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Decarbonylative Coupling of Fluorobenzoyl Chlorides with Hexamethyldisilane in the Presence of a Palladium Complex Catalyst: Extremely Facile Decarbonylation of Pentafluorobenzoyl−Pd Complex Relevant to $C_6F_5SiMe_3$ Formation

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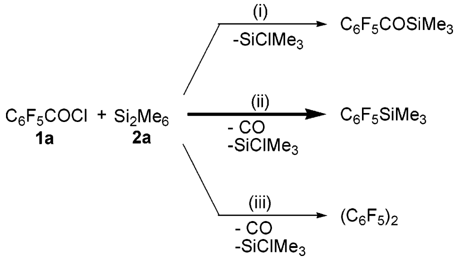
Palladium−phosphite complexes catalyze the reaction of pentafluorobenzoyl chloride with hexamethyldisilane to selectively form pentafluorophenytrimethylsilane as virtually the sole product. The reaction of 3,5-difluoro- or 4-fluorobenzoyl chloride was less selective, giving a mixture of corresponding benzoyl- and phenylsilanes. Oxidative addition of pentafluorobenzoyl chloride with $Pd(PPh_3)_4$ or with $Pd[P(OEt)_3]_2$ generated in situ proceeds readily, but decarbonylation occurs, giving *trans*-$C_6F_5PdClL_2$ (L = PPh_3, $P(OEt)_3$), selectively.

Introduction

We previously reported a rhodium-catalyzed addition reaction of perfluorinated acid chlorides across alkynes, which affords 2-chloroalken-1-yl perfluoroorganyl ketones.[1] This reaction is quite different from the reaction of nonfluorinated aroyl chloride with alkynes, which gives (2-chloroalken-1-yl)arenes,[2] in that it is a nondecarbonylative addition reaction. This observation seems to suggest that the ease of decarbonylation of aroyl−rhodium species is highly dependent on the electronic nature of the aroyl group, as electronegative groups bound to the carbonyl prevent the decarbonylation. With the significant effect of the fluorine substituent in mind, we became interested in decarbonylation in palladium-catalyzed reactions. We chose the reaction of pentafluorobenzoyl chloride with hexamethyldisilane as a probe. Palladium-catalyzed reactions of aroyl chlorides with disilanes, first reported by Yamamoto and Tsuji using $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ as a precatalyst[3] and later by Rich using $PdCl_2(PhCN)_2$,[4] are straightforward and high-yielding synthetic routes for aroylsilanes.[5] To our knowledge, pentafluorobenzoyl chloride has never been examined as a substrate for the reaction. At least three reactions could have taken place: (i) the nondecarbonylative metathesis leading to fluorinated aroylsilanes,[6] which are valuable in synthetic applications;[7] (ii) decarbonylative metathesis forming fluorinated arylsilanes, which are also useful in organic and inorganic syntheses;[8] (iii) decarbonylative reductive coupling leading to fluorinated biaryls, similarly to the desulfonylative reductive coupling of arenesulfonyl chloride.[9] The real event observed in practice was the second, which will be reported in this paper. Very rapid decarbonylation of the pentafluorobenzoyl−palladium species, different from the slow decarbonylation of the pentafluorobenzoyl−rhodium complex, is also described.

Scheme 1



Results and Discussion

Catalytic Reactions. In a representative reaction (entry 1, Table 1), pentafluorobenzoyl chloride and hexamethyldisilane

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[5] Both $[Pd(\eta^3\text{-allyl})Cl]_2$ and $PdCl_2(PhCN)_2$ are envisioned to be converted to the same PdL_n species upon treatment with hexamethyldisilane in the presence of a phosphorus ligand (L). On the basis of this assumption, we presume it reasonable to compare current results obtained using $PdCl_2(PhCN)_2$ with those in ref 3. However, we cannot rule out the possibility that catalytic activity may be dependent on the structure of the precursor complex, in view of the difference in the quantity of the coproduct ($SiClMe_3$) generated during the conversion of the precursor to the active species.

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Table 1. Ligand Effect in the Reaction of 1a with 2a[a]

$$\underset{\mathbf{1a}}{C_6F_5COCl} + \underset{\mathbf{2a}}{Si_2Me_6} \xrightarrow{\text{Pd catalyst}} \underset{\mathbf{4aa}}{C_6F_5SiMe_3} + ClSiMe_3$$

entry	ligand	time (day)	conversion of **1a** (%)[b]	yield of **4aa** (%)[b]
1	$P(OEt)_3$	5	97	94 (85)
2[c]	$P(OMe)_3$	5	40	40
3[c]	$P[O(n\text{-}Pr)]_3$	3	100	95
4[c]	$P[O(i\text{-}Pr)]_3$	3	78	68
5[c]	$P[O(n\text{-}Bu)]_3$	3	45	42
6[d]	$P(OPh)_3$	5	5	3
7[c]	$PPh(OEt)_2$	3	69	62
8[c]	$PPh_2(OEt)$	3	55	53
9[d]	PPh_3	5	5	5
10[e]	PPh_3	5	38	30
11[d]	$P(p\text{-}FC_6H_4)_3$	5	2	2
12	$P(p\text{-}Tol)_3$	5	10	10
13[c]	$P(Mes)_3$[f]	5	44	40
14[c]	dppe	0.5	5	3
15[c]	dppp	0.5	2	2
16[c]	dppp	0.5	5	5
17[c]	PMe_3	1	2	2
18[c]	$P(t\text{-}Bu)_3$	5	20	1
19[g]	$P(OEt)_3$	5	58	42

[a] Reaction conditions: **1a** (2 mmol), **2a** (2 mmol), toluene 2 mL, $PdCl_2(PhCN)_2$ (5 mol %), ligand/Pd = 2, 110 °C. [b] Determined by ^{19}F NMR spectroscopy. The figure in parentheses is isolated yield. [c] Pd mirror was formed. [d] Reaction mixture became heterogeneous as the reaction proceeded. [e] Run in *sym*-tetrachloroethane. [f] Mes = 2,4,6-trimethylphenyl. [g] Run under a CO atmosphere (10 atm).

in toluene were heated at 110 °C in the presence of $PdCl_2(PhCN)_2$ and triethyl phosphite (P/Pd = 2). ^{19}F NMR spectroscopy showed that the reaction proceeded cleanly to give pentafluorophenyltrimethylsilane (**4aa**) as nearly the sole product in 94% yield after 5 days, eq 1. Unlike the reaction of plain benzoyl chloride in the presence of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ as precatalyst,[3] nondecarbonylative coupling forming pentafluorobezoylsilane (**3aa**) did not proceed at all. Decafluorobiphenyl, a possible product of decarbonylative reductive coupling,[9a] was not formed either. The reaction was slow, taking 5 days for completion, compared with only 24 h for the reaction of plain benzoyl chloride[3,4] under similar conditions.

$$\underset{\mathbf{1a}}{C_6F_5COCl} + \underset{\mathbf{2a}}{Si_2Me_6} \xrightarrow{\text{Pd catalyst}} \underset{\mathbf{3aa}}{C_6F_5COSiMe_3} + \underset{\mathbf{4aa}}{C_6F_5SiMe_3} \qquad (1)$$

Various catalyst systems comprising a phosphorus ligand and $PdCl_2(PhCN)_2$ promote the decarbonylative silylation as summarized in Table 1. The performance depended on the nature of the ligand, but none of the ligands listed in Table 1 promoted the formation of **3aa**.

As observed by Yamamoto in the CO-retentive metathesis of aroyl chloride with disilane forming aroylsilane, the present decarbonylative silylation is also best accomplished using phosphites, particularly trialkyl phosphites (entries 2−5).[3] Of the trialkyl phosphites, tri-*n*-propyl phosphite is the ligand of choice, which generates the most active palladium species, while higher or lower alkyl phosphites are somewhat inferior, and triphenyl phosphite displays only a marginal activity. Phosphonite and phosphinite ligands are moderately active (entries 7, 8). Phosphines in general are not capable ligands, as compared with phosphites. As far as triarylphosphines are concerned, a more donating phosphine is better performing than a less donating phosphine (entries 9, 11−13). However, more electron-donating trialkylphosphines and more strongly coordinating diphosphines are much more inferior (entries 14−18). Tris(2-furyl)phosphine, triphenylarsine, and triphenylstibine are completely ineffective.

Table 2. Dependence of the Extent Fluorine Substitution on the Selectivity[a]

$$\underset{\mathbf{1a\text{-}c}}{Ar^fCOCl} + \underset{\mathbf{2a}}{Si_2Me_6} \xrightarrow[\text{- ClSiMe}_3]{\text{Pd catalyst}} \underset{\mathbf{3xa}}{Ar^fCOSiMe_3} + \underset{\mathbf{4xa}}{Ar^fSiMe_3}$$

entry	Ar^fCOCl	solvent	time (day)	conversion of **1** (%)[b]	yield (%)[b] **3xa**	yield (%)[b] **4xa**
1	C_6F_5COCl **1a**	toluene	5	97	~0	94 (85)
2[c]	$3,5\text{-}F_2C_6H_3COCl$ **1b**	toluene	2	69	15	32
3[c,d]	$4\text{-}FC_6H_4COCl$ **1c**	none	2	90	57 (51)	2

[a] Ar^f stands for a fluorinated aryl group. Reaction was carried out at 110 °C using **1** (2 mmol), **2a** (2 mmol), $PdCl_2(PhCN)_2$ (5 mol %), $P(OEt)_3$ (10 mol %), and solvent (2 mL) in a sealed tube. [b] Determined by ^{19}F NMR spectroscopy. The figure in parentheses is isolated yield. [c] Pd mirror was formed. [d] The quantity of $PdCl_2(PhCN)_2$ and $P(OEt)_3$ was doubled.

In the reactions with the Pd−$P(OPh)_3$, −PPh_3, and −$P(p\text{-}FC_6H_4)_3$ catalyst systems, a white precipitate was observed soon after the reaction started. With the Pd−PPh_3 catalyst system, the precipitate was *trans*-$C_6F_5PdCl(PPh_3)_2$, an intermediate involved in the catalytic cycle (vide infra). It is reasonable to assume that the low solubility of this intermediate was responsible, at least in part, for the yield being poor (5% yield). When *sym*-tetrachloroethane, a better solvent than toluene, was used, the conversion of the acid chloride and the yield of **4aa** after 5 days improved to 38% and 30%, respectively (entry 10).

Finally, an attempted reaction under pressurized CO (10 atm) to prevent decarbonylation was run using the $PdCl_2(PhCN)_2$−$P(OEt)_3$ catalyst system. However, only a decrease in catalytic activity resulted (entry 19).

The above results clearly suggest that the pentafluorophenyl group strongly promotes decarbonylation. This conclusion is further reinforced by the following results observed in the reactions of partially fluorinated aroyl chlorides (Table 2). The reaction of 3,5-difluorobenzoyl chloride (**1b**) gave 3,5-difluorophenylsilane (**4ba**) in 32% yield, together with 3,5-difluorobenzoylsilane (**3ba**) in 15% yield, suggesting less decarbonylation (entry 2). The reaction of 4-fluorobenzoyl chloride (**1c**) carried out without solvent afforded the corresponding aroylsilane (**3ca**) more selectively (entry 3).[10] In these reactions of 3,5-difluorobenzoyl chloride and 4-fluorobenzoyl chloride, material balance was not so satisfactory as compared with the reaction of pentafluorobenzoyl chloride. A careful search for minor byproducts formed in the reaction of 4-fluorobenzoyl chloride revealed the presence of chlorofluorobenzene (3%), 4,4′-difluorobiphenyl (4%), and diethyl 4-fluorobenzoylphosphonate (3%). However, neither fluorobenzene nor 4,4′-difluorobenzophenone was detected.[11]

The reaction of tetrafluoroterephthaloyl dichloride smoothly conformed to the decarbonylative coupling at both acid chloride moieties to afford bis(trimethylsilyl)tetrafluorobenzene (**5**) in a high yield, eq 2.

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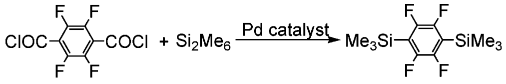
(10) When the reaction was run in a toluene solution under the standard conditions, the catalyst species decomposed rapidly, as judged by the development of a palladium mirror, and the yield of **3ca** was only 7% after 4 days. Another reaction using $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ and $P(OEt)_3$ under the standard conditions afforded **3ca** and **4ca** in yields of 27% and 3%, respectively.

(11) The ^{19}F NMR spectrum and gas chromatogram of the reaction mixture showed the formation of other byproducts. Despite much effort, including performing GC-MS analyses, we were unable to identify the byproducts. However, integration of the ^{19}F NMR signals of all unknown byproducts accounted for the discrepancy between the conversion of the acid chloride and the yield of the identified products. For the ^{19}F NMR spectrum of the reaction mixture, see Supporting Information.



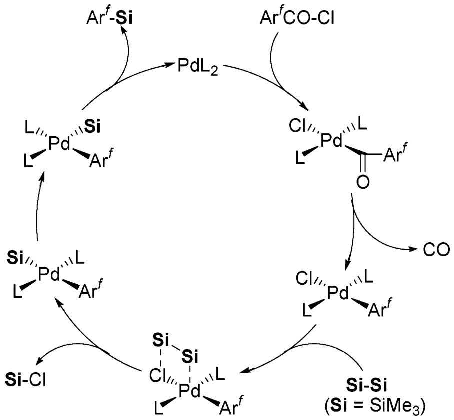
1d **5** 82% (2)

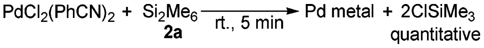
On the other hand, the reaction of heptafluorobutyryl chloride under the standard conditions was not clean, resulting in a messy mixture; although complete consumption of the starting heptafluorobutyryl chloride was confirmed by ^{19}F NMR spectroscopy, neither heptafluorobutyrylsilane nor heptafluoropropylsilane was detected.

Unlike hexamethyldisilane, *sym*-dichlorotetramethyldisilane was quite reluctant to react with fluorinated benzoyl chloride when the reaction was effected in the presence of the phosphite−Pd catalysts or $PdCl_2(PPh_3)_2$ under similar conditions. Only traces (<7%) of decarbonylative coupling products were formed in the reactions of 3,5-difluorobenzoyl chloride and 4-fluorobenzoyl chloride. Pentafluorobenzoyl chloride was even less reactive. This is somewhat peculiar in view of the successful formation of benzoylsilane from plain benzoyl chloride and *sym*-dichlorotetramethyldisilane reported by Rich. The low reactivity of *sym*-dichlorotetramethyldisilane in the reaction with pentafluorobenzoyl chloride is presumably associated with the difficulty of Si−C reductive elimination from C_6F_5−Pd−$SiMe_2$-Cl species (vide infra), in which both C_6F_5−Pd[12] and Pd−$SiMe_2$-Cl[13] are thermodynamically strong bonds.

Mechanistic Aspects of the Reaction. As Yamamoto suggested, the reaction mechanism is best explained by Scheme 2, which is well supported by the following observations. Pd(II) precatalyst is readily reduced to catalytically active Pd(0) species, as evidenced by the quantitative formation of chlorotrimethylsilane (30.1 ppm in ^{29}Si{^{1}H} NMR spectroscopy) upon treatment of $PdCl_2(PhCN)_2$ with hexamethyldisilane (1 equiv) in toluene at room temperature, eq 3.

Scheme 2





$$PdCl_2(PhCN)_2 + \underset{\mathbf{2a}}{Si_2Me_6} \xrightarrow[\text{rt., 5 min}]{} \text{Pd metal} + \underset{\text{quantitative}}{2ClSiMe_3} \qquad (3)$$

Oxidative addition of pentafluorobenzoyl chloride with $Pd(PPh_3)_4$ took place readily and cleanly at both 110 °C and room temperature. In striking contrast with the reaction of plain benzoyl chloride, in which benzoyl−palladium complex is formed,[14] the present reaction afforded *trans*-$C_6F_5PdCl(PPh_3)_2$ (**6**)[15] in excess of 80% isolated yield, suggesting that the pentafluorobenzoyl complex initially generated rapidly extruded carbon monoxide even at room temperature, eq 4. The structure of complex **6** was characterized by X-ray crystallography. The ORTEP drawing and selected bond lengths and angles are shown in Figure 1. The sum of the bond angles around Pd being 360° indicates that the complex has a square planar configuration. The length of the Pd−C bond is 2.011 Å, which, as anticipated, is remarkably shorter than that in *trans*-$C_6H_5PdCl(PPh_3)_2$ (2.407 Å).[16]

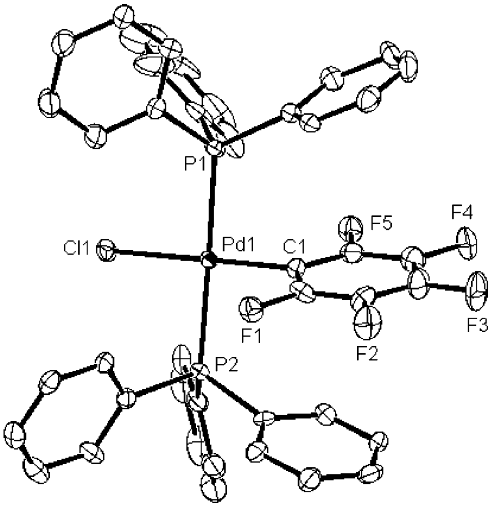
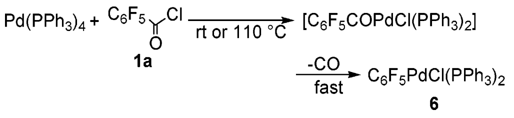


Figure 1. Molecular structure of complex **6**. Thermal ellipsoids are drawn at the 30% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd1−C1 = 2.011(2), Pd1−Cl1 = 2.3552(5), Pd1−P1 = 2.3228(7), Pd1−P2 = 2.3264(7), Cl1−Pd1−P1 = 89.68(2), Cl1−Pd1−P2 = 88.47(2), Cl1−Pd1−C1 = 179.58(7), P1−Pd1−P2 = 177.93(2), P1−Pd1−C1 = 90.61(7), P2−Pd1−C1 = 91.23(7).



(4)

To gain a more realistic view of the mechanism, oxidative addition of pentafluorobenzoyl chloride with a Pd−phosphite complex was also examined. In our literature search for relevant precedents, we have found only two articles describing oxidative addition of organic halides with Pd−phosphite complexes,[17] one of which reports that benzoyl chloride reacts with $[Pd\{P(OPh)_3\}_2]_n$.[17a] In our experiment, a benzene solution of $PdCl_2(PhCN)_2$, $P(OEt)_3$ (2.0 equiv), hexamethyldisilane (1.0 equiv), and C_6F_5COCl (1.0 equiv) was heated at 80 °C. The reaction was slow at this temperature, and ^{19}F NMR spectroscopy

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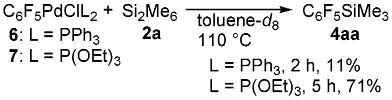
revealed that only a trace of *trans*-$C_6F_5PdCl[P(OEt)_3]_2$ (**7**) had formed after 14 h. In another experiment run at 110 °C for 12 h, C_6F_5COCl was completely consumed and complex **7** was formed in 48% yield, although extensive metallic palladium precipitation was visible and decafluorobiphenyl was also formed in 34% yield (in terms of the C_6F_5 group). Since complex **7** turned out to be an oil, it could be only partially purified. However, the purity of complex **7** obtained after partial purification was >90%, slightly contaminated with decafluorobiphenyl and other unknown compounds, and provided satisfactory ^{31}P NMR and HRMS data to support the structure. The result suggests that, as was observed in the above reaction with $Pd(PPh_3)_4$, the initial adduct, $C_6F_5COPdCl[P(OEt)_3]_2$, is labile, allowing it to undergo decarbonylation under the oxidative addition reaction conditions. Furthermore, in view of decafluorobiphenyl being formed in the absence of extra hexamethyldisilane, complex **7** appears somewhat more labile than complex **6**.

Pentafluorophenyl−palladium complex **6** was found to react with hexamethyldisilane (10 equiv), forming **4aa** in 11% yield (110 °C, 2 h; estimated by ^{19}F NMR spectroscopy), eq 5. Complex **7** behaved similarly (110 °C, 5 h) to give **4aa** and decafluorobiphenyl in yields of 71% and 6%, respectively. The mechanism of this transformation is as yet unclear, but presumably proceeds via *trans*-C_6F_5−Pd−Si species formed by σ-bond metathesis (only this possibility is illustrated in Scheme 1) or oxidative addition−reductive elimination involving Si−Si and C_6F_5−Pd−Cl linkages, isomerization to *cis*-C_6F_5−Pd−Si species, and Si−C reductive elimination.[18]



$$\underset{\substack{\mathbf{6}: L = PPh_3\\ \mathbf{7}: L = P(OEt)_3}}{C_6F_5PdClL_2} + \underset{\mathbf{2a}}{Si_2Me_6} \xrightarrow[\substack{\text{toluene-}d_8\\ 110\ ^\circ C}]{} \underset{\mathbf{4aa}}{C_6F_5SiMe_3} \qquad (5)$$

$L = PPh_3$, 2 h, 11%
$L = P(OEt)_3$, 5 h, 71%

In summary, pentafluorobenzoyl chloride reacts cleanly with hexamethyldisilane in the presence of trialkyl phosphite−palladium complexes to give pentafluorophenyltrimethylsilane as nearly the sole product. The reaction proceeds with concomitant decarbonylation, which is very rapid even at room temperature, as evidenced by the selective formation of *trans*-$C_6F_5PdCl(PPh_3)_2$ in the reaction of pentafluorobenzoyl chloride with $Pd(PPh_3)_4$.

Experimental Section

General Procedures. All manipulations involving air- and moisture-sensitive compounds were carried out under an atmosphere of dry argon or nitrogen, by using standard Schlenk tube techniques. All solvents were distilled over appropriate drying agents prior to use. IR spectra were recorded on a HORIBA FT/IR 730 spectrometer. ^{1}H NMR (300 MHz), ^{13}C{^{1}H} NMR (75 MHz), ^{19}F NMR (282 MHz), and ^{29}Si{^{1}H} NMR (60 MHz) spectra were recorded on a Bruker DPX300 spectrometer at ambient temperatures. ^{31}P{^{1}H} NMR (162 MHz) spectra were recorded on a JEOL JNM-EX400 spectrometer. ^{1}H, ^{13}C{^{1}H}, and ^{29}Si{^{1}H} NMR chemical shifts were reported in ppm relative to internal Me_4Si. ^{19}F NMR chemical shifts were reported in ppm relative to external $CFCl_3$. ^{31}P{^{1}H} NMR chemical shifts were reported in ppm relative to external aqueous 85% H_3PO_4. GC was run on a GL Sciences GC390B chromatograph (silicone OV17 5% on Chromosorb W (60/80 mesh), SUS column 2.0 mm $\phi \times 2.0$ m). GC-MS was run on a Shimadzu GC-MS QP-1100EX mass spectrometer. High-resolution mass spectra were obtained with a JEOL JMS-700 mass spectrometer at an ionization potential of 70 eV. Melting points were measured on a IA9100 micro melting point apparatus (Iuchi-Seieido Ltd.). X-ray crystal structure was determined on a Rigaku AFC10 diffractometer.

Acid chlorides, hexamethyldisilane, and liquid phosphorus-containing ligands were distilled before use. Solid phosphine ligands were recrystallized from EtOH or hexane. The following ligands/complexes were prepared according to the literature: $PhP(OEt)_2$,[19] $Ph_2P(OEt)$,[20] $P(O^nBu)$,[21] $P(O^nPr)$,[21] PMe_3,[22] $PdCl_2(PhCN)_2$,[23] $Pd(PPh_3)_4$,[24] $Pd_2(dba)_3{\cdot}CHCl_3$,[25] $Si_2Me_4Cl_2$.[26]

Typical Procedure for the Catalytic Silylation: The Reaction of Pentafluorobenzoyl Chloride with Hexamethyldisilane Affording 4aa. In a 5 mL Schlenk tube equipped with a three-way stopcock and a magnetic stirring bar were placed $PdCl_2(PhCN)_2$ (39.2 mg, 0.10 mmol), toluene (2 mL), triethyl phosphite (34 μL, 0.20 mmol), pentafluorobenzoyl chloride (0.3 mg, 2.0 mmol), hexamethyldisilane (0.41 mL, 2.0 mmol), and hexafluorobenzene (62.1 mg, an internal standard for ^{19}F NMR analysis) under argon. The mixture was stirred at 110 °C for 5 days. After NMR analysis of the reaction mixture, volatiles were removed under reduced pressure. The residue was purified by Kugelrohr distillation to afford pentafluorophenyltrimethylsilane (**4aa**) as a pale yellow oil in 85% yield, bp 37−38 °C/3 mmHg (lit.[27] 43−45 °C/5 mmHg). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.39 (t, 9H, $^5J_{FH} = 1.3$ Hz, $SiMe_3$). ^{19}F NMR (282.4 Hz, $CDCl_3$): δ −127.6 (quart, 2F, $J = 14.2$ Hz, *o*-F), −152.52 (t, 1F, $J = 19.7$ Hz, *p*-F), −161.9 (m, 2F, *m*-F). The structure was further confirmed by comparing the spectral data with those of an authentic sample prepared via a different route.[27]

(3,5-Difluorobenzoyl)trimethylsilane (3ba). An authentic sample was synthesized from ethyl 3,5-difluorobenzoate by the procedure reported for benzoyltrimethylsilane.[28] The yellow oil we obtained, even after repeated fractional distillation (bp 40−42 °C/0.1 mmHg), was an approximately 1:2 mixture of ethyl 3,5-difluorobenzoate and **3ba**. However, careful analysis of the mixture by comparing with pure ethyl 3,5-difluorobenzoate allowed us to characterize **3ba** as follows. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.31 (m, 2H, *o*-Ph), 6.97 (m, 1H, *p*-Ph), 0.38 (s, 9H, Me). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 232.8 (CO), 163.1 (dd, $^1J_{CF} = 252$ Hz, $^3J_{CF} = 11.5$ Hz, *m*-Ph), 133.7 ($^3J_{CF} = 9.3$ Hz, *ipso*-Ph), 110.0 (AB coupling, $^2J_{CF} = 17.1$ Hz, $^4J_{CF} = 7.9$ Hz, *o*-Ph), 107.8 (t, $^2J_{CF} = 30.2$ Hz, *p*-Ph), −1.6 (TMS). ^{19}F NMR (282 MHz, $CDCl_3$): δ −108.1 (m). ^{29}Si{^{1}H} NMR (75 MHz, $CDCl_3$): δ −5.43 (br s). IR (neat, cm^{-1}): 1627 (ν_{CO}). MS (EI, 20 eV): *m/z* (relative intensity) 214 ([M]$^+$, 5), 199 (8), 171 (12), 73 (100). HRMS (EI, 70 eV): calcd for $C_{10}H_{12}F_2OSi$ 214.0625, found 214.0623. For ^{1}H and ^{13}C{^{1}H} NMR of **3ba** (an approximately 1:2 mixture of ethyl 3,5-difluorobenzoate and **3ba**), see Supporting Information.

(3,5-Difluorophenyl)trimethylsilane (4ba). The synthetic procedure reported by Dunogues and co-workers[29] afforded an

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authentic sample as a pale yellow oil, bp 75−77 °C/20 mmHg (lit.[29] 73 °C/20 mmHg). Spectroscopic data, which have not been described, are as follows. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.91 (m, 2H, *o*-H), 6.69 (m, 1H, *p*-H), 0.21 (s, 9H, Me). ^{19}F NMR (282 MHz, $CDCl_3$): δ −111.1 (t, J = 9.2 Hz).

(4-Fluorobenzoyl)trimethylsilane (3ca). 4-Fluorobenzoyl chloride (2 mmol) and hexamethyldisilane (2 mmol) were heated in a sealed tube at 110 °C for 2 days in the presence of $PdCl_2(PhCN)_2$ (10 mol %) and $P(OEt)_3$ (20 mol %). After ^{19}F NMR analysis of the reaction mixture (57% ^{19}F NMR yield), the mixture was subjected to Kugelrohr distillation to afford **3ca** as a pale yellow oil in 51% yield, bp 95−100 °C/20 mmHg. This compound has been documented[30] without spectral data, which are as follows. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.88−7.83 (m, 2H, *o*-H), 7.16−7.11 (m, 2H, *m*-H), 0.37 (s, 9H, Me). ^{19}F NMR (282 MHz, $CDCl_3$): δ −106.2 (m). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 233.5 (CO), 165.4 (d, J = 254.4 Hz, *p*-C), 130.0 (d, J = 9.1 Hz, *o*-C), 115.4 (d, J = 9.2 Hz, *m*-C), 115.3 (d, J = 21 Hz, *ipso*-Ph), −1.4 (s, Me). ^{29}Si{^{1}H} NMR (60 MHz, $CDCl_3$): δ −50.0. Anal. Calcd for $C_{10}H_{13}FOSi$: C, 61.19; H, 6.68. Found: C, 60.97; H, 6.64.

(4-Fluorophenyl)trimethylsilane (4ca). The synthetic procedure reported by Dunogues and co-workers[29] afforded an authentic sample as a yellow oil. Spectroscopic data, which have not been reported, are as follows. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.43−7.37 (dd, 2H, J_{FH} = 4.9 Hz, J_{HH} = 1.1 Hz, FCC*H*CHCSiMe$_3$), 6.93−6.87 (dd, 2H, J_{FH} = 8.5 Hz, J_{HH} = 1.1 Hz, FCCHC*H*CSiMe$_3$), 0.01 (s, 9H, Me). ^{19}F NMR (282 MHz, $CDCl_3$): δ −115.5 (m).

1,4-Bis(trimethylsilyl)tetrafluorobenzene (5). After the reaction of tetrafluoroterephthaloyl dichloride (1.0 mmol) with hexamethyldisilane (2.0 mmol) under the standard conditions for 10 days, the mixture was evaporated. Dichloromethane was added to the residue, and the mixture was filtered. The filtrate was evaporated and was purified by preparative TLC (hexane) to afford an analytically pure sample of compound **5**, 76% isolated yield, mp 53.5−54.7 °C (lit.[31] 53−55 °C). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.83 (t, J = 6.95 Hz, 18H, Me). ^{19}F NMR (282 MHz, $CDCl_3$): δ −128.5 (br s). Anal. Calcd for $C_{12}H_{18}F_4Si_2$: C, 48.95; H, 6.16. Found: C, 48.83; H, 6.28.

Reaction of $PdCl_2(PhCN)_2$ with Si_2Me_6. A mixture of $PdCl_2(PhCN)_2$ (15.7 mg, 0.041 mmol), Si_2Me_6 (0.041 mmol), and toluene (2.0 mL) was stirred at room temperature for 5 min. Metallic palladium precipitated immediately. Analysis of the resulting mixture by ^{29}Si{^{1}H} NMR spectroscopy ($CDCl_3$) revealed complete consumption of Si_2Me_6 and displayed only one singlet assignable to $SiClMe_3$ (30.1 ppm).

Synthesis of *trans*-$Pd(C_6F_5)Cl(PPh_3)_2$ (6). Pentafluorobenzoyl chloride (20 μL, 0.139 mmol) was added to a greenish-yellow solution of $Pd(PPh_3)_4$ (141 mg, 0.122 mol) in toluene (3.0 mL) placed in a Schlenk tube. Gas evolution started immediately, and the solution became colorless in less than 10 min to afford a white participate. The mixture was stirred for 1 h at room temperature under argon. Volatiles were removed in vacuo, and the residue was washed with Et_2O (5 mL × 2) to afford the title complex as a white powder in 85% yield, mp 233.0−235.0 °C (under Ar, dec). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.89−7.18 (m, 30H, Ph). ^{19}F NMR (282 MHz, $CDCl_3$): δ −119.17 (m, 2F, *o*-F), −164.6 (t, 1F, J = 19.8 Hz, *p*-F), −164.9 (t, 2F, J = 19.8 Hz, *m*-F). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 24.9 (t, J = 7.3 Hz). Anal. Calcd for $C_{42}H_{30}ClF_5P_2Pd$: C, 60.52; H, 3.63. Found: C, 60.15; H, 3.31.

Synthesis of *trans*-$Pd(C_6F_5)Cl[P(OC_2H_5)_3]_2$ (7). To a toluene (5.0 mL) solution of $PdCl_2(PhCN)_2$ (122.3 mg, 0.32 mmol) was added $P(OEt)_3$ (110 μL, 0.64 mmol) and Si_2Me_6 (65 μL, 0.32 mmol). After stirring at room temperature for 5 min, the mixture was treated with pentafluorobenzoyl chloride (46 μL, 0.32 mmol) and was heated at 110 °C for 12 h, while a black powdery material gradually precipitated. Volatiles were evaporated, and benzene-d_6 (1.0 mL) and hexafluorobenzene (26 μL, internal standard for ^{19}F NMR analysis) were added. Analysis of the mixture by ^{19}F NMR spectroscopy showed that complex **7** had been formed in 48% yield together with decafluorobiphenyl (34% in terms of the pentafluorophenyl group). Addition of hexane (10 mL), filtration to remove the black powder and majority of decafluorobiphenyl, and evaporation of volatiles (40 °C/0.01 mmHg) afforded a colorless oil (71 mg). Analysis by ^{31}P and ^{19}F NMR spectroscopies confirmed its purity being in excess of 90%. ^{1}H NMR (300 MHz, benzene-d_6): δ 4.19 (m, 12H, OCH_2CH$_3$), 1.08 (m, 18H, OCH$_2$CH_3). ^{13}C{^{1}H} NMR (75 MHz, benzene-d_6): δ 62.5 (br s, O*C*H$_2$CH$_3$), 16.1 (virtual t, J = 3.17 Hz, OCH$_2$*C*H$_3$). Signals associated with carbons in the pentafluorophenyl group were too weak to be observable due presumably to multiple couplings with F nuclei. ^{19}F NMR (282 MHz, benzene-d_6): δ −139.6 (m, 2F, *o*-F), −162.3 (m, 1F, *p*-F), −165.4 (t, 2F, J = 19.7 Hz, *m*-F). ^{31}P{^{1}H } NMR (162 MHz, benzene-d_6): δ 105.2 (t, J = 11.6 Hz). HRMS (FAB, matrix = 3-nitrobenzyl alcohol): calcd for $C_{18}H_{31}ClF_5O_6P_2{}^{106}Pd$ (value for $[M + 1]^+$) 641.0239, found 641.0233. For ^{1}H, ^{13}C{^{1}H}, ^{19}F, and ^{31}P{^{1}H} NMR spectra of this material of >90% purity, see Supporting Information.

Reaction of *trans*-$Pd(C_6F_5)Cl(PPh_3)_2$ with Si_2Me_6. A mixture of *trans*-$Pd(C_6F_5)Cl(PPh_3)_2$ (4.2 mg, 5.0 μmol), Si_2Me_6 (10 μL, 49 μmol), and toluene-d_8 (0.5 mL) was heated in a sealed NMR tube at 110 °C for 2 h. ^{19}F NMR spectroscopy revealed the formation of $C_6F_5SiMe_3$ in 11% yield.

Reaction of *trans*-$Pd(C_6F_5)Cl[P(OC_2H_5)_3]_2$ with Si_2Me_6. To *trans*-$Pd(C_6F_5)Cl[P(OEt)_3]_2$ (>90% purity, 25.6 mg, 0.0399 mmol on the assumption of 100% purity) placed in an NMR tube were added toluene-d_8 (0.5 mL), Si_2Me_6 (5.6 μL, 0.03 mmol), and hexafluorobenzene (2.2 mg, internal standard for ^{19}F NMR analysis). Heating the mixture at 80 °C for 1 h did not promote the reaction to an appreciable extent. Further heating for 5 h at 110 °C resulted in deposition of palladium mirror. ^{19}F NMR analysis showed signals arising from $C_6F_5SiMe_3$ (71% based on Si_2Me_6), decafluorobiphenyl (approximately 6% based on complex **7**), and a trace of unreacted **7** (approximately 3%).

Molecular Structure Analysis of Complex 6. Single crystals were grown from a CH_2Cl_2 solution. A suitable colorless crystal (0.18 × 0.15 × 0.10 mm) was used for X-ray diffraction data collection with Mo Kα radiation (λ = 0.7107 Å). Crystal data for **6**: $Cl_2F_{10}P_2Pd_2C_{84}H_{60}$, M = 1605.04, monoclinic, space group = $P2_1/a$ (#14), a = 23.287(4) Å, b = 11.9507(17) Å, c = 25.667(4) Å, β = 90.019(2)°, V = 7143.1(18) Å^3. Z = 4, density(calc) = 1.492, $2\theta_{max}$ = 55.0°. Total reflections collected = 16 228, GOF = 1.031. The final R factor was 0.0747 (R_w = 0.0773 for all data). The structure was solved by direct methods (SIR97) and refined by full-matrix least-squares method by using the SHELXL program.

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Supporting Information Available: ^{1}H and ^{13}C{^{1}H} NMR spectra of compound **3ba**, ^{1}H, ^{13}C{^{1}H}, ^{19}F, and ^{31}P{^{1}H} NMR spectra of complex **7**, ^{19}F NMR spectrum of the reaction mixture of entry 3, Table 2, and crystallographic data for **6** in CIF format. The material is available free of charge via the Internet at http://pubs.acs.org.

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