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Activator-Free Palladium-Catalyzed Silylation of Aryl Chlorides with Silylsilatranes

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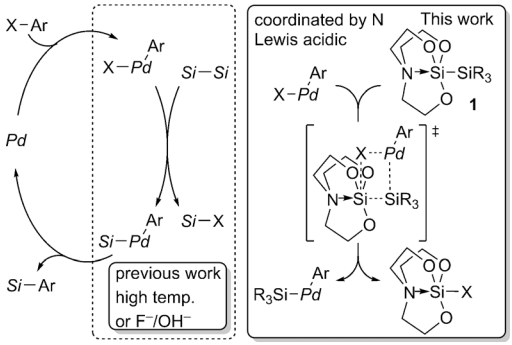
Abstract: The palladium-catalyzed silylation of aryl chlorides with silylsilatranes proceeds under activator-free conditions; hence, wide functional group compatibility is displayed and boryl and siloxy groups are able to survive. Experimental and computational studies revealed that smooth transmetalation from the silylsilatrane to the arylpalladium chloride is facilitated by strong interaction between the Lewis acidic silicon and the chloride.

Keywords: aryl chlorides · palladium · silylation · silylsilatranes · transmetalation

Introduction

Owing to the important roles that organosilicon compounds play in organic chemistry, chemists have devoted much time to develop new efficient reactions for carbon–silicon bond formation.[1] Given that conventional nucleophilic attack of chlorosilanes with organomagnesium or organolithium reagents suffers from functional group compatibility,[2] silylation under milder conditions has been drawing significant attention.[1a,3–12] The transition-metal-catalyzed silylation of aryl halides with disilanes is an attractive method (Scheme 1, left).[4–6,11,12] However, silylation with disilane generally requires very high temperatures such as 140–170 °C[4] or highly basic reaction conditions.[6] Milder protocols for achieving efficient silylation with wider functional group compatibility are therefore highly sought.

The palladium-catalyzed silylation with disilanes consists of the oxidative addition of an aryl halide to palladium(0), transmetalation between the arylpalladium halide and the disilane, and reductive elimination. Taking the low reactivity of disilanes into consideration, one should focus on the transmetalation step to achieve activator-free mild silylation.[5,13] To this end, we designed unsymmetrical disilane silylsilatrane **1** (Scheme 1, right). We initially envisioned that internal coordination of the nitrogen atom would facilitate Si–Si bond cleavage for facile transmetalation.[14–16] Indeed, in the literature, arylstannatranes and arylgermatranes are known to be more reactive in activator-free cross-coupling reactions than the corresponding trialkyl analogs.[15] We also expected that the silatrane moiety of **1** would be more Lewis acidic than a triorganosilyl group to realize efficient interaction with the halide on the palladium for both smooth transmetalation and selective transfer of the triorganosilyl group of **1**.



Scheme 1. Catalytic cycle for the Pd-catalyzed silylation reaction with disilanes and our design of silylsilatrane **1**.

Results and Discussion

Synthesis of **1** was easy and scalable (see the Experimental Section). For instance, nucleophilic substitution of readily available ethoxysilatrane with dimethylphenylsilyllithium afforded dimethylphenylsilylsilatrane (**1a**) on a 12 g scale

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(Figure 1). Silylsilatranes **1** are fairly stable and can be stored in air for more than one year without detectable decomposition. Therefore, silylsilatranes **1** have practical advantages over the corresponding simpler trialkoxydisilanes such as $R_3Si–Si(OMe)_3$.[17] X-ray crystallographic analysis of **1a** (Figure 1) revealed that the length of the Si–Si bond [2.3426(9) Å] is close to that of a typical symmetrical disilane [2.354(2) Å for $(FpCH_2)Me_2Si–SiMe_2(CH_2Fp)$, Fp = $(\eta^5\text{-}C_5H_5)Fe(CO)_2$].[18] This similarity indicates that the transannular coordination of the nitrogen atom to the bridgehead silicon is not so effective as to elongate the Si–Si bond, despite a short transannular N–Si distance of 2.153(2) Å.

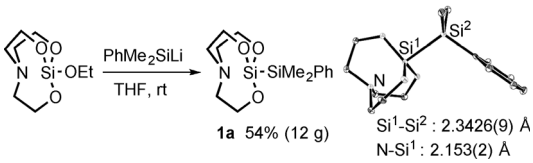
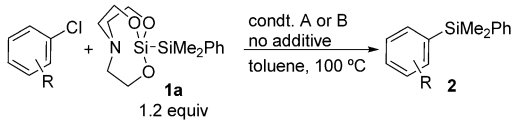


Figure 1. Synthesis and ORTEP drawing of silylsilatrane **1a**. Thermal ellipsoids represent 50% probability.

With silylsilatrane **1** in hand, we examined the silylation of aryl halides under palladium catalysis. To our delight, the reaction of electron-rich aryl chlorides with **1a** proved to proceed at 100 °C under $Pd_2(dba)_3$/SPhos[19] (dba = dibenzylideneacetone, SPhos = 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl) catalysis in the absence of an additive (Table 1, entries 1–5). As we expected, the dimethylphenylsilyl group of **1a** was selectively transferred and none of arylsilatranes were detected. Under the fluoride-free conditions, a siloxy group was naturally compatible (Table 1, entry 2). Arylsilane **2d** bearing a substituent in the *ortho* position was obtained in good yield after 30 h (Table 1, entry 4). Unfortunately, the $Pd_2(dba)_3$/SPhos catalyst did not work for the reaction of electron-deficient aryl chlorides (Table 1, entry 7). After rescreening a series of catalysts, $Pd(PtBu_3)_2$[20,21] showed excellent catalytic activity in converting electron-deficient aryl chlorides (Table 1, entries 8–11). Notably, the chloro group of 4-chlorophenylboronate was substituted with the silyl group and the boronate moiety remained intact (Table 1, entry 12). Both catalytic systems are effective in silylating electronically neutral chlorotoluenes (Table 1, entries 6, 13, and 14).

Table 1. Silylation of aryl chlorides with silylsilatrane **1a**.

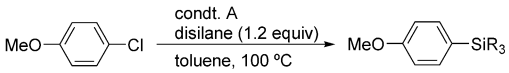


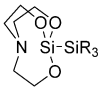
Entry	R[a]	Conditions[b]	2	Yield [%]
1	4-MeO	A	**2a**	89
2	4-TBDMSO	A	**2b**	91
3[c]	4-AcHN	A	**2c**	78
4[d]	2-MeO	A	**2d**	71
5[e]	3-chlorothiophene	A	**2e**	74
6	4-CH_3	A	**2f**	77
7	4-CF_3	A	**2g**	0[f]
8	4-CF_3	B	**2g**	99
9	4-CO_2Et	B	**2h**	96
10	3-CN	B	**2i**	96
11[g]	3-NO_2	B	**2j**	71
12[h]	4-Bpin	B	**2k**	69
13[h]	3-CH_3	B	**2l**	71
14	4-CH_3	B	**2f**	77

[a] TBDMSO = *tert*-butyldimethylsilyloxy, pin = pinacolato. [b] Conditions A: $Pd_2(dba)_3$ (3 mol%), SPhos (9 mol%), 12 h; conditions B: $Pd(PtBu_3)_2$ (5 mol%), 10 h. [c] **1a** (1.0 equiv.). [d] 30 h. [e] 8 h. [f] > 90% recovery of the starting material. [g] 40 h. [h] Catalyst (10 mol%).

The scope of silylsilatrane **1** was surveyed (Table 2). Bulkier silyl groups were transferred efficiently (Table 2, entries 1 and 2). Trimethylsilylsilatrane (**1d**) was less reactive, yet it participated in the silylation with the aid of RuPhos[19] (2-dicyclohexylphosphino-2′,6′-diisopropoxybiphenyl) at a higher temperature in DMF. The silatrane skeleton of **1** is important for efficient silyl transfer: simple hexaorganodisilane and monoalkoxydisilane reacted sluggishly (Table 2, entries 4 and 5).

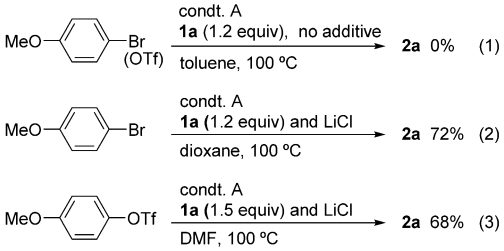
Table 2. Scope of the disilanes.



Entry	Disilane		Product	Yield [%]
1		$SiMePh_2$ (**1b**)	**3**	81
2[a]		$SiMe_2$(*o*-tolyl) (**1c**)	**4**	90
3[b]		$SiMe_3$ (**1d**)	**5**	54 (74[c])
4	$Me_2PhSi–SiMe_2Ph$		**2a**	11
5	$(iPrO)Me_2Si–SiMe_2Ph$		**2a**	16

[a] $Pd_2(dba)_3$ (5 mol%) and SPhos (15 mol%). [b] RuPhos was used instead of SPhos. Performed in DMF at 120 °C. [c] Yield determined by NMR spectroscopy.

Surprisingly, attempts to silylate aryl bromides and aryl triflates failed and resulted in the recovery of the starting materials under the standard conditions [Scheme 2, Eq. (1)].[22] Considering that oxidative addition of aryl bromides and aryl triflates should be much easier than that of aryl chlorides, we speculated that the transmetalation step would be problematic and that chloride on palladium would play a crucial role in smooth transmetalation. Indeed, lithium chloride as an additive promoted the silylation



Scheme 2. Silylation of aryl bromides and aryl triflates.

[Scheme 2, Eqs. (2) and (3)], probably through halide–ligand exchange between the arylpalladium bromide or arylpalladium triflate and lithium chloride. We confirmed this ligand-exchange process by ^{31}P NMR spectroscopy analysis (see the Supporting Information).

To investigate the effect of the chloride ligand in the smooth transmetalation step, DFT calculations were performed by using Gaussian 09.[23,24] We chose transmetalation between PhPdX($PtBu_3$) and **1d** (trimethylsilylsilatrane) as a model reaction for computational simplicity (Figure 2). Transmetalation between PhPdCl($PtBu_3$) and **1d** was calculated to proceed via four-membered transition state **TS_Cl** in a concerted manner with an activation barrier of 98.7 kJ mol^{-1}. Transmetalation results in the formation of **Prod_Cl**, in which the chloride weakly coordinates to palladium. The overall reaction is slightly endothermic by 14.7 kJ mol^{-1}. On the other hand, the activation energy for transmetalation between PhPdBr($PtBu_3$) and **1d** was calculated to be 114.1 kJ mol^{-1}; thus, it is more difficult to reach **TS_Br** than **TS_Cl** by 15.4 kJ mol^{-1}. The formation of product **Prod_Br** is significantly endothermic (44.2 kJ mol^{-1}), which correlates with the higher activation energy for late transition state **TS_Br**. These results show that the efficient silylation of aryl chlorides is based on intrinsically strong interaction between the silicon and chlorine atoms in the transmetalation step.[25,26]

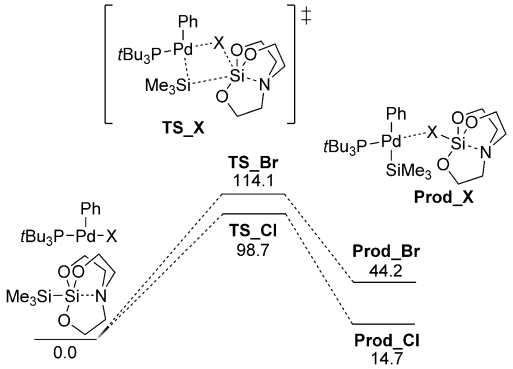


Figure 2. Energy profile of the transmetalation reaction obtained by DFT calculations at the M06/6-311G**+ECP(Pd,P,Si,Cl,Br) level. Energies are in kJ mol^{-1}.

Conclusions

We developed silylsilatranes as promising silylating agents in the palladium-catalyzed silylation of aryl chlorides under activator-free conditions. A variety of functional groups such as boryl and siloxy groups were tolerant owing to the absence of a basic activator. Experimental and computational investigations revealed that the success of the activator-free silylation relies on smooth transmetalation between the arylpalladium chloride and the silylsilatranes, which takes advantage of the affinity between the chloride on the palladium and the Lewis acidic silicon. These findings contain important information on still-unexplained transmetalation in general and have a significant impact on the development of new activator-free reactions of moderately reactive organometalloid reagents of low toxicity. These studies are currently underway in our laboratory to realize ultimate activator-free cross-coupling reactions.

Experimental Section

General Methods

^1H NMR (600 MHz), ^{13}C NMR (151 MHz), ^{31}P NMR (243 MHz), and ^{29}Si NMR (119 MHz) spectra were taken with a JEOL ECA-600 spectrometer. Chemical shifts are reported relative to $CHCl_3$ ($\delta=7.26$) for ^1H NMR, relative to $CDCl_3$ ($\delta=77.16$) for ^{13}C NMR, relative to H_3PO_4 ($\delta=0.00$) for ^{31}P NMR, and relative to tetramethylsilane ($\delta=0.00$) for ^{29}Si NMR. Spectroscopic-grade solvents were used for all spectroscopic studies without further purification. IR spectra were determined with a JASCO IR-810. High-resolution APCI-TOF mass spectra were taken with a Bruker microTOF. TLC analyses were performed on commercial glass plates bearing a 0.25 mm layer of Merck Silica gel $60F_{254}$. Preparative separations were performed by silica gel chromatography (Wako gel C-200, C-300, or C-400). Crystallographic data were collected with a Rigaku RAXIS-RAPID apparatus at −180 °C by using graphite-monochromated CuK_α radiation ($\lambda=1.54187$ Å). The structures were solved by direct methods (SHELXS-97) and refined with the full-matrix least squares technique (SHELXL-97).[27]

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Toluene, *N*,*N*-dimethylformamide (DMF), and hexamethylphosphoric triamide (HMPA) were distilled from CaH_2. Tris(dibenzylideneacetone)dipalladium [$Pd_2(dba)_3$], SPhos, RuPhos, and lithium wire were purchased from Sigma–Aldrich. Pd($PtBu_3$)$_2$ was purchased from Strem and was stored and weighed in a glove box filled with nitrogen. Anhydrous THF was purchased from Wako Pure Chemical Industries, Ltd. and stored under an atmosphere of nitrogen.

Syntheses

*Dimethylphenylsilylsilatrane (**1a**)*

Ethoxysilatrane[28] (14.6 g, 72 mmol) was placed in a reaction flask. The flask was purged with nitrogen, and THF (120 mL) was added. Dimethylphenylsilyllithium[29] (≈1.0 M in THF, 72 mL, 72 mmol) was added to the solution by cannula. The mixture was stirred at room temperature. After 20 min, the reaction was quenched with a saturated solution of NH_4Cl and extracted with EtOAc. The organic layer was washed with brine, dried (anhydrous Na_2SO_4), filtered, and concentrated in vacuo to afford a white solid. The solid was suspended in hexane (10 mL), and the suspension was then filtered off. The solid was washed on the filter paper with hexane to afford **1a** (12.0 g, 38.9 mmol, 54%). Colorless solid; m.p. 164–165 °C; ^1H NMR ($CDCl_3$): $\delta=7.66$–7.63 (m, 2H), 7.31–7.23 (m, 3H), 3.75 (t, $J=5.5$ Hz, 6H), 2.78 (t, $J=5.5$ Hz, 6H), 0.52 ppm (s, 6H); ^{13}C NMR ($CDCl_3$): $\delta=142.80$, 134.58, 127.68, 127.35, 58.10, 51.42, −1.80 ppm; ^{29}Si NMR ($CDCl_3$, 60 °C): $\delta=-25.70$, −66.96 ppm; IR (neat): $\tilde{\nu}=1425$, 1109, 1072, 936, 807, 757, 733, 698, 617 cm^{-1}; MS (APCI-TOF): *m/z*: calcd for $C_{14}H_{23}NO_3Si_2$: 309.1211 $[M]^+$; found: 309.1202; crystal data: $C_{14}H_{23}NO_3Si_2$, from CCl_4/EtOH, $M=309.51$; monoclinic, $P2_1/n$ (No. 14), $a=6.613(2)$, $b=21.9028(4)$, $c=10.7275(2)$ Å; $\beta=94.0357(17)°$; $V=1561.27(6)$ Å^3; $Z=4$; $T=93$ K; $\rho_{calcd}=1.317$ g cm^{-3}; $R_1=0.0573$ [$I>2.0\,\sigma(I)$]; $wR_2=0.1547$ (all data); GOF = 1.142.

*Methyldiphenylsilylsilatrane (**1b**)*

Ethoxysilatrane (2.44 g, 12 mmol) was placed in a reaction flask. The flask was purged with nitrogen, and THF (20 mL) was added to the flask. Methyldiphenylsilyllithium[30] (≈1.0 M in THF, 18 mL, 18 mmol) was

added to the solution by cannula. The mixture was stirred at room temperature. After 20 min, the reaction was quenched with a saturated solution of NH_4Cl and extracted with EtOAc. The organic layer was washed with brine, dried (anhydrous Na_2SO_4), filtered, and concentrated in vacuo to afford a white solid. The solid was suspended in hexane (5 mL), and the suspension was then filtered off. The solid was washed on the filter paper with hexane to afford **1b** (1.02 g, 2.75 mmol, 23%). Colorless solid; m.p. 170–171 °C; ^{1}H NMR ($CDCl_3$): δ = 7.71–7.66 (m, 4H), 7.32–7.27 (m, 6H), 3.77 (t, J = 5.5 Hz, 6H), 2.76 (t, J = 5.5 Hz, 6H), 0.57 ppm (s, 3H); ^{13}C NMR ($CDCl_3$): δ = 140.91, 135.47, 127.83, 127.35, 57.95, 51.33, −2.87 ppm; ^{29}Si NMR ($CDCl_3$, 60 °C): δ = −26.56, −69.02 ppm; IR (neat): $\tilde{\nu}$ = 1427, 1271, 1108, 1067, 910, 748, 735, 700, 629 cm^{-1}; MS (APCI-TOF): m/z: calcd for $C_{19}H_{25}NO_3Si_2$: 371.1367 $[M]^+$; found: 371.1360; crystal data: $C_{19}H_{25}NO_3Si_2$, from 1,2-dichloroethane/EtOH, M = 371.58; orthorhombic, *Pbca* (No. 61), a = 11.4397(3), b = 24.7612(6), c = 13.1386(3) Å; V = 3721.65(16) Å^3; Z = 8; T = 93 K; ρ_{calcd} = 1.326 g cm^{-3}; R_1 = 0.0516 [$I > 2.0\,\sigma(I)$]; wR_2 = 0.1183 (all data); GOF = 1.077.

*Dimethyl(o-tolyl)silylsilatrane (**1c**)*

Et_2O (15 mL) and dichlorodimethylsilane (60 mmol, 9.0 mL) were added to a reaction flask purged with nitrogen. The mixture was cooled to 0 °C. 2-Methylphenylmagnesium bromide (0.62 M in THF, 81 mL, 50 mmol) was added at 0 °C by cannula to the solution, which was warmed to room temperature. The mixture was stirred overnight, and the resulting suspension was filtered off and washed on the filter with hexane to collect the filtrate. After evaporation of the solvent, chlorodimethyl(*o*-tolyl)silane was distilled under reduced pressure (0.4 kPa, 78 °C, 5.37 g, 29.0 mmol, 58%). Lithium wire (500 mg, 70 mmol) in oil was cut into 4 mm cubes with scissors. These lithium cubes were stirred vigorously for 10 min in hexane (5 mL) under an atmosphere of nitrogen. The hexane was removed and the lithium was suspended in THF (15 mL). The mixture was stirred rapidly with chlorodimethyl(*o*-tolyl)silane (3.0 mL, 18 mmol) at room temperature for 6 h to give a deep red solution of Me_2(*o*-tolyl)SiLi (≈1.0 M). Ethoxysilatrane (2.44 g, 12 mmol) was placed in a reaction flask. The reaction flask was purged with nitrogen, and THF (20 mL) was added to the reaction flask. Dimethyl(*o*-tolyl)silyllithium (≈1.0 M in THF, 18 mL, 18 mmol) was added to the solution by cannula. The mixture was stirred at room temperature. After 30 min, the reaction was quenched with a saturated solution of NH_4Cl and extracted with EtOAc. The organic layer was washed with brine, dried (anhydrous Na_2SO_4), filtered, and concentrated in vacuo to afford a white solid. The solid was suspended in hexane (5 mL), and the suspension was then filtered off. The solid was washed on the filter paper with hexane to afford **1c** (486 mg, 1.50 mmol, 13%). Colorless solid; m.p. 143–144 °C; ^{1}H NMR ($CDCl_3$): δ = 7.56 (d, J = 6.4 Hz, 1H), 7.17 (t, J = 7.8 Hz, 1H), 7.13–7.07 (m, 2H), 3.72 (t, J = 5.5 Hz, 6H), 2.76 (t, J = 5.5 Hz, 6H), 2.52 (s, 3H), 0.35 ppm (s, 6H); ^{13}C NMR ($CDCl_3$): δ = 144.52, 140.72, 135.21, 129.29, 128.11, 124.58, 58.32, 51.57, 23.35, −1.06 ppm; ^{29}Si NMR ($CDCl_3$, 60 °C): δ = −25.62, −65.51 ppm; IR (neat): $\tilde{\nu}$ = 1453, 1274, 1110, 1075, 874, 812, 740, 624, 588 cm^{-1}; MS (APCI-TOF): m/z: calcd for $C_{15}H_{25}NO_3Si_2$: 323.1367 $[M]^+$; found: 323.1352.

*Trimethylsilylsilatrane (**1d**)*

Ethoxysilatrane (6.58 g, 30 mmol) and THF (40 mL) were added to a reaction flask under an atmosphere of nitrogen. Trimethylsilyllithium[31] (≈0.24 M in THF, 62 mL, 15 mmol) was added to the solution by cannula. The mixture was stirred overnight at room temperature. The reaction was quenched with a saturated solution of NH_4Cl and extracted with EtOAc. The organic layer was washed with brine, dried (anhydrous Na_2SO_4), filtered, and concentrated to afford a white solid. The solid was suspended in hexane (5 mL) and then filtered off. The solid was washed on the filter paper with hexane to afford **1d** (1.04 g, 4.2 mmol, 28%). Colorless solid; m.p. 171–174 °C; ^{1}H NMR ($CDCl_3$): δ = 3.73 (t, J = 5.5 Hz, 6H), 2.76 (t, J = 5.5 Hz, 6H), 0.04 ppm (s, 9H); ^{13}C NMR ($CDCl_3$): δ = 58.29, 51.47, −0.81 ppm; ^{29}Si NMR ($CDCl_3$, 60 °C): δ = −23.85, −64.03 ppm; IR (neat): $\tilde{\nu}$ = 1110, 1077, 935, 849, 824, 744, 726, 640, 613 cm^{-1}; MS (APCI-TOF): m/z: calcd for $C_9H_{21}NO_3Si_2$: 247.1054 $[M]^-$; found: 247.1061.

1,1,2,2-Tetramethyl-1-phenyl-2-isopropoxydisilane

Ether (100 mL) and 1,2-dichloro-1,1,2,2-tetramethyldisilane (30 mmol, 5.56 mL) were added to a reaction flask purged with nitrogen. The mixture was cooled to 0 °C. PhMgBr (0.47 M in Et_2O, 60 mL, 28.2 mmol) was added. After stirring at 0 °C for 8 h, the resulting suspension was filtered off and washed on the filter with hexane to collect the filtrate. After evaporation, 1-chloro-2-phenyl-1,1,2,2-tetramethyldisilane was distilled under reduced pressure (0.4 kPa, 89 °C, 4.29 g, 18.7 mmol, 62%). 4-Dimethylaminopyridine (2.5 mmol, 305.4 mg), imidazole (6.0 mmol, 408.5 mg), and 1-chloro-2-phenyl-1,1,2,2-tetramethyldisilane (5.0 mmol, 1.14 mL) were placed in a flask. The flask was purged with nitrogen, and DMF (25 mL) was added. The mixture was cooled to 0 °C, and *i*PrOH (10 mmol, 0.77 mmol) was added dropwise. The mixture was stirred at room temperature for 3 h and then quenched by the addition of water. The mixture was diluted with ether. The layers were separated, and the aqueous layer was extracted with ether. The organic extracts were washed with brine (3×), dried (anhydrous Na_2SO_4), filtered, and concentrated in vacuo to afford a colorless liquid. The product was distilled under reduced pressure (0.3 kPa, 73–74 °C, 757 mg, 3.0 mmol, 60%). Colorless liquid; ^{1}H NMR ($CDCl_3$): δ = 7.53–7.48 (m, 2H), 7.37–7.30 (m, 3H), 3.87 (sept., J = 5.9 Hz, 1H), 1.09 (d, J = 5.9 Hz, 6H), 0.39 (s, 6H), 0.23 ppm (s, 6H); ^{13}C NMR ($CDCl_3$): δ = 139.40, 134.04, 128.59, 127.92, 66.05, 25.96, 0.26, −3.34 ppm; ^{29}Si NMR ($CDCl_3$, 60 °C): δ = 10.65, −25.08 ppm; IR (neat): $\tilde{\nu}$ = 1244, 1120, 1106, 1018, 876, 825, 786, 763, 731, 679, 633 cm^{-1}; MS (APCI-TOF): m/z: calcd for $C_{13}H_{24}OSi_2$: 251.1282 $[M]^-$; found: 251.1270.

Representative procedure for the silylation of electron-rich and electron-neutral aryl chlorides

$Pd_2(dba)_3$ (0.015 mmol, 13.7 mg) and SPhos (0.045 mmol, 18.5 mg) were added to a flask. The flask was purged with argon, and toluene (0.5 mL) was added. The mixture was then stirred at room temperature for 10 min. 4-Chloroanisole (0.50 mmol, 71.2 mg) was added, and then the mixture was stirred at room temperature for 5 min. Dimethylphenylsilylsilatrane (**1a**; 0.60 mmol, 185.7 mg) and toluene (1.0 mL) were added. The mixture was then stirred at 100 °C for 12 h. The resulting mixture was diluted with EtOAc and passed through a short column of alumina by washing copiously with EtOAc. Chromatographic purification (silica gel, EtOAc/hexane = 1:40) afforded **2a** (108 mg, 0.444 mmol, 89%).

Representative procedure for the silylation of electron-deficient and electron-neutral aryl chlorides

Under an inert atmosphere, Pd(P*t*Bu$_3$)$_2$ (0.025 mmol, 12.8 mg) was added to a flask. Toluene (1.0 mL) and 1-chloro-4-trifluoromethyltoluene (0.50 mmol, 90.9 mg) were added, and then the mixture was stirred at room temperature for 5 min. Dimethylphenylsilylsilatrane (**1a**; 0.60 mmol, 185.7 mg) was added, and the mixture was then stirred at 100 °C for 10 h. The resulting mixture was diluted with EtOAc and passed through a short column of alumina by washing copiously with EtOAc. Chromatographic purification (silica gel, hexane) afforded **2g** (140 mg, 0.499 mmol, 99%).

Products **2a**,[32] **2d**,[33] **2f**,[34] **2g**,[32] **2h**,[32] **2l**,[32] **3**,[33] **4**,[35] and **5**[36] are known compounds and showed spectral data that were identical to those given in the literature.

*(4-tert-Butyldimethylsiloxyphenyl)dimethylphenylsilane (**2b**)*

Colorless oil; ^{1}H NMR ($CDCl_3$): δ = 7.53–7.48 (m, 2H), 7.39–7.31 (m, 5H), 6.83 (d, J = 8.3 Hz, 2H), 0.98 (s, 9H), 0.52 (s, 6H), 0.20 ppm (s, 6H); ^{13}C NMR ($CDCl_3$): δ = 156.84, 138.92, 135.76, 134.30, 129.74, 129.11, 127.90, 119.79, 25.83, 18.34, −2.01, −4.20 ppm; ^{29}Si NMR ($CDCl_3$, RT): δ = 20.62, −8.45 ppm; IR (neat): $\tilde{\nu}$ = 1591, 1500, 1428, 1253, 1175, 1109,

911, 802, 774, 699, 653 cm^{-1}; MS (APCI-TOF): *m*/*z*: calcd for $C_{20}H_{31}OSi_2$: 343.1908 $[M+H]^+$; found: 343.1899.

*(4-Acetylaminophenyl)dimethylphenylsilane (**2c**)*

Colorless solid; m.p. 115–116 °C; ^1H NMR ($CDCl_3$): $\delta = 7.59$–7.44 (m, 7H), 7.39–7.32 (m, 3H), 2.17 (s, 3H), 0.54 ppm (s, 6H); ^{13}C NMR ($CDCl_3$): $\delta = 168.67$, 138.85, 138.35, 135.13, 134.25, 133.80, 129.22, 127.93, 119.31, 24.73, −2.23 ppm; ^{29}Si NMR ($CDCl_3$, RT): $\delta = -8.25$ ppm; IR (neat): $\tilde{\nu} = 1669$, 1590, 1530, 1371, 1322, 1292, 1247, 1112, 806, 778, 728, 701 cm^{-1}; MS (APCI-TOF): *m*/*z*: calcd for $C_{16}H_{20}NOSi$: 270.1309 $[M+H]^+$; found: 270.1316.

*Dimethylphenyl(3-thienyl)silane (**2e**)*

Colorless oil; ^1H NMR ($CDCl_3$): $\delta = 7.58$–7.51 (m, 2H), 7.50–7.47 (m, 1H), 7.43–7.34 (m, 4H), 7.21 (d, $J = 4.6$ Hz, 1H), 0.57 ppm (s, 6H); ^{13}C NMR ($CDCl_3$): $\delta = 139.07$, 138.50, 134.08, 132.98, 132.05, 129.30, 127.98, 125.94, −1.64 ppm; ^{29}Si NMR ($CDCl_3$, 60 °C): $\delta = -12.42$ ppm; IR (neat): $\tilde{\nu} = 1248$, 1105, 821, 795, 769, 730, 697, 655, 607 cm^{-1}; MS (APCI-TOF): *m*/*z*: calcd for $C_{12}H_{14}SSi$: 217.0502 $[M-H]^-$; found: 217.0492.

*(3-Cyanophenyl)dimethylphenylsilane (**2i**)*

Colorless oil; ^1H NMR ($CDCl_3$): $\delta = 7.78$ (s, 1H), 7.74–7.71 (m, 1H), 7.66–7.62 (m, 1H), 7.53–7.49 (m, 2H), 7.47–7.37 (m, 4H), 0.59 ppm (s, 6H); ^{13}C NMR ($CDCl_3$): $\delta = 140.86$, 138.32, 137.77, 136.53, 134.20, 132.58, 129.79, 128.48, 128.23, 119.28, 112.29, −2.57 ppm; ^{29}Si NMR ($CDCl_3$, RT): $\delta = -7.08$ ppm; IR (neat): $\tilde{\nu} = 2227$, 1428, 1391, 1250, 1111, 850, 829, 793, 774, 733, 701 cm^{-1}; MS (APCI-TOF): *m*/*z*: calcd for $C_{15}H_{16}NSi$: 238.1047 $[M+H]^+$; found: 238.1043.

*Dimethyl(3-nitrophenyl)phenylsilane (**2j**)*

Colorless oil; ^1H NMR ($CDCl_3$): $\delta = 8.37$ (s, 1H), 8.21 (d, $J = 8.4$ Hz, 1H), 7.81 (d, $J = 7.3$ Hz, 1H), 7.58–7.48 (m, 3H), 7.44–7.36 (m, 3H), 0.64 ppm (s, 6H); ^{13}C NMR ($CDCl_3$): $\delta = 148.00$, 141.58, 140.30, 136.49, 134.19, 129.83, 128.92, 128.61, 128.25, 124.11, −2.52 ppm; ^{29}Si NMR ($CDCl_3$, RT): $\delta = -6.75$; IR (neat): $\tilde{\nu} = 1522$, 1346, 875, 833, 816, 778, 726, 700, 680, 662 cm^{-1}; MS (APCI-TOF): *m*/*z*: calcd for $C_{14}H_{16}NO_2Si$: 258.0945 $[M+H]^+$; found: 258.0944.

*Dimethyl(4-pinacolatoborylphenyl)phenylsilane (**2k**)*

Colorless solid; m.p. 87–94 °C; ^1H NMR ($CDCl_3$): $\delta = 7.79$ (d, $J = 7.8$ Hz, 2H), 7.54 (d, $J = 7.8$ Hz, 2H), 7.52–7.49 (m, 2H), 7.38–7.31 (m, 3H), 1.35 (s, 12H), 0.55 ppm (s, 6H); ^{13}C NMR ($CDCl_3$): $\delta = 142.01$, 138.20, 136.27, 134.32, 134.03, 133.62, 129.25, 127.94, 83.91, 24.99, −2.34 ppm; ^{29}Si NMR ($CDCl_3$, RT): $\delta = -7.87$ ppm; IR (neat): $\tilde{\nu} = 1357$, 1139, 1075, 808, 776, 746, 732, 700, 656 cm^{-1}; MS (APCI-TOF): *m*/*z*: calcd for $C_{20}H_{28}BO_2Si_2$: 339.1950 $[M+H]^+$; found: 339.1960.

Crystallographic data

CCDC-985696 (for **1a**) and -985697 (for **1b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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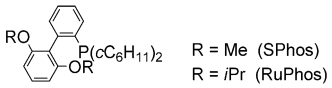

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FULL PAPER

A Si of relief: The Pd-catalyzed silylation of aryl chlorides with silylsilatranes proceeds under activator-free conditions and hence displays wide functional group compatibility and allows boryl and siloxy groups to survive. The chloride on palladium is revealed to play an important role in transmetalation from the silylsilatrane to the arylpalladium chloride through strong interaction between the Lewis acidic silicon and the chloride.

Silylation

Yutaro Yamamoto, Hiroshi Matsubara, Kei Murakami, Hideki Yorimitsu,* Atsuhiro Osuka* _____ ▮▮▮▮–▮▮▮▮

Activator-Free Palladium-Catalyzed Silylation of Aryl Chlorides with Silylsilatranes