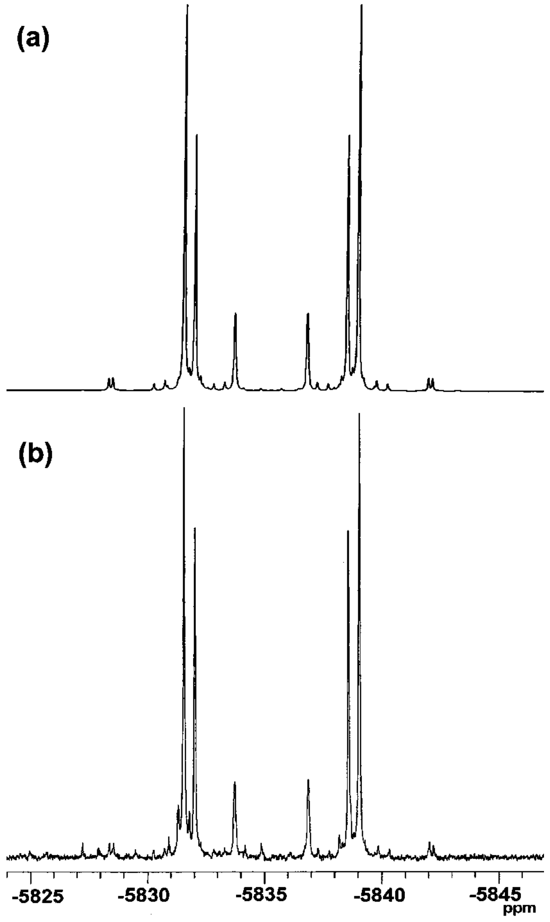
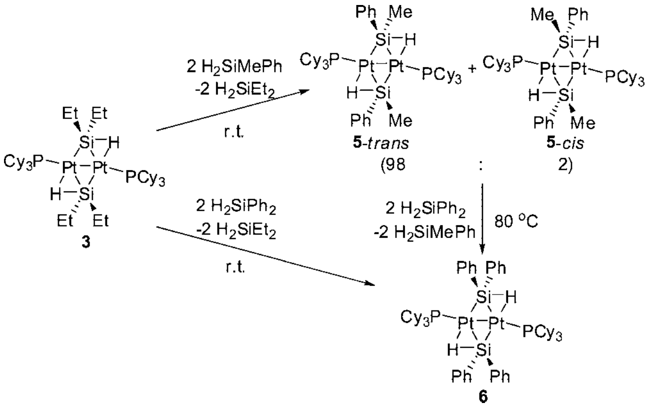


Figure 3. (a) Computer-simulated and (b) observed ^{195}Pt{^{1}H} NMR spectra of **4** in C_6D_6 at 25 °C.

Scheme 2



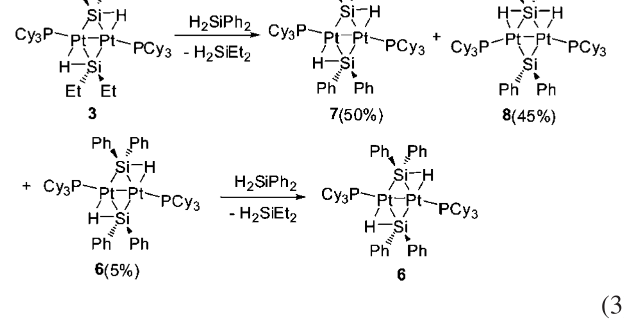
52.8, while ^{1}H and ^{31}P NMR signals of the minor isomer are observed at δ 8.16 and 52.5, respectively. These isomers can be assigned to the complex with different orientation of two phenyl (and methyl) groups on the Si atoms. The major isomer is assigned to **5**-*trans*, having two phenyl groups at the opposite sides of the Pt_2Si_2 plane because recrystallization of the product from toluene/hexane afforded the isomer. Figure 1c shows the molecular structure of **5**-*trans* determined by X-ray crystallography. The mixture of **5**-*cis* and **5**-*trans* reacts with H_2SiPh_2 at 80 °C to produce [{Pt(PCy$_3$)}$_2$(μ-η^2-HSiPh$_2$)$_2$] (**6**) in 81% yield. Direct reaction of H_2SiPh_2 with **3** at room temperature also forms **6** in 97% yield. Complex **6**, with two bridging diphenylsilyl ligands, was prepared initially from the reaction of H_2SiPh_2 with [Pt(C_2H_4)(PCy$_3$)$_2$].[2] A zero-valent complex without an ethylene ligand, [Pt(PCy$_3$)$_2$], is not a good precursor for **6**, and the reaction of [Pt(PCy$_3$)$_2$] with excess H_2SiPh_2 at 80 °C gave a mixture of the Pt complexes including **6**, which was difficult to isolate in pure form.

Table 1. Selected Bond Distances (Å) and Angles (deg) of 3–6

	3	4	5-*trans*	6
Pt–Pt*	2.7011 (3)	2.6988 (6)	2.6982 (3)	2.6985 (3)
Pt–Si	2.323 (2)	2.317 (2)	2.324 (2)	2.326 (2)
	2.423 (2)	2.413 (3)	2.409 (2)	2.385 (2)
Pt–P	2.256 (2)	2.255 (2)	2.223 (2)	2.268 (2)
Pt–H	1.91 (7)	1.92 (9)	1.83 (1)	1.94 (8)
Si–H	2.07 (5)	2.0 (1)	1.99 (1)	1.88 (7)
Si–Pt–Si*	110.66 (6)	110.4 (1)	110.51 (7)	110.13 (7)
Pt–Si–Pt*	69.34 (6)	69.54 (9)	69.49 (6)	69.87 (5)

Figure 1d displays the molecular structure of complex **6** determined by X-ray crystallography. Table 1 summarizes selected bond distances and bond angles of **3**–**6**. Molecules of these complexes have a crystallographic C_2 symmetry center at the midpoint of two Pt centers. Distances between the two Pt centers of **3**–**6** (2.6982(3)–2.7011(3) Å) are within the range of Pt–Pt bonds of dinuclear Pt(I) complexes with bridging silyl ligands.[2–4] The four-membered Pt_2Si_2 core contains two Pt–Si σ-bonds and two Pt–H–Si 3c-2e bonds. The Pt–Si distances of the 3c-2e bonds (2.385(2)–2.423(2) Å) of **3**–**6** are significantly longer than the Pt–Si σ-bond distances (2.317(2)–2.326(2) Å). The former bond distances are shortened in the order **3** (2.423(2) Å) > **4** (2.413(3) Å) > **5** (2.409(2) Å) > **6** (2.385(2) Å), while the latter bonds vary in almost reverse order, **6** (2.326(2) Å) > **5** (2.324(2) Å) > **3** (2.323(2) Å) > **4** (2.317(2) Å). Thus, phenyl substituents on the Si center promote exchange of the bridging silyl ligand shown in Scheme 2 and result in the elongation of the Pt–Si σ-bonds of the complexes and shortening of the Pt–Si distances of the Pt–H–Si 3c-2e bonds.

An equimolar reaction of H_2SiPh_2 with **3** yields a mixture of diplatinum complexes with two different bridging silyl ligands, [{Pt(PCy$_3$)}$_2$(μ-η^2-HSiPh$_2$)(μ-η^2-HSiEt$_2$)] (**7**), and with bridging diethylsilane and diphenylsilylene ligands, [{Pt(PCy$_3$)}$_2$(μ-η^2:η^2-H$_2$SiEt$_2$)(μ-SiPh$_2$)] (**8**) (eq 3). A small amount of **6** is also formed in the reaction, although complexes having diethylsilylene or diphenylsilane ligands are not observed. The ratio of the products is determined by ^{1}H NMR spectroscopy as [**7**]:[**8**]:[**6**] = 50:45:5. Further addition of H_2SiPh_2 to the reaction mixture at room temperature ([Si]:[Pt] = 3:1) causes exchange of the remaining $SiHEt_2$ or SiH_2Et_2 ligands of **7** and **8** with the $SiHPh_2$ group to afford **6** as a single product (67% isolated yield).



(3)

Repeated recrystallization of the initial reaction products from toluene/hexane (1:7) at −20 °C yielded a solid containing **7** and **8** in 6:94 molar ratio, although isolation of **8** by further recrystallization was not feasible. Molecular structures of **7** and **8** were determined by X-ray crystallography of single crystals

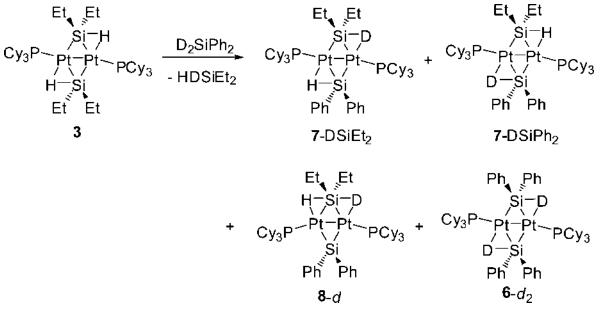
Table 2. Selected NMR and IR Data of Complexes 3–10[a]

	$^{31}P\{^1H\}$[b]				$^{29}Si\{^1H\}$[b]		IR[c] (ν_{H-Si})
3	52.6	$J_{P-Pt} = 3957$ $^2J_{P-Pt} = 260$ $^3J_{P-P} = 60$			188.1	$J_{P-Si} = 73$	1653
4	51.8	$J_{P-Pt} = 3969$ $^2J_{P-Pt} = 264$ $^3J_{P-P} = 60$			183.2	$J_{P-Si} = 73, 7$ $J_{Pt-Si} = 1451, 273$	1655
5-*trans*	52.8	$J_{P-Pt} = 3972$ $^2J_{P-Pt} = 239$ $^3J_{P-P} = 57$	52.5[d]				1670
7[e]	53.2	$J_{P-Pt} = 3858$ $^2J_{P-Pt} = 252$ $^3J_{P-P} = 59$	53.5	$J_{P-Pt} = 4027$ $^2J_{P-Pt} = 237$ $^3J_{P-P} = 59$	163.7 195.5	$J_{P-Si} = 66, 12$ $J_{P-Si} = 60, 11$	
8[f]	51.8	$J_{P-Pt} = 3849$ $^2J_{P-Pt} = 362$ $^3J_{PP} = 55$			141.3 230.1	$J_{Pt-Si} = 418$, $J_{P-Si} = 72$ $J_{Pt-Si} = 1180$, $J_{P-Si} = 4$	1696
9	39.2	$J_{P-Pt} = 1263$ $^2J_{P-Pt} = 222$ $^3J_{P-P} = 29$			-95.5[g]	$J_{Pt-Si} = 789$[g]	
10	57.1	$J_{P-Pt} = 1511$ $^2J_{P-Pt} = 275$ $^3J_{P-P} = 28$					

[a] Complex **6** shows the NMR data, which are identical with the reported value. See ref 2. [b] Chemical shifts given in ppm, coupling constants in Hz, data collected in C_6D_6 or C_7D_8 solvents. [c] cm^{-1} in KBr disks. [d] NMR data of **5**-*cis*. [e] Data were obtained from the mixture of **7** and **8** in 55:45 ratio. [f] Data were obtained from the mixture of **7** and **8** in 6:94 ratio. [g] Solid-state CPMAS $^{29}Si\{^1H\}$ NMR measurement.

carefully chosen from the mixtures.[21] There have been only a limited number of reports on the bridging silane coordination to two transition metals in the dinuclear complexes of Re,[26] Mn,[27] Fe,[28] and Ru.[29] Results of theoretical calculations on hydrido(silyl) complexes (dhpe)M(H)Si(R^1)(R^2)(R^3) (dhpe = 1,2-bis(dihydrophosphino)ethane; M = Pd, Pt; R = H, Me, Ph, F, Cl)[30] suggest that silyl ligands with electron-negative substituents (i.e., aryl and halogen groups) stabilize the M−Si bonds more significantly than the alkylsilyl ligands.

The NMR data of **7** and of **8** were obtained from comparison of the spectra of the mixtures containing these complexes in 6:94 and 55:45 molar ratios. The ^1H NMR signals of the Pt−H−Si hydrogens of **7** and **8** are buried in the broad PCy_3 hydrogen signals, while diplatinum complex **6** shows the Si−H signal at δ 2.47 in C_6D_6 accompanied by ^{195}Pt satellites (J_{Pt-H} = 86 and 605 Hz). Table 2 summarizes NMR ($^{31}P\{^1H\}$ and $^{29}Si\{^1H\}$) and IR data of the complexes. The ^{31}P NMR signals of PCy_3-coordinated diplatinum complexes **3**–**8** are observed in the range δ 51.8–53.5. Complex **7**, with different μ-silyl groups, displays two signals at δ 53.2 and 53.5 with the same P−P coupling (59 Hz). Existence of the magnetically inequivalent ^{31}P nuclei suggests that migration of the Si−H hydrogen between the Pt centers does not occur or occurs much more slowly than the NMR time scale. Two $^{29}Si\{^1H\}$ NMR signals of **7** show two doublets of doublets at δ 163.7 and 195.5 with similar $^2J_{P-Si}$ values (66, 12 Hz and 60, 11 Hz), while **8** gives rise to two signals at δ 230.1 and 141.3 with different coupling patterns from each other. The signal at lower magnetic field is assigned to the bridging $SiPh_2$ ligand and shows a coupling pattern with a large J_{Pt-Si} value (1180 Hz) and a small $^2J_{P-Si}$ value (4 Hz). The signal at δ 141.3 is assigned to the μ-SiH_2Et_2 group, and it is symmetrical due to the presence of ^{195}Pt nuclei (J_{Pt-Si} = 418 Hz) and two ^{31}P nuclei ($^2J_{P-Si}$ = 72 Hz). The ^{29}Si resonance of the bridging silylene ligands in diruthenium complexes $[Ru_2(CO)_6\{\mu\text{-}Si(C_6H_4Me)_2\}(\mu\text{-}PPh_2CH_2PPh_2)]$ appears at lower magnetic field (δ 172.6), compared with that of the bridging silane ligand, $[Ru_2(CO)_4\{SiH(C_6H_4Me)\}_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}H_2Si(C_6H_4Me)_2\}(\mu\text{-}PPh_2CH_2PPh_2)]$ (δ 154.8).[29b]



(4)

An equimolar reaction of D_2SiPh_2 with **3** produces a mixture of the complexes, as shown in eq 4. The $^2H\{^1H\}$ NMR spectrum of the products contains signals at δ 2.43 (J_{Pt-D} = 87 Hz), 1.44 (J_{Pt-D} = 95 Hz), and 1.01 (J_{Pt-D} = 99 Hz). Since nondeuterated complex **6** shows ^1H NMR signals for the Si−H hydrogen peak at δ 2.47 (J_{Pt-H} = 86 and 605 Hz), the ^2H NMR peak at δ 2.43 is assigned to the $DSiPh_2$ ligand of $[\{Pt(PCy_3)\}_2(\mu\text{-}\eta^2\text{-}DSiPh_2)(\mu\text{-}\eta^2\text{-}HSiEt_2)]$ (**7**-$DSiPh_2$) and $[\{Pt(PCy_3)\}_2(\mu\text{-}\eta^2\text{-}DSiPh_2)_2]$ (**6**-*d_2*). Complex **6**-*d_2*, however, is contained in a much smaller amount than **7**-$DSiPh_2$, which is shown by the $^{31}P\{^1H\}$ NMR spectrum of the mixture. Further repeated recrystallization of the products of the above reaction yields $[\{Pt(PCy_3)\}_2(\mu\text{-}SiPh_2)(\mu\text{-}\eta^2\text{:}\eta^2\text{-}DHSiEt_2)]$ (**8**-*d*) mainly (**7**-*d*:**8**-*d* = 7:93, yield 4%). The $^2H\{^1H\}$ NMR signal of **8**-*d* observed in the mixture appears at δ 1.01 flanked with ^{195}Pt satellites (J_{Pt-D} = 99 Hz), which is assigned to the deuterium of the bridging diethylsilane ligand. Thus, the ^2H NMR signal at δ 1.44 of the above reaction mixture is assigned to the $DSiEt_2$ ligand of $[\{Pt(PCy_3)\}_2(\mu\text{-}\eta^2\text{-}HSiPh_2)(\mu\text{-}\eta^2\text{-}DSiEt_2)]$ (**7**-$DSiEt_2$). Formation of **7**-$DSiEt_2$ is attributed to intramolecular hydrogen exchange of **7**. Intermolecular hydrogen

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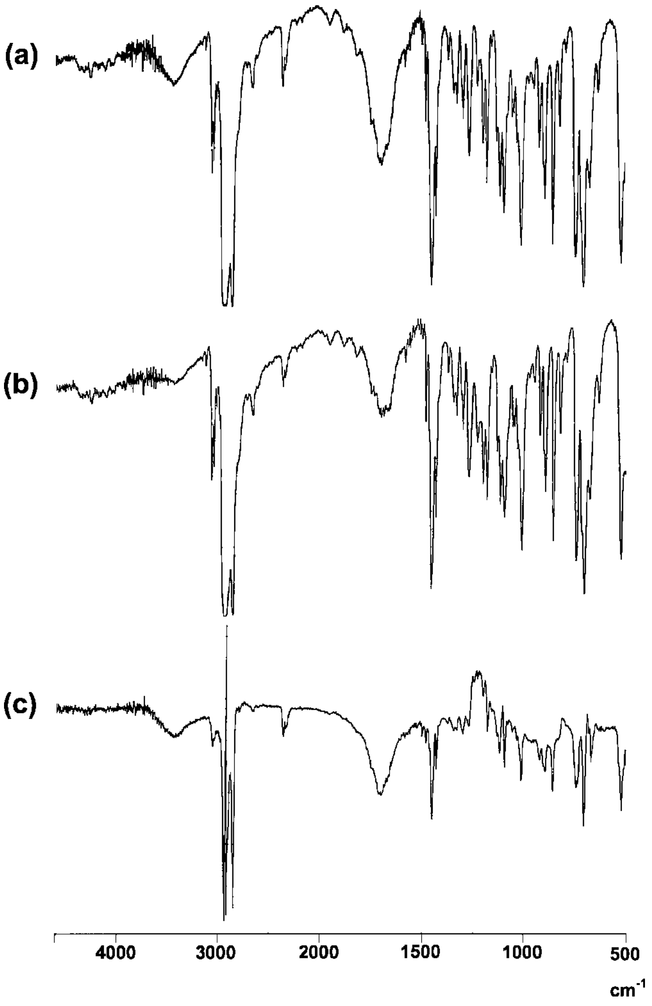


Figure 4. Infrared spectra of (a) **8** and (b) **8**-*d* and (c) a differential spectrum of them.

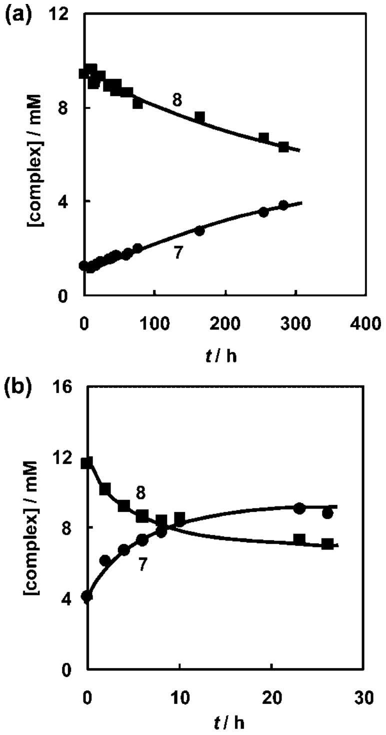
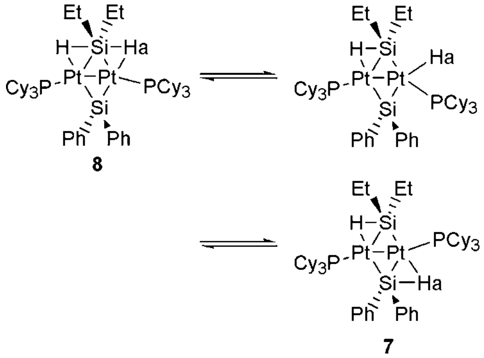


Figure 5. Change in amounts of **7** and **8** during the isomerization starting from a mixture of **7** and **8** in 6:94 ratio in C_6D_6 at 25 °C (a) in the absence of PCy_3, [**7**+**8**] = 11 mM, and (b) in the presence of 0.2 equiv of PCy_3 (3.5 mM), [**7**+**8**] = 16 mM. Change of the amount of the complexes was monitored by ^{1}H NMR using dibenzyl as an internal standard (10 mM).

Scheme 3



migration might form [{Pt(PCy_3)}$_2$(μ-η^2-$HSiPh_2$)(μ-η^2-$HSiEt_2$)] (**7**) and [{Pt(PCy_3)}$_2$(μ-η^2-$DSiPh_2$)(μ-η^2-$DSiEt_2$)] (**7**-d_2). The above NMR data, however, did not provide any information for the presence or absence of these complexes.

Figure 4 shows the IR spectra of complexes **8** and **8**-*d*, and their differential spectrum in the region containing M−H−Si and M−D−Si bond stretching vibrations. The ν(Pt−H−Si) band of **8** is observed at 1696 cm^{-1} (Figure 4a), which is at a higher wavenumber than the corresponding peaks of **3**–**5**, with two bridging silyl ligands (1653–1670 cm^{-1}) (Table 2). The IR spectrum of **8**-*d* contains a broad peak due to ν(Pt−H−Si) vibration at ca. 1685 cm^{-1}. Peaks of the ν(Pt−D−Si) vibration are not observed clearly in Figure 4b due to weak peak intensity and overlapping with other peaks in this region. The differential spectrum of **8** from **8**-*d* shows an inversed peak (1225 cm^{-1}), which can be assigned as a Si−D−Pt stretching frequency of **8**-*d*. A μ-silane ligand of diruthenium complex [{(η^5-C_5Me_5)Ru(μ-H)}$_2$(μ-η^2:η^2-$H_2Si^tBu_2$)] was reported to show a stretching frequency of the ν(Ru−H−Si) bond at 1790 cm^{-1} and the ν(Ru−D−Si) bond of the deuterated complex at 1280 cm^{-1}.[29a]

Complex **8** undergoes isomerization into **7** in solution at room temperature. The reaction using a mixture with [**8**]:[**7**] = 94:6 as the starting material was monitored by ^{1}H NMR spectroscopy, as shown in Figure 5a. Gradual decrease of **8** and concomitant increase of **7** give a mixture of 62:38 ratio after 238 h at room temperature, and the mixture reaches an equilibrium with a 45:55 ratio in 2 weeks. Addition of PCy_3 to the solutions ([Pt]:[PCy_3] = 1:0.2) enhances the isomerization, and the equilibrium is attained in 23 h (Figure 5b). The isomerization of **8** to **7** obeys first-order kinetics ($k_{obsd} = 5.0 \times 10^{-7}$ s^{-1} at 25 °C), and the addition of PCy_3 increases the rate constant to 1.0×10^{-5} s^{-1}. A plausible pathway for the isomerization from **8** to **7** is illustrated in Scheme 3. Activation of the Si−Ha bond of **8** produces a platinum−hydride intermediate with the bridging diethylsilyl ligand. Transfer of the hydrogen atom with exchange of the positions of PCy_3 and hydride ligands forms a new Si−Ha bond on the Si atom of the bridging $SiPh_2$ ligand. The Si−H bonds in Pt−H−Si groups are activated easily by coordination of the additional phosphine to the Pt atom. The Pd−Pt and Pt−Pt complexes with hydride and bridging silylene ligands, [{M(H)(PR_3)$_2$}{M′(PR_3)}(μ-SiR_2)(μ-η^2-$HSiR_2$)] (M = Pt, M′ = Pt or Pd), reported so far, contain two phosphine ligands at a metal center.[4c,d,6b] Enhancement of the isomerization caused by addition of PCy_3 can be attributed to facile generation of the intermediates having hydride and bridging silylene ligands.

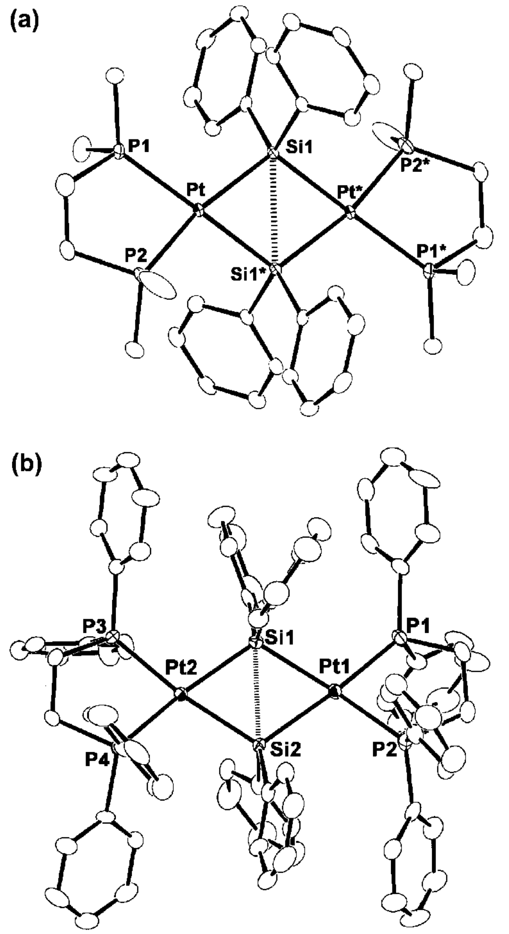
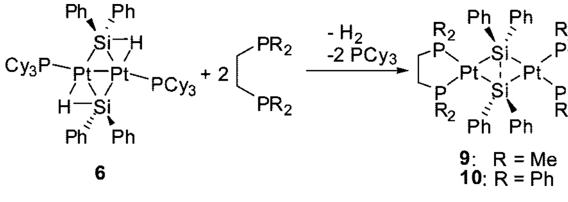


Figure 6. ORTEP drawings of (a) **9** and (b) **10** with thermal ellipsoids shown at the 50% probability level. The molecule of **9** has a C_2 symmetry center at the midpoint of two Pt centers. Atoms with asterisks are crystallographically equivalent to those having the same number without asterisks. Hydrogen atoms are omitted for clarity.

Braddock-Wilking and co-workers reported that a diplatinum complex with two bridging diarylsilyl ligands, $[\{Pt(PPh_3)\}_2\{\mu\text{-}\eta^2\text{-HSiH(IMP)}\}_2]$ (IMP = 2-isopropyl-6-methylphenyl), reacted with dppe to produce the Pt complex with two bridging silylene ligands, $[\{Pt(dppe)\}_2\{\mu\text{-SiH(IMP)}\}_2]$.[31] Reactions of dmpe or dppe with complex **6** also cause elimination of hydrogens of the silyl ligand to afford the diplatinum complexes with two bridging silylene ligands, $[\{Pt(dmpe)\}_2(\mu\text{-SiPh}_2)_2]$ (**9**) and $[\{Pt(dppe)\}_2(\mu\text{-SiPh}_2)_2]$ (**10**), in 98% and 91% yields, respectively (eq 5).



(5)

Figure 6 displays molecular structures of **9** and **10** determined by X-ray crystallography. Complex **9** has a crystallographic C_2 symmetry at the midpoint of two Pt atoms, while the two Pt centers of **10** are crystallographically independent. Selected bond distances and angles are listed in Table 3. The Si$\cdots$Si distance of **9** (2.718(2) Å) is slightly longer than the Si–Si single bond of $^t\text{Bu}_3\text{Si–Si}^t\text{Bu}_3$ (2.697 Å),[32] which suggests a weak interaction between the two Si atoms. The corresponding distance of **10** (2.646(2) Å) is slightly shortened compared with that of **9**, while the Pt–Si bonds of **9** and **10** are not dispersed (2.374(1)–2.395(1) Å). Acute Si–Pt–Si angles in the Pt_2Si_2 ring of **9** (69.48(4)°) and of **10** (67.49(4)° and 67.12(4)°) also suggest a Si$\cdots$Si interaction, although it is larger than the Si–Pd–Si angle (63.92(2)°) of $[\{Pd(dmpe)\}_2(\mu\text{-SiPh}_2)_2]$.[12]

Table 3. Selected Bond Distances (Å) and Angles (deg) of 9 and 10

	9	10
Pt$\cdots$Pt*	3.9193 (2)	3.9723 (2)
Pt–Si	2.385 (1) 2.3847 (9)	2.374 (1), 2.391 (1) 2.389(1) , 2.395 (1)
Pt–P	2.3053 (8) 2.299 (1)	2.309 (1), 2.307 (1) 2.303 (1), 2.317 (1)
Si$\cdots$Si*	2.718 (2)	2.646 (2)
Si–Pt–Si*	69.48 (4)	67.49 (4), 67.12 (4)
Pt–Si–Pt*	110.52 (4)	112.96 (5), 112.25 (5)
P–Pt–P	85.48 (3)	84.77 (4), 85.56 (4)

The solid-state $^{29}Si\{^1H\}$ NMR measurement of **9** was carried out because the complex has too low solubility for the measurement in solution. The ^{29}Si resonance of the bridging silylene ligands was observed at highly negative position (δ −95.5) flanked with satellite signals of the ^{195}Pt nucleus (J_{Pt-Si} = 789 Hz). The diplatinum complexes, having a close Si$\cdots$Si contact between the silylene ligands, exhibit ^{29}Si NMR signals in the region with negative chemical shifts ($SiMe_4$ standard), as shown by *trans*-$[\{Pt(P^nPr_3)_2\}_2\{\mu\text{-SiH(Hex)}\}_2]$ (δ −92.3)[3] and *trans*-$[\{Pt(dppe)\}_2\{\mu\text{-SiH(IMP)}\}_2]$ (δ −132),[31] and a dipalladium analogue, $[\{Pd(dmpe)\}_2(\mu\text{-SiPh}_2)_2]$ (δ −51.0).[12] Coordination of a bidentate phosphine to the Pt center activates the Si–H bond of the bridging silyl ligands to form a diplatinum intermediate with μ-silyl and μ-silylene ligands and facilitates the hydrogen migration prior to reductive elimination of H_2.

Conclusion

This paper revealed details in the structure of the diplatinum complexes with bridging silyl ligands as well as in the exchange reactions of the bridging silyl ligands caused by addition of secondary silanes. Phenyl groups at the Si atoms influence Pt–Si lengths in the Pt–H–Si 3c-2e bonds and those of the Pt–Si σ-bond. The two bridging dialkylsilyl ligands of the diplatinum complexes undergo stepwise replacement with the silyl group with the added H_2SiPh_2 or $H_2SiMePh$. Exchange of a bridging diethylsilyl group of **3** with equimolar H_2SiPh_2 affords not only **7**, having μ-silyl ligands, but also **8**, having μ-silylene and μ-silane ligands. Results of the reaction using D_2SiPh_2 and of the isomerization of **8** into **7** suggest intramolecular migration of the Si–H hydrogens during the reaction. Coordination of chelating diphosphine ligands to the silyl-bridged diplatinum complexes causes Si–H bond activation and then H_2 elimination to form the complexes with bridging silylene ligands. This reaction as well as those reported previously may be induced by Si–H bond activation of the bridging silyl ligand caused by additional phosphines, as depicted in Scheme 4.

Experimental Section

General Procedures. All manipulations of the complexes were carried out using standard Schlenk techniques under an argon or

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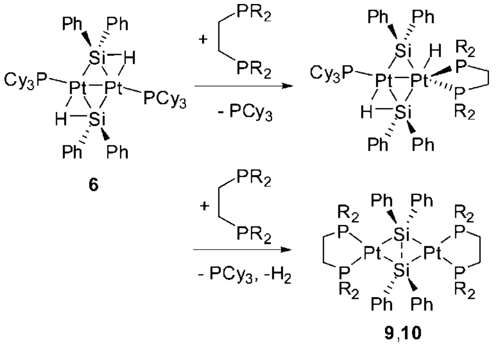
Scheme 4



nitrogen atmosphere. Hexane and toluene were purified by passing through a solvent purification system (Glass Contour). ^{1}H, ^{2}H{^{1}H}, ^{13}C{^{1}H}, ^{29}Si{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on Varian Mercury 300 or JEOL EX-400 spectrometers. Chemical shifts in ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to the residual peaks of the solvents used. The peak positions of the ^{29}Si{^{1}H} and ^{31}P{^{1}H} NMR spectra were referenced to external $SiMe_4$ (δ 0) and external 85% H_3PO_4 (δ 0) in C_6D_6, respectively. The ^{29}Si{^{1}H} NMR spectrum was acquired using a DEPT pulse sequence.[33] The ^{29}Si{^{1}H}, ^{31}P{^{1}H}, and ^{195}Pt{^{1}H} NMR measurements of **4** were performed on a JEOL ECA-600 spectrometer. Solid-state CPMAS ^{29}Si{^{1}H} NMR measurement was carried out at 79.3 MHz on a JEOL ECA-400 spectrometer using a spinning speed of 6849 Hz. The ^{29}Si chemical shift was referenced to poly(dimethylsilane)s (δ −34.0). The reagents H_2SiEt_2, D_2SiPh_2, and dppe (Sigma-Aldrich), $H_2SiMePh$ and H_2SiPh_2 (Wako Pure Chemical), and dmpe (Strem) are commercially available products. The compounds $[Pt(PCy_3)_2]$,[22] H_2SiHex_2,[34] and $[PtH_2(PCy_3)_2]$[35] were prepared according to the reported procedure. IR absorption spectra were recorded on a Shimadzu FT/IR-8100 spectrometer. Elemental analysis was carried out using a LECO CHNS-932 or Yanaco MT-5 CHN autorecorder.

Preparation of [{Pt(PCy$_3$)}$_2$(μ-η^2-HSiEt$_2$)$_2$] (3). A toluene solution (16 mL) of *cis*-$[PtPh_2(PCy_3)_2]$ (413 mg, 0.45 mmol) was heated at 60 °C for 1 h to produce $[Pt(PCy_3)_2]$, accompanied by reductive elimination of biphenyl. Addition of excess H_2SiEt_2 (438 μL, 3.4 mmol) to the reaction mixture produced *cis*-$[PtH(SiHEt_2)(PCy_3)_2]$ (**1**), which was characterized by comparison of the ^{1}H and ^{31}P{^{1}H} NMR spectra with the reported data.[23] Further heating of the reaction mixture at 80 °C for 1 h and removal of the solvent and volatile compounds under reduced pressure gave a colorless solid, which was washed with 10 mL of hexane twice and dried *in vacuo* to give **3** as a white solid (234 mg, 91%). Crystals of **3** suitable for X-ray crystallography were obtained by recrystallization from THF at −20 °C. Data for **1**: ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ −3.39 (dd, 1H, Pt*H*, $J_{\mathrm{Pt-H}} = 870$ Hz, $^{2}J_{\mathrm{P-H}} = 26, 141$ Hz), 0.4–2.6 (P*Cy*$_3$ and Si*Et*$_2$), 4.41 (m, 1H, Si*H*). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6, 25 °C): δ 38.5 (d, $P_{trans\ \mathrm{to\ H}}$, $J_{\mathrm{Pt-P}} = 2681$ Hz, $^{2}J_{\mathrm{P-P}} = 11$ Hz), 46.0 (d, $P_{trans\ \mathrm{to\ Si}}$, $J_{\mathrm{Pt-P}} = 1544$ Hz, $^{2}J_{\mathrm{P-P}} = 11$ Hz). Data for **3**: Anal. Calcd for $C_{44}H_{88}P_2Pt_2Si_2$: C, 46.96; H, 7.88. Found: C, 47.29; H, 7.63. ^{1}H NMR (400 MHz, C_7D_8, 80 °C): δ 1.26–1.30 (m, 18H, PCHCH$_2$C*H*$_2$ and PCHCH$_2$CH$_2$C*H*$_2$), 1.35 (t, 12H, SiCH$_2$C*H*$_3$, $^{3}J_{\mathrm{H-H}} = 8.0$ Hz), 1.40–1.52 (m, 4H, SiC*H*$_2$), 1.55–1.68 (m, 24H, PCHC*H*$_2$, PCHCH$_2$CH$_2$C*H*$_2$, SiC*H*$_2$, and Pt−*H*−Si), 1.78 (m, 12H, PCHCH$_2$C*H*$_2$), 2.04–2.11 (m, 18H, PC*H* and PCHC*H*$_2$). ^{13}C{^{1}H} NMR (100 MHz, C_7D_8, 80 °C): δ 12.2 (SiCH$_2$*C*H$_3$, $^{3}J_{\mathrm{Pt-C}} = 24, 9.3$ Hz), 17.6 (Si*C*H$_2$, $^{2}J_{\mathrm{Pt-C}} = 76, 43$ Hz), 27.1 (PCHCH$_2$CH$_2$*C*H$_2$), 28.0 (m, PCHCH$_2$*C*H$_2$, $^{3}J_{\mathrm{P-C}} = 6$ Hz), 31.0 (apparent triplet, PCH*C*H$_2$, $^{2}J_{\mathrm{P-C}} = 14$ Hz), 39.2 (m, P*C*H, $J_{\mathrm{P-C}} = 12$ Hz). DEPT ^{29}Si{^{1}H} NMR (79 MHz, C_7D_8, 80 °C): δ 188.1 (apparent triplet due to virtual coupling, $^{2}J_{\mathrm{P-Si}} = 73$ Hz). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6, 25 °C): δ 52.6 ($J_{\mathrm{Pt-P}} = 3957$ Hz, $^{2}J_{\mathrm{Pt-P}} = 260$ Hz, $^{3}J_{\mathrm{P-P}} = 60$ Hz). IR (KBr): 1653 ($\nu_{\mathrm{H-Si}}$) cm^{-1}. All ^{1}H NMR signals were assigned on the basis of the results of 2D ^{1}H−^{13}C NMR measurements.

Preparation of [{Pt(PCy$_3$)}$_2${μ-η^2-HSi(Hex)$_2$}$_2$] (4). Complexes **2** and **4** were obtained with a similar procedure for the preparation of **3**. The reaction of *cis*-$[PtPh_2(PCy_3)_2]$ (286 mg, 0.31 mmol) and H_2SiHex_2 (350 μL, 1.2 mmol) in toluene solution (5 mL) gave **4** as a white solid (192 mg, 90%). Crystals of **4** suitable for X-ray crystallography were obtained from slow diffusion of the toluene solution to hexane (1:33) at room temperature. Data for **2**: ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ −3.42 (dd, 1H, Pt*H*, $J_{\mathrm{Pt-H}} = 875$ Hz, $^{2}J_{\mathrm{P-H}} = 143, 25$ Hz), 0.5–2.6 (P*Cy* and Si*Hex*), 4.41 (m, 1H, Si*H*). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6, 25 °C): δ 38.5 (d, $P_{trans\ \mathrm{to\ H}}$, $J_{\mathrm{P-Pt}} = 2670$ Hz, $^{2}J_{\mathrm{P-P}} = 11$ Hz), 45.9 (d, $P_{trans\ \mathrm{to\ Si}}$, $J_{\mathrm{P-Pt}} = 1531$ Hz, $^{2}J_{\mathrm{P-P}} = 11$ Hz). Data for **4**: Anal. Calcd for $C_{60}H_{120}P_2Pt_2Si_2$: C, 53.39; H, 8.96. Found: C, 52.91; H, 8.62. ^{1}H NMR (400 MHz, C_7D_8, 25 °C): δ 0.96 (t, 12H, Si(CH$_2$)$_5$C*H*$_3$, $^{3}J_{\mathrm{H-H}} = 7.0$ Hz), 1.25–1.85 (90H, PCHCH$_2$CH$_2$C*H*$_2$, PCHCH$_2$C*H*$_2$, PCHC*H*$_2$, Si(C*H*$_2$)$_5$CH$_3$, and Pt−*H*−Si), 2.09 (m, 18H, PC*H* and PCHCH$_2$C*H*$_2$). ^{13}C{^{1}H} NMR (100 MHz, C_7D_8, 80 °C): δ 14.4 (Si(CH$_2$)$_5$*C*H$_3$), 23.2 (Si(CH$_2$)$_2$*C*H$_2$ or Si(CH$_2$)$_3$*C*H$_2$), 26.6 (Si*C*H$_2$, $^{2}J_{\mathrm{Pt-C}} = 69, 40$ Hz), 27.1 (PCHCH$_2$CH$_2$*C*H$_2$), 28.2 (m, PCHCH$_2$*C*H$_2$, $^{3}J_{\mathrm{P-C}} = 5$ Hz), 29.1 (SiCH$_2$*C*H$_2$, $^{3}J_{\mathrm{Pt-C}} = 21, 8$ Hz), 31.0 (apparent triplet, PCH*C*H$_2$, $^{2}J_{\mathrm{P-C}} = 13$ Hz), 32.7 (Si(CH$_2$)$_2$*C*H$_2$ or Si(CH$_2$)$_3$*C*H$_2$), 34.4 (Si(CH$_2$)$_4$*C*H$_2$), 39.2 (m, P*C*H, $^{2}J_{\mathrm{P-C}} = 12$ Hz). ^{31}P{^{1}H} NMR (243 MHz, C_6D_6, 25 °C): δ 51.8 ($J_{\mathrm{Pt-P}} = 3969$ Hz, $^{2}J_{\mathrm{Pt-P}} = 264$ Hz, $^{3}J_{\mathrm{P-P}} = 60$ Hz). ^{29}Si{^{1}H} NMR (119 MHz, C_6D_6, 25 °C): δ 183.2 ($J_{\mathrm{Pt-Si}} = 1451, 273$ Hz, $^{2}J_{\mathrm{P-Si}} = 73, 7$ Hz). ^{195}Pt{^{1}H} NMR (561 MHz, C_6D_6, 25 °C): δ −5835 ($J_{\mathrm{Pt-Pt}} = 2995$ Hz, $J_{\mathrm{Pt-P}} = 3969, 264$ Hz, $J_{\mathrm{Pt-Si}} = 1451, 273$ Hz). IR (KBr): 1655 ($\nu_{\mathrm{H-Si}}$) cm^{-1}. All signals in the ^{1}H and ^{13}C{^{1}H} NMR spectra were assigned on the basis of the results of 2D ^{1}H−^{1}H and ^{1}H−^{13}C NMR measurements.

Reaction of H$_2$SiEt$_2$ with *trans*-[PtH$_2$(PCy$_3$)$_2$]. Preparation of *trans*-$[PtH_2(PCy_3)_2]$ was conducted by a modified procedure of the previous report.[35] The solution of $[Pt(PCy_3)_2]$, obtained from heating *cis*-$[PtPh_2(PCy_3)_2]$ (170 mg, 0.19 mmol) in toluene (4 mL) solution at 60 °C, was stirred under H_2 atmosphere for 30 min to yield *trans*-$[PtH_2(PCy_3)_2]$ quantitatively. Excess H_2SiEt_2 (120 μL, 0.94 mmol) was added *in situ* to the reaction mixture, and the solution was stirred for 1 h at 80 °C. Removal of the solvent and volatile compounds under reduced pressure gave a solid, which was washed with 5 mL of hexane twice and dried *in vacuo* to give **3** as a white solid (36 mg, 34%).

Preparation of [{Pt(PCy$_3$)}$_2$ (μ-η^2-HSiMePh)$_2$] (5). Complex **3** (290 mg, 0.26 mmol) was dissolved in toluene (5 mL) with heating at 60 °C for 5 min. A 3-fold molar amount of $H_2SiMePh$ (106 μL, 0.77 mmol) was added to the solution, and the solution was stirred for 12 h at room temperature. The solvent and volatile compounds were removed under reduced pressure to give a solid, which was washed with 5 mL of hexane twice and dried *in vacuo* to give **5** as a pale yellow solid (270 mg, 88%). The NMR spectra of the product indicated the mixture of **5**-*trans* and **5**-*cis* in 98:2 ratio. Crystals of **5**-*trans* were obtained by recrystallization from toluene/hexane (3:5) at room temperature. Anal. Calcd for $C_{50}H_{84}P_2Pt_2Si_2$: C, 50.32; H, 7.09. Found: C, 50.40; H, 6.79. ^{1}H NMR (400 MHz, C_7D_8, 25 °C): δ 1.15–1.38 (18H, PCHCH$_2$CH$_2$C*H*$_2$ and PCHCH$_2$C*H*$_2$), 1.51–1.59 (18H, SiC*H*$_3$, PCHC*H*$_2$), 1.73 (14H, PCHCH$_2$CH$_2$C*H*$_2$, PCHCH$_2$C*H*$_2$, and Pt−*H*−Si), 1.82 (d, 6H, PCHCH$_2$C*H*$_2$, $J_{\mathrm{H-H}} = 11$ Hz), 1.94 (d, 6H, PCHC*H*$_2$, $J_{\mathrm{H-H}} = 12$ Hz), 2.12 (d, 12H, PCHC*H*$_2$ and PCHCH$_2$C*H*$_2$, $J_{\mathrm{H-H}} = 10$ Hz), 7.29 (t, 2H, C$_6$*H*$_5$ *para*, $J_{\mathrm{H-H}} = 7.2$ Hz), 7.43 (t, 4H, C$_6$*H*$_5$ *meta*, $J_{\mathrm{H-H}} = 7.2$ Hz), 7.99 (d, 4H, C$_6$*H*$_5$ *ortho*, $J_{\mathrm{H-H}} = 7.2$ Hz). ^{13}C{^{1}H}

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Table 4. Crystallographic Data and Details of Refinement of 3, 4, 5-*trans*, 6, 9, and 10

	3	**4**	**5**-*trans*	**6**	**9**	**10**
formula	$C_{44}H_{88}P_2Si_2Pt_2$	$C_{60}H_{120}P_2Si_2Pt_2$	$C_{50}H_{84}P_2Si_2Pt_2$	$C_{60}H_{88}P_2Si_2Pt_2$	$C_{36}H_{52}P_4Si_2Pt_2$	$C_{76}H_{68}P_4Pt_2Si_2+C_4H_8O$
formula wt	1125.44	1349.87	1193.48	1317.62	1055.02	1623.68
cryst size/mm	0.02 × 0.08 × 0.14	0.10 × 0.15 × 0.17	0.20 × 0.20 × 0.24	0.35 × 0.40 × 0.40	0.40 × 0.40 × 0.50	0.08 × 0.12 × 0.18
cryst syst	triclinic	triclinic	monoclinic	monoclinic	triclinic	triclinic
cryst color	colorless	colorless	yellow	yellow	yellow	yellow
space group	$P\bar{1}$ (*No.* 2)	$P\bar{1}$ (*No.* 2)	$P2_1/a$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a/Å	9.695 (3)	9.427 (3)	10.053 (2)	10.218 (3)	9.183 (2)	12.388 (2)
b/Å	9.826 (2)	13.635 (4)	18.213 (4)	13.957 (4)	11.193 (3)	13.734 (2)
c/Å	14.461 (5)	13.746 (4)	13.751 (3)	20.078 (6)	11.320 (3)	20.297 (3)
α/deg	75.28 (1)	113.132 (4)			102.781 (2)	85.119 (4)
β/deg	82.66 (1)	90.197 (3)	91.150 (3)	93.089 (4)	112.877 (3)	86.097 (4)
γ/deg	61.14 (1)	105.053 (3)			104.3217 (5)	89.294 (4)
V/Å^3	1166.8 (6)	1558.0 (8)	2517.3 (9)	2859 (1)	970.9 (5)	3433 (1)
Z	1	1	2	2	1	2
D_{calcd}/g cm^{-3}	1.602	1.439	1.572	1.530	1.804	1.511
F(000)	566	694	1192	1324	512	1556
μ/mm^{-1}	6.1123	4.5908	5.6716	5.0017	7.4187	4.1809
no. of reflns measd	8585	10 874	17 633	16 989	6669	26 131
no. of unique reflns	4963	6587	5670	6144	4019	14 745
R_{int}	0.035	0.033	0.029	0.029	0.023	0.031
no. of obsed reflns ($I > 2.00\sigma(I)$)	4363	5130	4326	5042	3745	11 116
no. of variables	273	381	295	345	225	878
R1 ($I > 2.00\sigma(I)$)	0.0390	0.0612	0.0603	0.0521	0.0223	0.0360
wR2 ($I > 2.00\sigma(I)$)	0.1005	0.1364	0.1554	0.1230	0.0553	0.0757
GOF	0.998	1.061	0.958	1.032	1.013	1.019

NMR (100 MHz, C_7D_8, 80 °C): δ 6.58 (SiCH$_3$, $^2J_{\mathrm{Pt-C}} = 56$, 84 Hz), 26.8 (PCHCH$_2$CH$_2$$CH_2$), 27.9 (m, PCHCH$_2$$CH_2$), 30.6 (apparent triplet, PCHCH$_2$), 31.0 (apparent triplet, PCHCH$_2$), 39.0 (m, PCH, $J_{\mathrm{P-C}} = 12$ Hz), 127.3 (C_6H$_5$ *meta*), 135.5 (br, C_6H$_5$ *ortho*), 150.3 (C_6H$_5$ *ipso*). The *para* carbon signal of C_6H$_5$ group was overlapped with the solvent signals. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 25 °C): δ 52.8 ($J_{\mathrm{Pt-P}} = 3972$ Hz, $^2J_{\mathrm{Pt-P}} = 239$ Hz, $^3J_{\mathrm{P-P}} = 57$ Hz). IR (KBr): 1670 ($\nu_{\mathrm{H-Si}}$) cm^{-1}. All signals in the ^{1}H and ^{13}C{^{1}H} NMR spectra were assigned on the basis of the results of 2D ^{1}H$-^{13}$C NMR measurements. NMR data of **5**-*cis* in the product mixture were obtained only in part due to low peak intensity and overlapping with **5**-*trans*; ^{1}H NMR: δ 8.16 (d, C$_6$$H_5$ *ortho*, $J_{\mathrm{H-H}} = 7.2$ Hz). ^{31}P{^{1}H} NMR: δ 52.5.

Preparation of [{Pt(PCy$_3$)}$_2$(μ-η^2-HSiPh$_2$)$_2$] (6). Complex **5** (147 mg, 0.12 mmol) was dissolved in toluene (5 mL) with heating at 60 °C for 5 min. Addition of excess H_2SiPh_2 (120 μL, 0.65 mmol) to the solution and further heating of the mixture at 80 °C for 2 h gave **6**. The product was obtained by removal of the solvent and volatile compounds under reduced pressure and by washing with 5 mL of hexane twice and drying *in vacuo* (131 mg, 81%). The NMR data were identical with those reported.[2] Crystals of **6** suitable for X-ray crystallography were obtained by recrystallization from toluene/hexane (3:5) at room temperature.

Reaction of H_2SiPh_2 with 3. To a toluene suspension (5 mL) of **3** (280 mg, 0.25 mmol) was added excess H_2SiPh_2 (170 μL, 0.92 mmol). The reaction mixture was stirred at room temperature for 3 h. The solvent and volatile compounds were removed under reduced pressure to give a solid, which was washed with 5 mL of hexane twice and dried *in vacuo* to give **6** (317 mg, 97%).

Equimolar Reaction of H_2SiPh_2 with 3. To a toluene solution (25 mL) of **3** (801 mg, 0.71 mmol) was added a slightly smaller amount of H_2SiPh_2 (122 μL, 0.66 mmol). The reaction mixture was stirred for 3 h at room temperature. Removal of the solvent under reduced pressure afforded 842 mg of a yellow solid, which contained [{Pt(PCy$_3$)}$_2$(μ-η^2-HSiEt$_2$)(μ-η^2-HSiPh$_2$)] (**7**), [{Pt(PCy$_3$)}$_2$(μ-η^2:η^2-H$_2$SiEt$_2$)(μ-SiPh$_2$)] (**8**), and **6** in a 50:45:5 ratio. Repeated recrystallization from toluene/hexane solution (1:7) of the products at −20 °C gave yellow crystals (94 mg, 11%), whose ^{1}H NMR spectrum showed the presence of **7** and **8** in 6:94 ratio. Dissolution of the mixture in C_6D_6 and leaving the solution for 2 weeks gave rise to an equilibrium of **7** and **8** (55:45). Anal. Calcd for $C_{52}H_{88}P_2Pt_2Si_2$ (**7**:**8** = 6:94): C, 51.13; H, 7.26. Found: C, 51.46; H, 7.48. Data of **8**: ^{1}H NMR (400 MHz, C_7D_8, 80 °C): δ 1.03 (br, 20H, PCHCH$_2$CH$_2$CH_2, PCHCH$_2$CH_2, and Pt$-H-$Si), 1.33 (t, 6H, SiCH$_2$CH_3, $J_{\mathrm{H-H}} = 8.0$ Hz), 1.37 (br, 12H, PCHCH_2), 1.50 (br, 6H, PCHCH$_2$CH$_2$CH_2) 1.58 (br, 16H, SiCH_2 and PCHCH$_2$CH_2), 1.83 (br, 12H, PCHCH_2), 1.98 (m, 6H, PCH), 7.07 (t, 2H, C$_6$$H_5$ *para*, $J_{\mathrm{H-H}} = 7.2$ Hz), 7.20 (t, 4H, C$_6$$H_5$ *meta*, $J_{\mathrm{H-H}} = 7.2$ Hz), 8.00 (d, 4H, C$_6$$H_5$ *ortho*, $J_{\mathrm{H-H}} = 7.2$ Hz). ^{13}C{^{1}H} NMR (100 MHz, C_7D_8, 80 °C): δ 11.8 (SiCH$_2$$CH_3$, $^3J_{\mathrm{Pt-C}} = 11$ Hz), 16.8 (SiCH$_2$, $^2J_{\mathrm{Pt-C}} = 61$ Hz), 26.8 (PCHCH$_2$CH$_2$$CH_2$), 27.8 (m, PCHCH$_2$$CH_2$, $^3J_{\mathrm{P-C}} = 6$ Hz), 30.8 (apparent triplet, PCHCH$_2$, $^2J_{\mathrm{P-C}} = 13$ Hz), 38.9 (m, PCH, $J_{\mathrm{P-C}} = 12$ Hz), 127.2 (C_6H$_5$ *meta*), 127.5 (C_6H$_5$ *para*), 137.4 (C_6H$_5$ *ortho*, $^3J_{\mathrm{Pt-C}} = 15$ Hz), 151.0 (C_6H$_5$ *ipso*, $^2J_{\mathrm{Pt-C}} = 63$ Hz). DEPT ^{29}Si{^{1}H} NMR (162 MHz, C_7D_8, 45 °C): δ 141.3 (t, H$_2$$SiEt_2$, $J_{\mathrm{Pt-Si}} = 418$ Hz, $^2J_{\mathrm{P-Si}} = 72$ Hz), 230.1 (t, SiPh$_2$, $J_{\mathrm{Pt-Si}} = 1180$ Hz, $^2J_{\mathrm{P-Si}} = 4$ Hz). ^{31}P{^{1}H} NMR (162 MHz, C_7D_8, 80 °C): δ 51.8 ($J_{\mathrm{Pt-P}} = 3849$ Hz, $^2J_{\mathrm{Pt-P}} = 362$ Hz, $^2J_{\mathrm{Si-P}} = 72$ Hz, $^3J_{\mathrm{P-P}} = 55$ Hz). IR (KBr): 1696 ($\nu_{\mathrm{H-Si}}$) cm^{-1}. The ^{1}H NMR signals in the aliphatic region were characterized using 2D ^{1}H$-^1$H and ^{1}H$-^{13}$C NMR measurements. Addition of PCy$_3$ (0.2 equiv) to the mixture accelerated the conversion of **8** to **7** to an almost equal ratio (45:55) in 23 h. The NMR spectroscopic data of **7** were obtained from the mixture of **7** and **8**. The crystals of **7** and **8** suitable for X-ray crystallography were obtained by carefully selecting the crystals from the mixture. Data of **7**: ^{1}H NMR (400 MHz, C_7D_8, 80 °C): δ 0.7–1.8 (PC$_6$$H_{11}$ and Pt$-H-$Si), 6.88 (C$_6$$H_5$ *para*), 7.00 (C$_6$$H_5$ *meta*), 7.60 (C$_6$$H_5$ *ortho*). ^{13}C{^{1}H} NMR (100 MHz, C_7D_8, 80 °C): δ 12.4 (SiCH$_2$$CH_3$, $^3J_{\mathrm{Pt-C}} = 24$, 8 Hz), 18.0 (SiCH$_2$, $^2J_{\mathrm{Pt-C}} = 75$, 43 Hz), 26.7 (PCHCH$_2$CH$_2$$CH_2$), 27.6 (PCHCH$_2$$CH_2$), 30.5 (PCH$CH_2$), 38.5 (P$C$H), 127.4 ($C_6H_5$ *meta*), 127.7 (C_6H$_5$ *para*), 136.5 (C_6H$_5$ *ortho*, $^3J_{\mathrm{Pt-C}} = 12$ Hz), 146.8 (C_6H$_5$ *ipso*). DEPT ^{29}Si{^{1}H} NMR (162 MHz, C_7D_8, 45 °C): δ 163.7 (dd, $^2J_{\mathrm{P-Si}} = 12$, 66 Hz), 195.5 (dd, $^2J_{\mathrm{P-Si}} = 11$, 60 Hz). The $J_{\mathrm{Pt-Si}}$ values were not estimated due to small peak intensity. ^{31}P{^{1}H} NMR (162 MHz, C_7D_8, 25 °C): δ 53.2 ($J_{\mathrm{Pt-P}} = 3858$ Hz, $^2J_{\mathrm{Pt-P}} = 252$ Hz, $^3J_{\mathrm{P-P}} = 59$ Hz), 53.5 ($J_{\mathrm{Pt-P}} = 4027$ Hz, $^2J_{\mathrm{Pt-P}} = 237$ Hz, $^3J_{\mathrm{P-P}} = 59$ Hz). ^{1}H and ^{13}C{^{1}H} NMR signals of **7** in aliphatic region were severely overlapped with those of **8**.

Equimolar Reaction of D_2SiPh_2 with 3. To a toluene solution (25 mL) of **3** (753 mg, 0.67 mmol) was added an equimolar amount of D_2SiPh_2 (125 μL, 0.67 mmol). The reaction mixture was stirred for 3 h at room temperature. Removal of the solvent under reduced pressure yielded a yellow solid (782 mg), which contained [{Pt(PCy$_3$)}$_2$-

(μ-η^2-DSiEt$_2$)(μ-η^2-HSiPh$_2$)] (**7**-DSiEt$_2$), [{Pt(PCy$_3$)}$_2$(μ-η^2-HSiEt$_2$)(μ-η^2-DSiPh$_2$)] (**7**-DSiPh$_2$), [{Pt(PCy$_3$)}$_2$(μ-η^2:η^2-HDSiEt$_2$)(μ-SiPh$_2$)] (**8**-*d*), and [{Pt(PCy$_3$)}$_2$(μ-η^2-DSiPh$_2$)$_2$] (**6**-d_2) in a 49:47:4 ratio (**7**-DSiEt$_2$+**7**-DSiPh$_2$:**8**-*d*:**6**-d_2). Repeated recrystallization from toluene/hexane solution (1:7) of the product at −20 °C gave yellow crystals containing **8**-*d* as the major component (32 mg, 4%, **7**-DSiEt$_2$+**7**-DSiPh$_2$:**8**-*d* = 7:93). Data of **8**-*d*: ^{2}H{^{1}H} NMR (61 MHz, toluene, 40 °C): δ 1.01 (H*D*SiEt$_2$, $J_{\mathrm{Pt-D}} = 99$ Hz). IR (KBr): 1685 ($\nu_{\mathrm{Pt-H-Si}}$), 1225 ($\nu_{\mathrm{Pt-D-Si}}$) cm^{-1}. The ^{2}H{^{1}H} NMR spectroscopic data of **7**-DSiEt$_2$+**7**-DSiPh$_2$ were obtained from the mixture containing **8**-*d* (61 MHz, toluene, 40 °C): 1.44 (*D*SiEt$_2$, $J_{\mathrm{Pt-D}} = 95$ Hz), 2.43 (*D*SiPh$_2$, $J_{\mathrm{Pt-D}} = 87$ Hz).

Reaction of H_2SiPh_2 with a Mixture of 7 and 8. To a toluene solution (5 mL) of a mixture of **7** and **8** (87 mg, 0.071 mmol), together with a tiny amount of complex **6** (**6**:**7**:**8** = 5:50:45), was added excess H$_2$SiPh$_2$ (40 μL, 0.21 mmol). The reaction mixture was stirred at room temperature for 12 h. The solvent was removed under reduced pressure to give a pale yellow solid, which was washed with 5 mL of hexane twice and dried *in vacuo* to give complex **6** (63 mg, 67%).

Preparation of [{Pt(dmpe)}$_2$(μ-SiPh$_2$)$_2$] (9). To a toluene suspension (13 mL) of **6** (497 mg, 0.38 mmol) was added twice the molar amount of dmpe (125 μL, 0.76 mmol). The reaction mixture was stirred for 1 h at room temperature. The solvent was removed under reduced pressure to give a solid, which was washed with 5 mL of hexane twice and dried *in vacuo* to give **9** as a yellow solid (391 mg, 98%). Yellow crystals of **9** suitable for X-ray crystallography were obtained by recrystallization from THF/hexane (2:1). Anal. Calcd for $C_{36}H_{52}P_4Pt_2Si_2$: C, 40.98; H, 4.97. Found: C, 40.60; H, 4.86. ^{1}H NMR (400 MHz, THF-d_8, 25 °C): δ 0.91 (d, 24H, PC*H*$_3$, $^2J_{\mathrm{P-H}} = 7.1$ Hz, $^3J_{\mathrm{Pt-H}} = 17$ Hz), 1.33 (m, 8H, PC*H*$_2$, $^2J_{\mathrm{P-H}} = 15$ Hz, $^3J_{\mathrm{Pt-H}} = 11$ Hz), 6.87 (t, 4H, C$_6$*H*$_5$ *para*, $^3J_{\mathrm{H-H}} = 7.5$ Hz), 6.98 (t, 8H, C$_6$*H*$_5$ *meta*, $^3J_{\mathrm{H-H}} = 7.5$ Hz), 7.66 (d, 8H, C$_6$*H*$_5$ *ortho*, $^3J_{\mathrm{H-H}} = 7.5$ Hz). ^{13}C{^{1}H} NMR (100 MHz, THF-d_8, 55 °C): δ 15.2 (m, P*C*H$_3$, $^2J_{\mathrm{Pt-C}} = 49$ Hz), 32.3 (m, P*C*H$_2$, $J_{\mathrm{P-C}} = 22$ Hz), 125.5 (Si*C*$_6$H$_5$ *para*), 126.3 (Si*C*$_6$H$_5$ *meta*), 138.1 (Si*C*$_6$H$_5$ *ortho*, $^3J_{\mathrm{Pt-C}} = 29$ Hz), 154.4 (Si*C*$_6$H$_5$ *ipso*, $^2J_{\mathrm{Pt-C}} = 12$ Hz). Solid-state CPMAS ^{29}Si{^{1}H} NMR (79 MHz, 25 °C): δ −95.5 ($J_{\mathrm{Pt-Si}} = 789$ Hz). ^{31}P{^{1}H} NMR (121 MHz, C$_6$D$_6$, 25 °C): δ 39.2 ($J_{\mathrm{Pt-P}} = 1263$ Hz, $^3J_{\mathrm{Pt-P}} = 222$ Hz, $^4J_{\mathrm{P-P}} = 29$ Hz).

Preparation of [{Pt(dppe)}$_2$(μ-SiPh$_2$)$_2$] (10). Complex **10** was obtained as a yellow solid (91%) from the reaction of **6** (154 mg, 0.12 mmol) and dppe (93 mg, 0.23 mmol) at 80 °C for 20 min. Recrystallization from THF/hexane (3:1) yielded crystals suited for X-ray crystallography. Anal. Calcd for $C_{76}H_{68}P_4Pt_2Si_2$: C, 58.83; H, 4.42. Found: C, 58.82; H, 4.76. ^{1}H NMR (400 MHz, THF-d_8, 25 °C): δ 1.83 (d, 8H, PC*H*$_2$, $^2J_{\mathrm{P-H}} = 15.2$ Hz), 6.67 (t, 8H, PC$_6$*H*$_5$ *para*, $^3J_{\mathrm{H-H}} = 7.6$ Hz), 6.81 (t, 4H, SiC$_6$*H*$_5$ *para*, $^3J_{\mathrm{H-H}} = 6.8$ Hz), 6.9–7.1 (m, 48H, PC$_6$*H*$_5$ *meta*, SiC$_6$*H*$_5$ *meta*, PC$_6$*H*$_5$ *ortho*, and SiC$_6$*H*$_5$ *ortho*). ^{13}C{^{1}H} NMR (100 MHz, THF-d_8, 25 °C): δ 29.8 (m, P*C*H$_2$, $J_{\mathrm{P-C}} = 21$ Hz), 125.4 (Si*C*$_6$H$_5$ *para*), 126.3 (Si*C*$_6$H$_5$ *meta*), 128.2 (apparent triplet, P*C*$_6$H$_5$ *meta*, $^3J_{\mathrm{P-C}} = 3$ Hz), 129.6 (P*C*$_6$H$_5$ *para*), 134.0 (m, P*C*$_6$H$_5$ *ortho*) 135.3 (m, P*C*$_6$H$_5$ *ipso*), 137.6 (Si*C*$_6$H$_5$ *ortho*, $^3J_{\mathrm{Pt-C}} = 22$ Hz), 151.6 (Si*C*$_6$H$_5$ *ipso*, $^2J_{\mathrm{Pt-C}} = 10$ Hz). ^{31}P{^{1}H} NMR (121 MHz, C$_6$D$_6$, 25 °C): δ 57.1 ($J_{\mathrm{Pt-P}} = 1511$ Hz, $^2J_{\mathrm{Pt-P}} = 275$ Hz, $^3J_{\mathrm{P-P}} = 28$ Hz).

X-ray Crystallography. Crystals of **3**, **4**, **5**-*trans*, **6**, **9**, and **10** suitable for an X-ray diffraction study were mounted on a glass capillary tube. The data were collected to a maximum 2θ value of 55.0°. A total of 720 oscillation images were collected on a Rigaku Saturn CCD area detector equipped with monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at −160 °C. Hydrogen atoms, except for the SiH hydrogens of **3**, **4**, **5**-*trans*, and **6** were located by assuming the ideal geometry and were included in the structure calculation without further refinement of the parameters. Crystallographic data and details of refinement of the complexes are summarized in Table 4.

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Supporting Information Available: Crystallographic data for **3**, **4**, **5**-*trans*, **6**, **9**, and **10** as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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