A New Reactive System for Catalytic Bis-Silylation of Acetylenes and Olefins

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Reaction of diphenylacetylene (**1a**) with Me_3SiSiF_2Ph (1 equiv) in toluene in the presence of a palladium catalyst (1 mol %) generated in situ by mixing $[Pd(\eta^3\text{-allyl})Cl]_2$ and PMe_2Ph (2.2 equiv/Pd) was completed in 1.4 h at room temperature to give the bis-silylation product (*Z*)-1-(difluorophenylsilyl)-1,2-diphenyl-2-(trimethylsilyl)ethene (**2a**) in 95% yield. In similar catalytic systems, a variety of acetylenes and olefins, including 3-hexyne, 1-phenyl-1-propyne, phenylacetylene, 1-octyne, norbornene, styrene, and 1-octene, were bis-silylated in 64–96% yields. The highly reactive nature of the present catalytic system was studied in stoichiometric systems. The presumed intermediates *trans*-$Pd(SiMe_3)(SiF_2Ph)L_2$ (L = PMe_3 (**4a**), PMe_2Ph (**4b**)) were prepared by oxidative addition of Me_3SiSiF_2Ph toward $Pd(styrene)L_2$ complexes (L = PMe_3 (**3a**), PMe_2Ph (**3b**)). Complex **4b** reacted with diphenylacetylene (3 equiv) in toluene-d_8 at −20 °C to give the bis-silylation product (*Z*)-**2a** in 82% yield together with $Pd(PhC{\equiv}CPh)(PMe_2Ph)_2$ (93%). Treatment of **4a** with dimethyl acetylenedicarboxylate (1 equiv) in toluene at −20 °C instantly formed a palladium(0) complex coordinated with bis-silylated olefin, $Pd\{(Z)\text{-}(MeO_2C)(Me_3Si)C{=}C(SiF_2Ph)(CO_2Me)\}(PMe_3)_2$ (**6**). The structure of **6** was determined by an X-ray diffraction study. Crystal data for **6**·THF: $C_{21}H_{38}O_4P_2F_2Si_2Pd{\cdot}C_4H_8O$, a = 15.585(2) Å, b = 12.438(2) Å, c = 17.652(2), β = 93.86(1)°, V = 3413.9(8) Å^3, monoclinic, $P2_1/n$, Z = 4.

Introduction

Organosilicon compounds have attracted considerable recent interest because of their potential applications in material science as well as in organic synthesis.[1] Bis-silylation of unsaturated hydrocarbons catalyzed by group 10 metals is a convenient synthetic means to obtain such compounds. Although this reaction has been extensively studied over the past two decades,[2–6] the scope of applications is still limited. Thus, the bis-silylation has not been successful for internal acetylenes except for dimethyl acetylenedicarboxylate,[2a–d] 3-pentyn-2-one,[2d] and diphenylacetylene,[2e] which all possess high reactivity. The bis-silylation of olefins is more scarce. Ito and his co-workers recently developed a novel palladium isocyanide catalyst that is active in intramolecular bis-silylation of olefins, while the catalyst is not applicable to intermolecular reactions.[3a,b] The only successful example of the intermolecular reaction of an olefin reported so far is the platinum-catalyzed bis-silylation of ethylene.[3c]

We report herein a highly reactive system for the catalytic bis-silylation of unsaturated hydrocarbons where a variety of acetylenes and olefins are bis-silylated in high yields under mild conditions. The combination of the unsymmetrically substituted disilane Me_3SiSiF_2Ph and a palladium catalyst coordinated with basic tertiary phosphine ligands, PMe_2Ph and PMe_3, was found to provide this highly reactive system.

Results and Discussion

Catalytic Bis-Silylation of Acetylenes and Olefins. Representative results for catalytic bis-silylation of acetylenes are summarized in eq 1 and Table 1. The bis-silylation of diphenylacetylene (**1a**) and 1-octyne (**1e**)

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Table 1. Palladium-Catalyzed Bis-Silylation of Acetylenes with $PhF_2SiSiMe_3$[a]

entry no.	acetylene	catalyst	reaction temp (°C)	reaction time (h)	yield[b] (%)	Z:E[c]
1	**1a**	A	room temp	1.4	95	>99:1
2	**1a**	B	room temp	2.3	95	>99:1
3	**1b**	B	60	20	76	>99:1
4	**1c**	B	40	10	96[d]	>99:1
5	**1d**	A	60	1.5	94	89:11
6	**1e**	A	room temp	0.9	94	87:13

[a] All reactions were run in a toluene solution in the presence of palladium catalysts generated in situ from $[Pd(\eta^3\text{-allyl})Cl]_2$ and tertiary phosphine ligands (PMe_2Ph for catalyst A; PMe_3 for catalyst B). The ratio acetylene:disilane:Pd:phosphine is 1.0:1.0:0.010:0.022 (entries 1, 4, and 6), 1.0:1.4:0.010:0.020 (entry 2), or 1.0:1.0:0.020:0.044 (entries 3 and 5). [b] Isolated yields after bulb-to-bulb distillation. [c] Determined by ^{19}F NMR spectroscopy. [d] The product (*Z*)-**2c** consists of the two regioisomers (*Z*)-(PhF_2Si)(Ph)C=C(Me)$(SiMe_3)$ and (*Z*)-(PhF_2Si)(Me)C=C(Ph)$(SiMe_3)$ in a 85:15 ratio.

$R^1C{\equiv}CR^2 + Me_3SiSiF_2Ph \xrightarrow[\text{toluene}]{[Pd]/L\ (1 \text{ or } 2 \text{ mol \%})} (L = PMe_2Ph \text{ or } PMe_3)$

1a: $R^1, R^2 = Ph$
1b: $R^1, R^2 = Et$
1c: $R^1 = Ph, R^2 = Me$
1d: $R^1 = Ph, R^2 = H$
1e: $R^1 = n\text{-Hex}, R^2 = H$

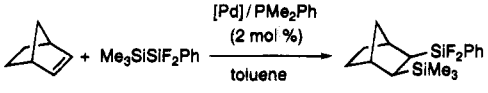
$PhF_2Si(R^1)C{=}C(R^2)SiMe_3$ + $PhF_2Si(R^1)C{=}C(R^2)SiMe_3$ (1)

(*Z*)-**2a–2e** (*E*)-**2a–2e**

with Me_3SiSiF_2Ph[7a] (1 equiv) readily proceeded at room temperature in the presence of 1 mol % of a palladium catalyst generated in situ by mixing $[Pd(\eta^3\text{-allyl})Cl]_2$ and a tertiary phosphine ligand (PMe_2Ph or PMe_3; 2.2 equiv/Pd), giving the bis-silylation products in around 95% yields (entries 1, 2, and 6 in Table 1). Internal acetylenes bearing alkyl substituent(s) (**1b,c**) were bis-silylated in good to excellent yields (entries 3 and 4). The catalytic bis-silylation was also successful for simple olefins (1-octene and styrene) as well as a strained olefin (norbornene) (eqs 2 and 3).[8,9]

$R{=}CH_2 + Me_3SiSiF_2Ph \xrightarrow[\text{toluene}]{[Pd]/PMe_2Ph\ (2 \text{ mol \%})} PhF_2Si(R)CH_2SiMe_3 + Me_3Si(R)CH_2SiF_2Ph$ (2)

R = *n*-Hex: at 100 °C, for 43 h; 64% (63 : 37)
R = Ph: at 80 °C, for 15 h; 67% (28 : 72)

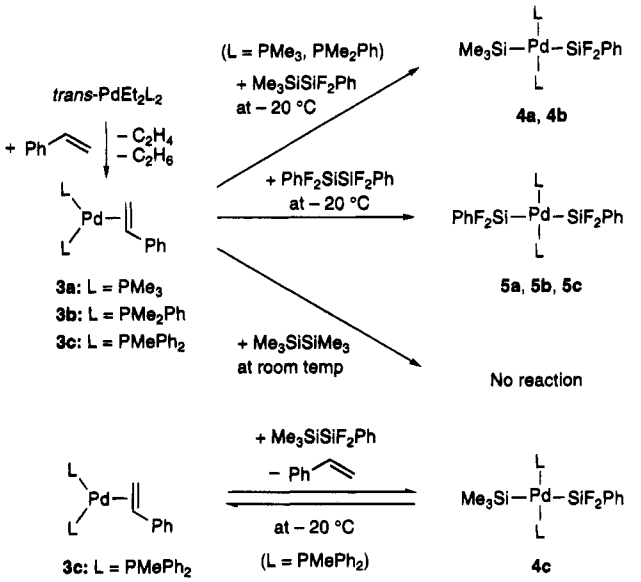


(3)

at 60 °C, for 7 h; 84%

The combination of Me_3SiSiF_2Ph and a basic tertiary phosphine ligand (PMe_2Ph or PMe_3) is essential for the high catalytic activity. For example, no bis-silylation of diphenylacetylene took place even at 60 °C when $Me_3SiSiMe_3$ or PhF_2SiSiF_2Ph[7b] was used in place of Me_3SiSiF_2Ph. Palladium catalysts coordinated with less basic phosphine ligands, such as $PMePh_2$ and PPh_3, exhibited much lower activity than the present catalysts.[10]

Scheme 1



[a] All reactions were performed in toluene-d_8.

Studies on the Catalytic Processes. The first step of the catalytic bis-silylation must be oxidative addition of disilane to a palladium(0) species, giving a bis(silyl)palladium complex.[11,12] This step was examined using three types of disilanes ($Me_3SiSiMe_3$, Me_3SiSiF_2Ph, and PhF_2SiSiF_2Ph) and palladium(0) styrene complexes bearing three kinds of tertiary phosphine ligands (Pd(styrene)L_2; L = PMe_3 (**3a**), PMe_2Ph (**3b**), $PMePh_2$ (**3c**))[13] (Scheme 1). Complexes **3a–c**, generated in situ from the corresponding *trans*-$PdEt_2L_2$ complexes and styrene (3 equiv) in toluene-d_8, were treated with the unsymmetrical disilane Me_3SiSiF_2Ph (3 equiv), and the reactions were followed by ^{31}P NMR spectroscopy. The reactions of **3a,b** instantly proceeded at −20 °C to give the unsymmetrical bis(silyl)palladium complexes *trans*-$Pd(SiMe_3)(SiF_2Ph)L_2$ (L = PMe_3 (**4a**), PMe_2Ph (**4b**)) in quantitative yields.[14] The reaction of **3c**, bearing PMe-

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(8) The reactions in eqs 2 and 3 were carried out using olefin and disilane in a 5:1 (for norbornene) or 20:1 ratio (for styrene and 1-octene). The yields of bis-silylation products are based on the amount of disilane used.

(9) Tanaka and his co-workers recently reported a platinum-catalyzed bis-silylation of norbornene with $FMe_2SiSiMe_2F$, giving 2-*exo*,3-*exo*-bis(fluorodimethylsilyl)norbornane in 26% yield.[3c]

(10) Reactions of diphenylacetylene with Me_3SiSiF_2Ph at room temperature in toluene in the presence of 2 mol % of palladium catalysts bearing $PMePh_2$ and PPh_3 ligands required 21 and 35 h, respectively, for their completion. Palladium complexes with P(*o*-tolyl)$_3$, dppe, dppp, and dppf ligands showed no catalytic activity under similar reaction conditions.

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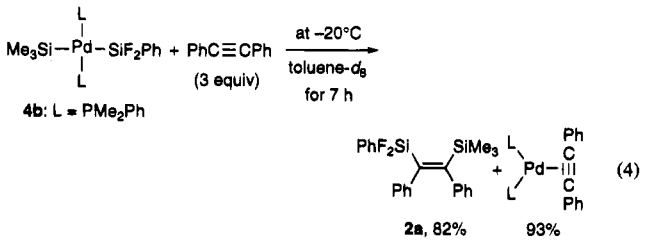
(14) Bis(silyl)palladium complexes **4a,b** and **5a–c** were isolated as white (**4a,b** and **5c**) or yellow solids (**5a,b**) and characterized by NMR spectroscopy and/or elemental analysis. Complex **4c** could not be isolated, owing to its low content in the reaction solution, while its formation was confirmed by ^1H, ^{19}F, and ^{31}P NMR spectroscopy (see Experimental Section).

Ph_2 ligands, with Me_3SiSiF_2Ph also took place instantly at −20 °C, but an equilibrium mixture of **3c** and *trans*-$Pd(SiMe_3)(SiF_2Ph)(PMePh_2)_2$ (**4c**) was obtained ([**4c**][styrene]/[**3c**][Me_3SiSiF_2Ph] = 0.87 ± 0.06). The palladium(0) complexes **3a**−**c** rapidly reacted also with PhF_2SiSiF_2Ph (3 equiv) in toluene-d_8 at −20 °C. In these cases, quantitative yields of *trans*-$Pd(SiF_2Ph)_2L_2$ (L = PMe_3 (**5a**), PMe_2Ph (**5b**), $PMePh_2$ (**5c**)) were formed independent of the tertiary phosphine ligands. On the other hand, $Me_3SiSiMe_3$ was totally inactive toward the palladium(0) complexes in toluene-d_8 at room temperature.

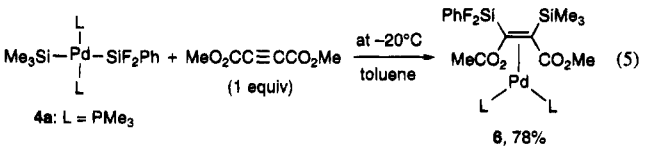
The unsymmetrical bis(silyl) complex **4b** reacted with diphenylacetylene in toluene-d_8 even at low temperature (−20 °C) to give the bis-silylation product (*Z*)-**2a** in 82% yield together with $Pd(PhC{\equiv}CPh)(PMe_2Ph)_2$ (eq 4). In



(4)

contrast, the symmetrical complex **5b** was totally inactive toward bis-silylation of diphenylacetylene; decomposition of **5b** giving a complicated mixture of unidentified palladium and silicon species proceeded in toluene-d_8 in the presence of 3 equiv of diphenylacetylene at room temperature.

The high reactivity of an unsymmetrical bis(silyl) complex toward bis-silylation was also observed in the reaction of **4a** with dimethyl acetylenedicarboxylate (eq 5). The reaction was completed within a few minutes



(5)

at −20 °C to give a novel palladium(0) complex coordinated with a bis-silylated olefin (**6**). The X-ray structure of **6** clearly showed the bis-silylation process via cis 1,2-addition (Figure 1).

Conclusion. It has been demonstrated that the stability and reactivity of bis(silyl)palladium intermediates are strongly affected by the starting disilanes and the tertiary phosphine ligands. $Me_3SiSiMe_3$ does not form bis(silyl) complexes. PhF_2SiSiF_2Ph undergoes rapid oxidative addition toward palladium(0) species, but the resulting *trans*-$Pd(SiF_2Ph)_2L_2$ complexes are inactive toward bis-silylation, probably because of the strong Pd−SiF_2Ph bonds. Me_3SiSiF_2Ph readily forms *trans*-$Pd(SiMe_3)(SiF_2Ph)L_2$ complexes when the basic ligands PMe_3 and PMe_2Ph are used. The unsymmetrical bis(silyl) complexes bearing a Pd−$SiMe_3$ bond are capable of bis-silylating a variety of acetylenes and olefins.

Experimental Section

General Procedures. All manipulations were carried out under a nitrogen atmosphere using conventional Schlenk techniques. Nitrogen gas was dried by passage through P_2O_5 (Merck, SICAPENT). NMR spectra were recorded on a JEOL JNM-EX270 spectrometer (^1H, 270.05 MHz; ^{31}P NMR, 109.25 MHz; ^{19}F NMR, 254.05 MHz; ^{13}C NMR, 67.80 MHz). Chemical shifts are reported in δ (ppm) referred to an internal $SiMe_4$ standard for ^1H NMR, to an external 85% H_3PO_4 standard for ^{31}P NMR, to an external CF_3COOH standard (100%) for ^{19}F NMR, and to the $CDCl_3$ signal (δ 77.23) for ^{13}C NMR. Elemental analyses were performed by the Hokkaido University Analytical Center. GLC analysis was carried out on a Shimadzu GC-3BT instrument, equipped with a TCD detector and a 1-m glass column packed with 5% silicone OV-1.

Me_3SiSiF_2Ph,[7a] PhF_2SiSiF_2Ph,[7b] and $[Pd(\eta^3\text{-allyl})Cl]_2$[15] were prepared according to literature methods. $Me_3SiSiMe_3$, acetylenes, and olefins were obtained from commercial sources and used without further purification. Diethylpalladium complexes *trans*-$PdEt_2L_2$ (L = PMe_3,[13c] PMe_2Ph,[13a] $PMePh_2$[13b]) were prepared as described previously. Toluene, THF, Et_2O, hexane, and pentane were dried over sodium benzophenone ketyl, distilled, and stored under a nitrogen atmosphere. Dichloromethane was dried over CaH_2, distilled, and stored under a nitrogen atmosphere.

Catalytic Bis-Silylation of Acetylenes. A typical procedure (entry 1 in Table 1) is as follows. Diphenylacetylene (49.9 mg, 0.280 mmol) and $[Pd(\eta^3\text{-allyl})Cl]_2$ (0.52 mg, 0.0014 mmol) were placed in a test tube equipped with a rubber septum cap, and the system was replaced with nitrogen gas. Toluene (0.6 mL), a toluene solution of PMe_2Ph (0.10 M, 62.5 μL, 0.00625 mmol), and Me_3SiSiF_2Ph (60.6 mg, 0.280 mmol) were successively added, and the resulting homogeneous solution was stirred at room temperature for 1.4 h. GLC analysis of the solution revealed the formation of (*Z*)-1-(difluorophenylsilyl)-1,2-diphenyl-2-(trimethylsilyl)ethene (**2a**) as the sole reaction product at 100% conversion of disilane and diphenylacetylene. Bulb-to-bulb distillation of the reaction solution (100−120 °C/0.09 mmHg) gave analytically pure (*Z*)-**2a** in 95% yield (104.6 mg).

(*Z*)-1-(Difluorophenylsilyl)-1,2-diphenyl-2-(trimethylsilyl)ethene ((*Z*)-2a). ^1H NMR ($CDCl_3$, room temperature

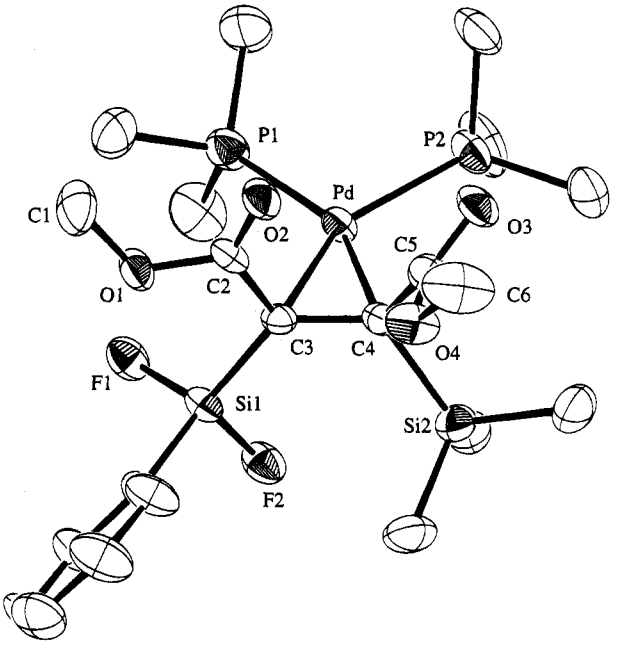


Figure 1. Molecular structure of **6**·THF. The THF molecule is omitted for simplicity. The ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (deg): Pd−C(3) = 2.139(7), Pd−C(4) = 2.087(7), C(3)−C(4) = 1.461(9), Pd−P(1) = 2.331(3), Pd−P(2) = 2.297(2); C(3)−Pd−C(4) = 40.4(3), P(1)−Pd−P(2) = 100.04(9), P(1)−Pd−C(3) = 111.8, P(2)−Pd−C(4) = 107.7(2).

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(RT)): δ 0.16 (t, $^6J_{H-F}$ = 1.0 Hz, 9H, $SiMe_3$), 6.65–6.79 (m, 4H, =CPh), 6.85–7.00 (m, 4H, =CPh), 7.00–7.08 (m, 2H, =CPh), 7.30–7.40 (m, 2H, SiPh), 7.42–7.51 (m, 1H, SiPh), 7.51–7.59 (m, 2H, SiPh). ^{19}F NMR ($CDCl_3$, RT): δ −56.9 (s, $^1J_{F-Si}$ = 300 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, RT): δ 0.7 (t, $^5J_{C-F}$ = 2 Hz, $SiMe_3$), 125.3 (s), 126.1 (s), 127.2 (s), 127.6 (s), 127.8 (s), 128.2 (s), 129.3 (t, $^2J_{C-F}$ = 20 Hz, *ipso-Ph*F_2Si), 129.4 (s), 131.8 (s), 134.6 (s), 140.9 (t, $^3J_{C-F}$ = 2 Hz, *ipso-Ph*(PhF_2Si)C=), 144.7 (s, *ipso-Ph*(Me_3Si)C=), 145.5 (t, $^2J_{C-F}$ = 18 Hz, (PhF_2Si)*C*=), 169.5 (s, (Me_3Si)*C*=). Anal. Calcd for $C_{23}H_{24}F_2Si_2$: C, 70.01; H, 6.13. Found: C, 70.18; H, 5.97.

(*Z*)-1-(Difluorophenylsilyl)-1,2-diethyl-2-(trimethylsilyl)ethene ((*Z*)-2b). ^1H NMR ($CDCl_3$, RT): δ 0.14 (t, $^6J_{H-F}$ = 1.0 Hz, 9H, $SiMe_3$), 1.00 (t, $^3J_{H-H}$ = 7.6 Hz, 3H, CH_3CH_2), 1.03 (t, $^3J_{H-H}$ = 7.6 Hz, 3H, CH_3CH_2), 2.35 (q, $^3J_{H-H}$ = 7.6 Hz, 2H, CH_3CH_2), 2.42 (q, $^3J_{H-H}$ = 7.6 Hz, 2H, CH_3CH_2), 7.33–7.46 (m, 2H, SiPh), 7.46–7.56 (m, 1H, SiPh), 7.57–7.71 (m, 2H, SiPh). ^{19}F NMR ($CDCl_3$, RT): δ −57.9 (s, $^1J_{F-Si}$ = 300 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, RT): δ 0.9 (t, $^5J_{C-F}$ = 3 Hz, $SiMe_3$), 15.1 (s), 24.5 (s), 26.2 (s), 128.3 (s), 130.8 (t, $^2J_{C-F}$ = 21 Hz, *ipso-Ph*F_2Si), 131.7 (s), 134.5 (s), 141.4 (t, $^2J_{C-F}$ = 16 Hz, (PhF_2Si)*C*=), 166.7 (s, (Me_3Si)*C*=). Anal. Calcd for $C_{15}H_{24}F_2Si_2$: C, 60.35; H, 8.10. Found: C, 60.45; H, 7.91.

(*Z*)-1-(Difluorophenylsilyl)-2-methyl-1-phenyl-2-(trimethylsilyl)ethene ((*Z*)-2c). ^1H NMR ($CDCl_3$, RT): δ 0.24 (s, 9H, $SiMe_3$), 1.74 (s, 3H, =CMe), 6.91–7.00 (m, 2H, =CPh), 7.17–7.22 (m, 1H, =CPh), 7.22–7.28 (m, 2H, =CPh), 7.32–7.38 (m, 2H, SiPh), 7.40–7.48 (m, 1H, SiPh), 7.48–7.55 (m, 2H, SiPh). ^{19}F NMR ($CDCl_3$, RT): δ −57.1 (s, $^1J_{F-Si}$ = 298 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, RT): δ 0.3 (t, $^5J_{C-F}$ = 2 Hz, $SiMe_3$), 22.9 (s), 126.6 (s), 128.1 (s), 128.6 (s), 129.0 (s), 129.8 (t, $^2J_{C-F}$ = 21 Hz, *ipso-Ph*F_2Si), 131.7 (s), 134.5 (s), 141.6 (t, $^3J_{C-F}$ = 2 Hz, *ipso-Ph*(PhF_2Si)C=), 144.0 (t, $^2J_{C-F}$ = 18 Hz, (PhF_2Si)*C*=), 163.5 (s, (Me_3Si)*C*=).

(*Z*)-1-(Difluorophenylsilyl)-1-methyl-2-phenyl-2-(trimethylsilyl)ethene ((*Z*)-2c'). ^1H NMR ($CDCl_3$, RT): δ 0.02 (s, 9H, $SiMe_3$), 1.66 (s, 3H, =CMe), 6.81–6.89 (m, 2H, =CPh), 7.17–7.22 (m, 1H, =CPh), 7.22–7.28 (m, 2H, =CPh), 7.32–7.38 (m, 2H, SiPh), 7.40–7.48 (m, 1H, SiPh), 7.69–7.76 (m, 2H, SiPh). ^{19}F NMR ($CDCl_3$, RT): δ −59.2 (s, $^1J_{F-Si}$ = 298 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, RT): δ 0.5 (t, $^5J_{C-F}$ = 2 Hz, $SiMe_3$), 20.3 (s), 125.7 (s), 126.3 (s), 128.6 (s), 129.0 (s), 129.7 (t, $^2J_{C-F}$ = 21 Hz, *ipso-Ph*F_2Si), 132.1 (s), 134.4 (s), 137.5 (t, $^2J_{C-F}$ = 18 Hz, (PhF_2Si)*C*=), 145.4 (s, *ipso-Ph*(Me_3Si)*C*=), 168.1 (s, (Me_3Si)*C*=). Anal. Calcd for a 6.1:1 mixture of (*Z*)-**2c** and (*Z*)-**2c'**, $C_{18}H_{22}F_2Si_2$: C, 65.01; H, 6.67. Found: C, 64.95; H, 6.80.

(*Z*)-1-(Difluorophenylsilyl)-1-phenyl-2-(trimethylsilyl)ethene ((*Z*)-2d). ^1H NMR ($CDCl_3$, RT): δ 0.20 (t, $^6J_{H-F}$ = 1.0 Hz, 9H, $SiMe_3$), 7.13 (t, $^4J_{H-F}$ = 1.8 Hz, 1H, =CH), 7.16–7.30 (m, 5H, =CPh), 7.31–7.41 (m, 2H, SiPh), 7.42–7.52 (m, 1H, SiPh), 7.56–7.63 (m, 2H, SiPh). ^{19}F NMR ($CDCl_3$, RT): δ −57.4 (s, $^1J_{F-Si}$ = 298 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, RT): δ 0.2 (t, J = 3 Hz), 127.1 (s), 127.6 (s), 128.4 (s), 128.7 (s), 129.4 (t, J = 20 Hz, *ipso-Ph*F_2Si), 132.1 (s), 134.4 (s), 144.7 (t, $^3J_{C-F}$ = 1 Hz, *ipso-Ph*(PhF_2Si)C=), 149.8 (t, $^2J_{C-F}$ = 18 Hz, (PhF_2Si)*C*=), 158.6 (s, (Me_3Si)*C*=).

(*E*)-1-(Difluorophenylsilyl)-1-phenyl-2-(trimethylsilyl)ethene ((*E*)-2d). ^1H NMR ($CDCl_3$, RT): δ −0.12 (s, 9H, $SiMe_3$), 6.89 (t, $^4J_{H-F}$ = 0.9 Hz, 1H, =CH), 7.16–7.30 (m, 5H, =CPh), 7.31–7.41 (m, 2H, SiPh), 7.42–7.52 (m, 1H, SiPh), 7.56–7.63 (m, 2H, SiPh). ^{19}F NMR ($CDCl_3$, RT): δ −66.1 (s, $^1J_{F-Si}$ = 299 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, RT): δ 0.0 (s, $SiMe_3$), 127.1 (s), 127.4 (s), 128.0 (s), 128.4 (s), 129.4 (t, J = 20 Hz, *ipso-Ph*F_2Si), 132.0 (s), 134.6 (s), 141.3 (t, $^3J_{C-F}$ = 1 Hz, *ipso-Ph*(PhF_2Si)C=), 153.6 (t, $^2J_{C-F}$ = 18 Hz, (PhF_2Si)*C*=), 155.2 (s, (Me_3Si)*C*=). Anal. Calcd for an 8.2:1 mixture of (*Z*)-**2d** and (*E*)-**2d**, $C_{17}H_{20}F_2Si_2$: C, 64.11; H, 6.33. Found: C, 64.29; H, 6.12.

(*Z*)-2-(Difluorophenylsilyl)-1-(trimethylsilyl)-1-octene ((*Z*)-2e). ^1H NMR ($CDCl_3$, RT): δ 0.09 (t, $^6J_{H-F}$ = 0.8 Hz, 9H, $SiMe_3$), 0.85 (t, $^3J_{H-H}$ = 6.6 Hz, 3H, Me), 1.14–1.34 (m, 6H, $CH_3(CH_2)_3$), 1.34–1.49 (m, 2H, =CCH_2CH_2), 2.22–2.31 (m, 2H, =CCH_2), 6.75–6.80 (m, 1H, =CH), 7.39–7.47 (m, 2H, SiPh), 7.47–7.57 (m, 1H, SiPh), 7.61–7.71 (m, 2H, SiPh). ^{19}F NMR ($CDCl_3$, RT): δ −59.9 (s, $^1J_{F-Si}$ = 300 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, RT): δ 0.1 (s, $SiMe_3$), 14.2 (s), 22.8 (s), 29.1 (s), 29.8 (s), 31.8 (s), 41.3 (s), 128.4 (s), 129.8 (t, $^2J_{C-F}$ = 20 Hz, *ipso-Ph*F_2Si), 132.0 (s), 134.4 (s), 149.8 (t, $^2J_{C-F}$ = 17 Hz, (PhF_2Si)*C*=), 154.0 (s, (Me_3Si)*C*=).

(*E*)-2-(Difluorophenylsilyl)-1-(trimethylsilyl)-1-octene ((*E*)-2e). ^1H NMR ($CDCl_3$, RT): δ 0.16 (s, 9H, $SiMe_3$), 0.86 (t, $^3J_{H-H}$ = 6.6 Hz, 3H, Me), 1.14–1.34 (m, 6H, $CH_3(CH_2)_3$), 1.34–1.49 (m, 2H, =CCH_2CH_2), 2.32–2.41 (m, 2H, =CCH_2), 6.49–6.51 (m, 1H, =CH), 7.39–7.47 (m, 2H, SiPh), 7.47–7.57 (m, 1H, SiPh), 7.61–7.71 (m, 2H, SiPh). ^{19}F NMR ($CDCl_3$, RT): δ −65.1 (s, $^1J_{F-Si}$ = 302 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, RT): δ 0.3 (s, $SiMe_3$), 14.2 (s), 22.8 (s), 29.1 (s), 29.8 (s), 30.5 (s), 35.7 (s), 128.4 (s), 129.2 (t, $^2J_{C-F}$ = 20 Hz, *ipso-Ph*F_2Si), 131.9 (s), 134.5 (s), 152.1 (s, (Me_3Si)*C*=), 153.6 (t, $^2J_{C-F}$ = 17 Hz, (PhF_2Si)*C*=). Anal. Calcd for a 6.1:1 mixture of (*Z*)-**2e** and (*E*)-**2e**, $C_{17}H_{28}F_2Si_2$: C, 62.52; H, 8.64. Found: C, 62.44; H, 8.52.

Catalytic Bis-Silylation of Norbornene. Norbornene (134 mg, 1.42 mmol) and [Pd(η^3-allyl)Cl]$_2$ (1.04 mg, 0.0028 mmol) were placed in a test tube equipped with a rubber septum cap, and the system was replaced with nitrogen gas. Toluene (1.5 mL), a toluene solution of PMe_2Ph (0.10 M, 125 μL, 0.0125 mmol), and Me_3SiSiF_2Ph (60.6 mg, 0.280 mmol) were successively added, and the resulting homogeneous solution was stirred at 60 °C for 7 h. GLC analysis of the solution revealed the formation of *exo,exo*-2-(difluorophenylsilyl)-3-(trimethylsilyl)norbornane as the sole reaction product at 100% conversion of disilane. Bulb-to-bulb distillation of the reaction solution (80–95 °C/0.09 mmHg) gave the analytically pure product in 84% yield (72.8 mg).

***exo,exo*-2-(Difluorophenylsilyl)-3-(trimethylsilyl)norbornane.** ^1H NMR ($CDCl_3$, RT): δ 0.06 (s, 9H, $SiMe_3$), 1.04 (dd, J = 1.3 and 11.2 Hz, 1H), 1.21 (dt, J = 1.7 and 9.6 Hz, 1H), 1.26–1.53 (m, 4H), 1.62–1.70 (m, 2H), 2.36 (s, 1H), 2.46 (s, 1H), 7.39–7.48 (m, 2H, SiPh), 7.48–7.57 (m, 1H, SiPh), 7.63–7.72 (m, 2H, SiPh). ^{19}F NMR ($CDCl_3$, RT): δ −55.1 (d, J = 22 Hz, $^1J_{F-Si}$ = 313 Hz), −62.4 (dd, J = 15 and 22 Hz, $^1J_{F-Si}$ = 311 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, RT): δ −1.0 (t, $^5J_{C-F}$ = 3 Hz, $SiMe_3$), 30.6 (t, $^2J_{C-F}$ = 15 Hz), 33.3 (s), 34.1 (s), 34.4 (s), 38.1 (s), 38.2 (s), 39.4 (s), 128.4 (s), 130.4 (t, $^2J_{C-F}$ = 20 Hz, *ipso-Ph*F_2Si), 131.7 (s), 134.1 (s). Anal. Calcd for $C_{16}H_{24}F_2Si_2$: C, 61.89; H, 7.79. Found: C, 62.01; H, 7.58.

The catalytic bis-silylation of 1-octene and styrene was carried out by a similar procedure using olefin and disilane in a 20:1 molar ratio. Reaction conditions: 100 °C, 43 h (1-octene); 80 °C, 15 h (styrene).

2-(Difluorophenylsilyl)-1-(trimethylsilyl)octane (Major Isomer). ^1H NMR ($CDCl_3$, RT): δ 0.01 (s, 9H, $SiMe_3$), 0.56 (dd, J = 14.8 and 9.2 Hz, 1H, (Me_3Si)C(H_a)(H_b)), 0.82 (dd, J = 14.8 and 4.6 Hz, 1H, (Me_3Si)C(H_a)(H_b)), 0.86 (t, J = 6.9 Hz, 3H, Me), 1.18–1.58 (m, 11H, CH_2 and CH), 7.40–7.47 (m, 2H, SiPh), 7.47–7.57 (m, 1H, SiPh), 7.62–7.69 (m, 2H, SiPh). ^{19}F NMR ($CDCl_3$, RT): δ −66.1 (d, $^2J_{F-F}$ = 22 Hz), −67.0 (d, $^2J_{F-F}$ = 22 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, RT): δ −0.8 (s, $SiMe_3$), 14.3 (s), 14.5 (s, (Me_3Si)CH_2), 18.9 (t, $^2J_{C-F}$ = 13 Hz, (PhF_2Si)*C*H), 22.8 (s), 28.9 (s), 29.8 (s), 31.6 (s), 31.8 (s), 128.4 (s), 129.0 (t, $^2J_{C-F}$ = 20 Hz, *ipso-Ph*F_2Si), 131.8 (s), 134.2 (s).

1-(Difluorophenylsilyl)-2-(trimethylsilyl)octane (Minor Isomer). ^1H NMR ($CDCl_3$, RT): δ −0.01 (s, 9H, $SiMe_3$), 0.86 (t, J = 6.9 Hz, 3H, Me), 0.92–1.02 (m, 1H, (PhF_2Si)C-(H_a)(H_b)), 1.03–1.14 (m, 1H, (PhF_2Si)C(H_a)(H_b)), 1.18–1.58 (m, 11H, CH_2 and CH), 7.40–7.47 (m, 2H, SiPh), 7.47–7.57 (m, 1H, SiPh), 7.62–7.69 (m, 2H, SiPh). ^{19}F NMR ($CDCl_3$, RT): δ −61.5 (m, $^2J_{F-F}$ = 22 Hz), −61.6 (m, $^2J_{F-F}$ = 22 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, RT): δ −2.5 (s, $SiMe_3$), 12.2 (t, $^2J_{C-F}$ = 15 Hz, (PhF_2Si)CH_2), 14.3 (s), 18.7 (s, (Me_3Si)*C*H), 22.9 (s), 29.0 (s), 29.8 (s), 31.9 (s), 32.9 (s), 128.5 (s), 130.0 (t, $^2J_{C-F}$ = 20 Hz, *ipso-Ph*F_2Si), 131.9 (s), 133.9 (s). Anal. Calcd for a 1.7:1

mixture of the two regioisomers, $C_{17}H_{30}F_2Si_2$: C, 62.14; H, 9.20. Found: 62.23; H, 9.15.

1-(Difluorophenylsilyl)-2-phenyl-2-(trimethylsilyl)-ethane (Major Isomer). ^{1}H NMR ($CDCl_3$, RT): δ −0.06 (s, 9H, $SiMe_3$), 1.42 (ddt, $^1J_{H-H}$ = 16.2 Hz, $^3J_{H-H}$ = $^3J_{F-H}$ = 4.3 Hz, 1H, $(PhF_2Si)C(H_a)(H_b)$), 1.55 (ddt, $^1J_{H-H}$ = 16.2 Hz, $^3J_{H-H}$ = 11.9 Hz, $^3J_{F-H}$ = 4.3 Hz, 1H, $(PhF_2Si)C(H_a)(H_b)$), 2.22 (dd, $^3J_{H-H}$ = 11.9 and 4.3 Hz, 1H, $(Me_3Si)CH$), 6.92−6.98 (m, 2H), 7.03−7.24 (m, 4H), 7.27−7.55 (m, 4H). ^{19}F NMR ($CDCl_3$, RT): δ −61.0 (dt, $^2J_{F-F}$ = 22 Hz, $^3J_{F-H}$ = 4 Hz, $^1J_{F-Si}$ = 305 Hz), −61.7 (dt, $^2J_{F-F}$ = 22 Hz, $^3J_{F-H}$ = 4 Hz, $^1J_{F-Si}$ = 303 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, RT): δ −3.2 (s, $SiMe_3$), 12.9 (t, $^2J_{C-F}$ = 15 Hz, $(PhF_2Si)CH_2$), 29.1 (s, $(Me_3Si)CH$), 125.1 (s), 127.7 (s), 128.2 (s), 128.3 (s, SiPh), 129.4 (t, $^2J_{C-F}$ = 18 Hz, *ipso-Ph*F_2-Si), 131.7 (s, SiPh), 133.7 (s, SiPh), 143.6 (s).

1-(Difluorophenylsilyl)-1-phenyl-2-(trimethylsilyl)-ethane (Minor Isomer). ^{1}H NMR ($CDCl_3$, RT): δ −0.18 (s, 9H, $SiMe_3$), 1.11 (m, $^1J_{H-H}$ = 14.8 Hz, $^3J_{H-H}$ = 4.6 Hz, 1H, $(Me_3Si)C(H_a)(H_b)$), 1.20 (m, $^1J_{H-H}$ = 14.8 Hz, $^3J_{H-H}$ = 11.6 Hz, 1H, $(Me_3Si)C(H_a)(H_b)$), 2.59 (dddd, $^3J_{H-H}$ = 11.6 and 4.6 Hz, $^3J_{H-F}$ = 4.6 and 2.0 Hz, 1H, $(PhF_2Si)CH$), 6.92−6.98 (m, 2H), 7.03−7.24 (m, 4H), 7.27−7.55 (m, 4H). ^{19}F NMR ($CDCl_3$, RT): δ −69.4 (dd, $^2J_{F-F}$ = 22 Hz, $^3J_{F-H}$ = 5 Hz, $^1J_{F-Si}$ = 311 Hz), −69.6 (dd, $^2J_{F-F}$ = 22 Hz, $^3J_{F-H}$ = 2 Hz, $^1J_{F-Si}$ = 311 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, RT): −1.0 (s, $SiMe_3$), 15.2 (s, (Me_3Si)-CH_2), 28.6 (t, $^2J_{C-F}$ = 15 Hz, $(PhF_2Si)CH$), 126.2 (s), 128.3 (s, SiPh), 128.7 (s), 128.8 (t, $^2J_{C-F}$ = 18 Hz, *ipso-Ph*F_2Si), 128.9 (s), 131.9 (s, SiPh), 134.5 (s, SiPh), 139.9 (s). Anal. Calcd for a 2.8:1 mixture of the two regioisomers, $C_{17}H_{22}F_2Si_2$: C, 63.70; H, 6.92. Found: C, 64.00; H, 6.92.

Oxidative Addition of Disilanes to Palladium(0) Styrene Complexes. NMR Sample Tube Reaction. The diethylpalladium complex *trans*-$PdEt_2L_2$ (0.015 mmol) was placed in an NMR sample tube equipped with a rubber septum cap, and the system was replaced with nitrogen gas. Styrene (0.045 mmol) and toluene-d_8 (500 μL) were added at −20 °C, and the mixture was allowed to stand for 2−4 h at 55 °C (for L = PMe_3), at 40 °C (for L = PMe_2Ph), or at room temperature (for L = $PMePh_2$). The resulting yellow homogeneous solution was cooled to −20 °C, and disilane (PhF_2SiSiF_2Ph, Me_3SiSiF_2-Ph, or $Me_3SiSiMe_3$; 0.045 mmol) was added by means of a syringe. The sample solution thus prepared was examined by ^{1}H, ^{19}F, and ^{31}P{^{1}H} NMR spectroscopy.

In the presence of $Me_3SiSiMe_3$, the Pd(styrene)L_2 complex was totally inactive in the reaction system at room temperature. When PhF_2SiSiF_2Ph was employed, *trans*-$Pd(SiF_2Ph)_2L_2$ species (L = PMe_3 (**5a**), PMe_2Ph (**5b**), $PMePh_2$ (**5c**)) were formed in quantitative yields at −20 °C. In the presence of Me_3SiSiF_2Ph, the PMe_3- and PMe_2Ph-coordinated palladium(0) complexes gave the corresponding *trans*-$Pd(SiMe_3)(SiF_2Ph)L_2$ (**4a**,**b**, respectively) in quantitative yields at −20 °C. On the other hand, the reaction of the $PMePh_2$-coordinated complex with Me_3SiSiF_2Ph at −20 °C gave an equilibrium mixture of Pd(styrene)$(PMePh_2)_2$ (**3c**; ^{31}P{^{1}H} NMR δ 5.0 (br)) and *trans*-$Pd(SiMe_3)(SiF_2Ph)(PMePh_2)_2$ (**4c**; ^{31}P{^{1}H} NMR δ −4.9 (t, $^3J_{P-F}$ = 31 Hz)). The equilibrium constant ([**4c**][styrene]/[**3c**][Me_3-$SiSiF_2Ph$]) measured at four different concentrations of disilane in the range 0.027−0.254 M was 0.87 ± 0.06.

Isolation and Characterization of Bis(silyl)palladium(II) Complexes. (a) Unsymmetrical Bis(silyl) Complexes. In a Schlenk tube containing *trans*-$PdEt_2(PMe_3)_2$ (126 mg, 0.397 mmol) were placed styrene (136 μL, 1.19 mmol) and hexane (8 mL) at −20 °C under a nitrogen atmosphere. The heterogeneous mixture was stirred at 55 °C for 3 h to give a yellow solution containing a small amount of black precipitate. The precipitate was removed by filtration through a short Al_2O_3 column. The resulting clear solution was cooled to −20 °C, and a hexane solution (2 mL) of Me_3SiSiF_2Ph (91.8 mg, 0.424 mmol) was added with stirring. A white solid was instantly formed. The mixture was stirred for an additional 30 min at the same temperature and then allowed to stand at −70 °C for 1 day. The white precipitate of *trans*-$Pd(SiMe_3)(SiF_2$-$Ph)(PMe_3)_2$ (**4a**) thus formed was filtered, washed with hexane (2 mL × 2) at −70 °C, and dried under vacuum at −20 °C (176.9 mg, 94% yield).

Similarly prepared was *trans*-$Pd(SiMe_3)(SiF_2Ph)(PMe_2Ph)_2$ (**4b**) (93% yield, white solid). Since complexes **4a**,**b** readily decompose at room temperature in the solid state, their elemental analyses were not feasible.

***trans*-Pd(SiMe$_3$)(SiF$_2$Ph)(PMe$_3$)$_2$ (4a).** ^{1}H NMR (CD_2Cl_2, −20 °C): δ 0.12 (s, 9H, SiMe), 1.30 (virtual triplet, J = 2.6 Hz, 18H, PMe), 7.26−7.37 (m, 3H, SiPh), 7.51−7.63 (m, 2H, SiPh). ^{19}F NMR (CD_2Cl_2, −20 °C): δ −31.4 (t, $^3J_{P-F}$ = 33 Hz, $^1J_{F-Si}$ = 360 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2, −20 °C): δ −30.5 (t, $^3J_{P-F}$ = 33 Hz).

***trans*-Pd(SiMe$_3$)(SiF$_2$Ph)(PMe$_2$Ph)$_2$ (4b).** ^{1}H NMR (CD_2Cl_2, −20 °C): δ 0.18 (s, 9H, SiMe), 1.11 (virtual triplet, J = 3.0 Hz, 12H, PMe), 7.19−7.29 (m, 4H, Ph), 7.29−7.39 (m, 9H, Ph), 7.57−7.68 (m, 2H, Ph). ^{19}F NMR (CD_2Cl_2, −20 °C): δ −31.1 (t, $^3J_{P-F}$ = 31 Hz, $^1J_{F-Si}$ = 362 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2, −20 °C): δ −19.5 (t, $^3J_{P-F}$ = 31 Hz).

The $PMePh_2$-coordinated complex **4c** could not be isolated because of its low content in the reaction solution (vide supra). Identification of **4c** was based on the following NMR data.

***trans*-Pd(SiMe$_3$)(SiF$_2$Ph)(PMePh$_2$)$_2$ (4c).** ^{1}H NMR (toluene-d_8, −20 °C): δ 0.63 (s, 9H, SiMe), 1.34 (br, 6H, PMe), 6.82−7.20 (m, 23H, Ph), 7.72−7.83 (m, 2H, Ph). ^{19}F NMR (toluene-d_8, −20 °C): δ −30.1 (t, $^3J_{F-P}$ = 31 Hz, $^1J_{F-Si}$ = 370 Hz). ^{31}P{^{1}H} NMR (toluene-d_8, −20 °C) δ −4.9 (t, $^3J_{P-F}$ = 31 Hz).

(b) Symmetrical Bis(silyl) Complexes. In a Schlenk tube containing *trans*-$PdEt_2(PMe_2Ph)_2$ (302 mg, 0.686 mmol) were placed styrene (235 μL, 2.05 mmol) and toluene (10 mL) at −20 °C under a nitrogen atmosphere. The mixture was stirred at 30 °C for 12 h. The resulting yellow solution was cooled to −20 °C, and a toluene solution (2.5 mL) of PhF_2SiSiF_2-Ph (386 mg, 1.34 mmol) was added. The homogeneous solution was stirred at room temperature for 1 h and then concentrated to dryness by pumping. The resulting solid was dissolved in CH_2Cl_2 (1.5 mL) at room temperature, layered with Et_2O (7 mL), and allowed to stand at −70 °C to give pale yellow needles of *trans*-$Pd(SiF_2Ph)_2(PMe_2Ph)_2$ (**5b**) (397 mg, 86% yield).

Similarly prepared were *trans*-$Pd(SiF_2Ph)_2(PMe_3)_2$ (**5a**) (90% yield, pale yellow needles) and *trans*-$Pd(SiF_2Ph)_2(PMePh_2)_2$ (**5c**) (78%, white crystals).

***trans*-Pd(SiF$_2$Ph)$_2$(PMe$_3$)$_2$ (5a).** ^{1}H NMR (CD_2Cl_2, −20 °C): δ 1.29 (virtual triplet, J = 3.6 Hz, 18H, PMe), 7.31−7.43 (m, 6H, SiPh), 7.57−7.69 (m, 4H, SiPh). ^{19}F NMR (CD_2Cl_2, −20 °C): δ −28.4 (t, $^3J_{P-F}$ = 33 Hz, $^1J_{F-Si}$ = 357 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2, −20 °C): δ −28.2 (quint, $^3J_{P-F}$ = 33 Hz). Anal. Calcd for $C_{18}H_{28}F_4P_2PdSi_2$: C, 39.67; H, 5.18. Found: C, 39.74; H, 5.26.

***trans*-Pd(SiF$_2$Ph)$_2$(PMe$_2$Ph)$_2$ (5b).** ^{1}H NMR (CD_2Cl_2, −20 °C): δ 1.12 (virtual triplet, J = 3.5 Hz, 12H, PMe), 7.03−7.20 (m, 4H, SiPh), 7.21−7.38 (m, 6H, SiPh), 7.39−7.50 (m, 6H, PPh), 7.62−7.80 (m, 4H, PPh). ^{19}F NMR (CD_2Cl_2, −20 °C): δ −27.6 (t, $^3J_{P-F}$ = 33 Hz, $^1J_{F-Si}$ = 357 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2, −20 °C): δ −17.0 (quint, $^3J_{P-F}$ = 33 Hz). Anal. Calcd for $C_{28}H_{32}F_4P_2PdSi_2$: C, 50.26; H, 4.82. Found: C, 50.14; H, 4.80.

***trans*-Pd(SiF$_2$Ph)$_2$(PMePh$_2$)$_2$ (5c).** ^{1}H NMR (CD_2Cl_2, −20 °C): δ 1.43 (virtual triplet, J = 3.0 Hz, 6H, PMe), 7.06−7.18 (m, 16H, Ph), 7.22−7.42 (m, 10H, Ph), 7.49−7.56 (m, 4H, Ph). ^{19}F NMR (CD_2Cl_2, −20 °C): δ −26.6 (t, $^3J_{P-F}$ = 33 Hz, $^1J_{F-Si}$ = 359 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2, −20 °C): δ −1.9 (quint, $^3J_{P-F}$ = 33 Hz). Because of the thermal instability of **5c**, a satisfactory elemental analysis was not obtained.

Reaction of 4b with Diphenylacetylene. Complex **4b** (9.1 mg, 0.015 mmol) and diphenylacetylene (8.3 mg, 0.047 mmol) were placed in an NMR sample tube equipped with a rubber septum cap, and the system was replaced with nitrogen gas. The sample was cooled to −20 °C, toluene-d_8 (750 μL) and anisole (1.65 μL) as an internal standard were added. The reaction was observed at intervals by ^{1}H, ^{19}F, and ^{31}P{^{1}H} NMR spectroscopy at the same temperature. The signals

Table 2. Crystal Data and Details of the Structure Determination for Complex 6

formula	$C_{21}H_{38}O_4P_2F_2Si_2Pd{\cdot}C_4H_8O$
fw	689.15
habit	prismatic
cryst size, mm	0.15 × 0.2 × 0.3
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
a, Å	15.585(2)
b, Å	12.438(2)
c, Å	17.652(2)
β, deg	93.86(1)
V, Å^3	3413.9(8)
Z	4
d_{calcd}, g cm^{-3}	1.341
μ(Mo Kα), cm^{-1}	7.48
$F(000)$	1432
radiation	Mo Kα (λ = 0.710 69 Å)
monochromator	graphite
data collected	$+h,+k,\pm l$
2θ range, deg	5.0−45.0
scan type	$\omega-2\theta$
$\Delta\omega$, deg	0.94 + 0.35 tan θ
scan speed, deg min^{-1}	16, fixed
temp, K	296
abs cor	empirical
min and max transmissn factors	0.899, 1.000
no. of rflns collected	4913
no. of unique rflns	4714 (R_{int} = 0.027)
no. of obsd rflns	2853 ($I \geq 2.5\sigma(I)$)
no. of variables	309
R	0.044
R_w	0.047
goodness of fit	1.59
max Δ/σ in final cycles	0.01
max and min peak, e Å^{-3}	+0.52, −0.47

Table 3. Positional Parameters and Equivalent Isotropic Thermal Parameters for Complex 6

atom	x	y	z	B_{eq}[a] (Å^2)
Pd	0.14226(4)	0.16667(5)	−0.14508(3)	3.83(1)
P(1)	0.0118(2)	0.2178(2)	−0.2071(1)	5.49(7)
P(2)	0.1982(2)	0.0648(2)	−0.2385(1)	5.07(6)
Si(1)	0.0721(1)	0.2109(2)	0.0230(1)	3.86(6)
Si(2)	0.2575(2)	0.0369(2)	−0.0004(1)	5.02(7)
F(1)	−0.0185(3)	0.2400(4)	−0.0164(2)	5.0(1)
F(2)	0.0660(3)	0.0853(4)	0.0341(2)	5.3(1)
O(1)	0.1025(3)	0.4109(4)	−0.0299(3)	4.8(2)
O(2)	0.2269(4)	0.4001(4)	−0.0856(3)	5.2(2)
O(3)	0.3511(3)	0.2129(5)	−0.1291(3)	5.4(2)
O(4)	0.3553(4)	0.2646(5)	−0.0071(3)	5.8(2)
C(1)	0.0972(6)	0.5244(7)	−0.0488(6)	7.3(3)
C(2)	0.1703(5)	0.3554(7)	−0.0541(4)	3.9(2)
C(3)	0.1616(5)	0.2406(6)	−0.0358(4)	3.3(2)
C(4)	0.2327(4)	0.1697(6)	−0.0524(4)	3.6(2)
C(5)	0.3168(5)	0.2197(7)	−0.0704(5)	4.3(2)
C(6)	0.4382(6)	0.310(1)	−0.0171(6)	9.1(4)
C(7)	0.0734(5)	0.2729(6)	0.1188(4)	4.3(2)
C(8)	0.0037(5)	0.2607(8)	0.1627(5)	5.4(2)
C(9)	0.0025(7)	0.3073(9)	0.2341(5)	6.7(3)
C(10)	0.0702(8)	0.367(1)	0.2612(5)	7.5(3)
C(11)	0.1391(7)	0.380(1)	0.2196(6)	7.9(3)
C(12)	0.1414(6)	0.3325(8)	0.1489(5)	5.9(3)
C(13)	0.1857(6)	−0.0737(7)	−0.0342(5)	5.9(3)
C(14)	0.2560(6)	0.0559(8)	0.1045(5)	6.8(3)
C(15)	0.3699(6)	−0.0028(8)	−0.0165(6)	7.4(3)
C(16)	0.0009(7)	0.230(1)	−0.3105(5)	8.9(3)
C(17)	−0.0298(6)	0.3488(9)	−0.1831(5)	7.8(3)
C(18)	−0.0756(6)	0.130(1)	−0.1972(6)	8.5(4)
C(19)	0.1274(7)	−0.0342(9)	−0.2833(6)	8.6(3)
C(20)	0.2946(6)	−0.0164(8)	−0.2203(5)	7.0(3)
C(21)	0.2311(6)	0.1469(8)	−0.3153(5)	6.9(3)
O(5)	0.141(1)	0.038(2)	0.368(1)	25.8(7)[b]
C(22)	0.202(2)	0.109(2)	0.333(1)	19.9(8)[b]
C(23)	0.226(1)	0.184(2)	0.388(1)	18.8(7)[b]
C(24)	0.180(1)	0.161(2)	0.452(1)	17.1(6)[b]
C(25)	0.143(1)	0.064(2)	0.445(1)	19.6(8)[b]

[a] $B_{eq} = (8\pi^2/3)\sum_i\sum_j[U_{ij}(a_i{*}a_j{*})] = {}^4/_3\sum_i\sum_j[\beta_{ij}(\mathbf{a}_i{\cdot}\mathbf{a}_j)]$. [b] Isotropic thermal parameters.

arising from **4b** ($^{31}P\{^1H\}$ NMR δ −20.2 (t, $^3J_{P-F}$ = 31 Hz); ^{19}F NMR δ −29.2 (t, $^3J_{F-P}$ = 31 Hz, $^1J_{F-Si}$ = 362 Hz)) gradually decreased, to be replaced by the signals due to Pd(PhC≡CPh)(PMe$_2$Ph)$_2$ ($^{31}P\{^1H\}$ NMR δ −10.2 (s)) and (*Z*)-1-(difluorophenylsilyl)-1,2-diphenyl-2-(trimethylsilyl)ethene ((*Z*)-**2a**; ^{19}F NMR δ −56.1 (s, $^1J_{F-Si}$ = 300 Hz)). After 7 h, complex **4b** disappeared. Amounts of the reaction products at this stage ((*Z*)-**2a**, 82% yield; Pd(PhC≡CPh)(PMe$_2$Ph)$_2$, 93% yield) were determined on the basis of the relative peak integration of the following proton signals: δ 0.29 (s, SiMe$_3$ in (*Z*)-**2a**), 1.24 (d, J = 4.0 Hz, PMe$_2$ in the palladium(0) complex), 3.26 (s, OMe in the anisole standard). The formation of (*Z*)-**2a** was also confirmed by GLC analysis.

An authentic sample of Pd(PhC≡CPh)(PMe$_2$Ph)$_2$ was prepared as follows. In a Schlenk tube containing *trans*-PdEt$_2$(PMe$_2$Ph)$_2$ (163 mg, 0.370 mmol) and diphenylacetylene (66.8 mg, 0.375 mmol) was placed toluene (3 mL) at −20 °C under a nitrogen atmosphere. The mixture was stirred for 2.3 h at 40 °C and concentrated to dryness at 0 °C. The resulting yellow, oily material was dissolved in a small amount of toluene, layered with hexane, and allowed to stand at −70 °C to give yellow crystals of Pd(PhC≡CPh)(PMe$_2$Ph)$_2$ (128 mg, 62% yield).

Pd(PhC≡CPh)(PMe$_2$Ph)$_2$. ^1H NMR (CD_2Cl_2, −20 °C): δ 1.40 (d, J = 5.6 Hz, 12H, PMe), 7.04−7.34 (m, 16H), 7.47−7.57 (m, 4H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −20 °C): δ −10.4 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −20 °C): δ 18.1 (t, J = 10 Hz, PMe), 119.7 (AXX′, $^2J_{C-P(1)} + {}^2J_{C-P(2)}$ = 74.7 Hz), 125.5 (s), 128.3 (s), 128.5 (t, J = 4 Hz), 128.8 (s), 129.2 (s), 131.2 (t, J = 7 Hz), 135.5 (t, J = 11 Hz), 141.2 (AXX′, $^3J_{C-P(1)} + {}^3J_{C-P(2)}$ = 26.8 Hz). Anal. Calcd for $C_{30}H_{32}P_2Pd$: C, 64.24; H, 5.75. Found: C, 64.06; H, 5.83.

Reaction of 4a with Dimethyl Acetylenedicarboxylate. The starting **4a** was prepared in situ from *trans*-PdEt$_2$(PMe$_3$)$_2$ and Me$_3$SiSiF$_2$Ph. In a Schlenk tube containing *trans*-PdEt$_2$(PMe$_3$)$_2$ (125 mg, 0.395 mmol) were placed styrene (140 μL, 1.22 mmol) and toluene (7 mL) at −20 °C under a nitrogen atmosphere. The mixture was stirred for 3 h at 55 °C. The resulting yellow solution was cooled to −20 °C, and Me$_3$SiSiF$_2$Ph (90.2 mg, 0.417 mmol) was added. After the solution was stirred for 25 min at −20 °C, dimethyl acetylenedicarboxylate (51.0 μL, 0.415 mmol) was added. The pale yellow color of the solution quickly turned to red and then to orange. The system was stirred for 20 min at −20 °C and then for 30 min at room temperature. Evaporation of the solution gave an oily material, which was dissolved in Et$_2$O, filtered through a short Celite column, layered with hexane, and allowed to stand at −70 °C to give yellow needles of Pd{(*Z*)-(MeO$_2$C)(Me$_3$Si)C=C(SiF$_2$Ph)(CO$_2$Me)}(PMe$_3$)$_2$ (**6**; 217.4 mg, 89%).

Complex 6. ^1H NMR (CD_2Cl_2, −20 °C): δ 0.01 (d, J = 2.6 Hz, 9H, SiMe$_3$), 1.31 (d, J = 6.9 Hz, 9H, PMe$_3$), 1.46 (d, J = 7.6 Hz, 9H, PMe$_3$), 3.38 (s, 3H, CO$_2$Me), 3.53 (s, 3H, CO$_2$Me), 7.32−7.52 (m, 3H, SiF$_2$Ph), 7.68−7.80 (m, 2H, SiF$_2$Ph). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −20 °C): δ −19.8 (dd, J = 16 and 7 Hz), −24.3 (dd, J = 15 and 9 Hz). ^{19}F NMR (CD_2Cl_2, −20 °C): δ −50.4 (d, J = 22 Hz, $^1J_{F-Si}$ = 279 Hz, 1F), −51.3 (d, J = 24 and 7 Hz, $^1J_{F-Si}$ = 279 Hz, 1F). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, RT): δ 2.5 (d, J = 6 Hz), 18.1 (dd, J = 18 and 2 Hz), 19.8 (dd, J = 20 and 4 Hz), 46.0 (dd, J = 18 and 6 Hz), 50.9 (s), 51.8 (s), 69.8 (d, J = 40 Hz), 128.2 (s), 131.1 (s), 133.7 (ddd, J = 26, 22 and 3 Hz), 135.0 (s), 173.0 (dd, J = 10 and 6 Hz), 176.1 (br). Anal. Calcd for $C_{21}H_{38}F_2O_4P_2PdSi_2$: C, 40 88; H, 6.21. Found: C, 40.63; H, 6.24.

X-ray Diffraction Study of 6·THF. Single crystals suitable for an X-ray diffraction study were grown from a THF−pentane solution. This product contained 1 equiv of THF in the crystal, as confirmed by ^1H NMR spectroscopy. A single crystal of dimensions ca. 0.15 × 0.2 × 0.3 mm was sealed in a glass capillary tube. Intensity data were collected on a Rigaku AFC5R four-circle diffractometer. Unit cell dimensions were

obtained from a least-squares treatment of the setting angles of 25 reflections in the range $20.5 < 2\theta < 28.3°$. The cell dimensions suggested a monoclinic cell, and systematic absences in the diffractometer data indicated the space group $P2_1/n$ (No. 14). Diffraction data were collected at 23 °C in the range $5.0 < 2\theta < 45.0°$ using the $\omega-2\theta$ scan technique at a scan rate of 16° min^{-1} in ω. Three standard reflections, monitored after every 150 reflection measurements, showed no significant decay in their intensities. The data were corrected for Lorentz and polarization effects and absorption (empirical, based on azimuthal scans of three reflections). Of the 4714 unique reflections measured, 2853 were classed as observed ($I > 2.5\sigma(I)$), and these were used for the solution and refinement of the structure.

All calculations were performed with the TEXSAN crystal structure analysis package provided by Rigaku Corp.[16] The scattering factors were taken from ref 17. The structure was solved by heavy-atom Patterson methods (SAPI91) and expanded using Fourier techniques (DIRDIF92). The structure was refined by full-matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms of the palladium moiety and with isotropic thermal parameters for the tetrahydrofuran fragment. In the final cycles of refinement, hydrogen atoms of the palladium moiety were located at idealized positions (d(C—H) = 0.95 Å) with isotropic temperature factors ($B_{iso} = 1.20B_{bonded\ atom}$) and were included in the calculation without refinement of their parameters. The function minimized in least squares was $\sum w(|F_o| - |F_c|)^2$ ($w = 1/[\sigma^2(F_o)]$). The final R index was 0.044 ($R_w = 0.047$, $S = 1.59$). $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. $S = [\sum w(|F_o| - |F_c|)^2/(N_o - N_p)]^{1/2}$, where N_o is the number of observed data and N_p is the number of parameters varied. Crystal data and details of data collection and refinement are summarized in Table 2. Positional parameters for all non-hydrogen atoms are listed in Table 3. Additional information is available as supplementary material.

(16) TEXSAN Structure Analysis Package, Molecular Structure Corp., The Woodlands, TX, 1985 and 1992.

(17) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

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Supplementary Material Available: Atomic numbering scheme (Figure S1), positional parameters for hydrogen atoms (Table S1), anisotropic thermal parameters (Table S2), and bond distances and angles (Table S3) for **6** (6 pages). Ordering information is given on any current masthead page.

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