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Transition-metal-free catalytic hydrodefluoronation of polyfluoroarenes via a concerted nucleophilic aromatic substitution with a hydrosilicate

Kotaro Kikushima, Mary Grellier, Masato Ohashi, and Sensuke Ogoshi*

Abstract: The transition-metal-free catalytic hydrodefluorination (HDF) reaction of polyfluoroarenes is described, which involves a direct hydride transfer from a hydrosilicate as the key intermediate, generated from a hydrosilane and a fluoride salt. The eliminated fluoride regenerates the hydrosilicate to complete the catalytic cycle. Dispersion-corrected density functional theory (DFT) calculations indicated that the HDF reaction proceeds via a concerted nucleophilic aromatic substitution (CS_NAr) reaction.

The demand for the development of an efficient methodology for the synthesis of organofluorine compounds is increasing.[1,2] So far, fluoroarenes have been synthesized by two complementary approaches: the introduction of a fluorine atom into an aromatic ring, or the substitution of a fluorine atom of polyfluoroarenes with other atoms/groups. As far as the former approach is concerned, aryl fluorides have been obtained from various fluorinations methods, including transition-metal-catalyzed C-F bond formations through the substitution of heteroatoms, or directing-group-assisted C-H bond activation methods,[3] both of which are alternatives to more traditional methods such as the Balz-Scheiman reaction[4] or the halex process.[5] These reactions, however, require the pre-installations of heteroatoms or directing groups, which renders polyfluorinations difficult. The second approach, i.e., the substitution of a fluorine atom of polyfluoro-arenes with other atoms/groups, which includes nucleophilic substitutions or the activation of C-F bonds in polyfluoroarenes[6–11] circumvents these obstacles. The hydrodefluorination (HDF), i.e., the substitution of a fluorine with a hydrogen atom, should be a promising approach for the synthesis of polyfluorinated building blocks from readily available fluorinated bulk chemicals.[7–12] Substantial efforts have been devoted to transition-metal-catalyzed HDF reactions via the activation of the inert C-F bond (Figure 1a).[7–9] However, these reactions should represent a severe drawback, given that employing elaborate catalysts
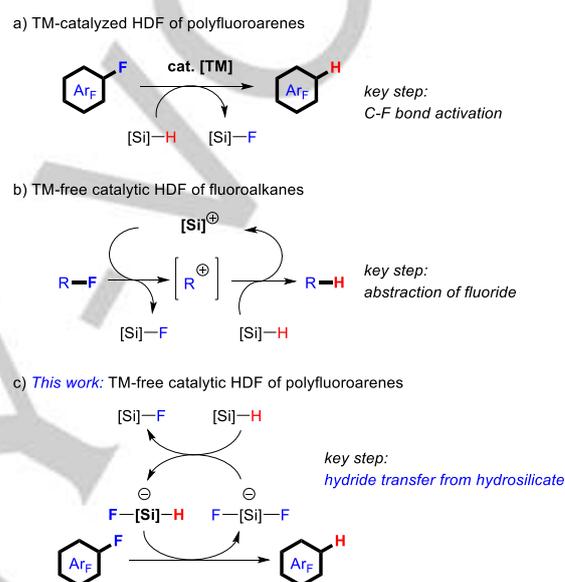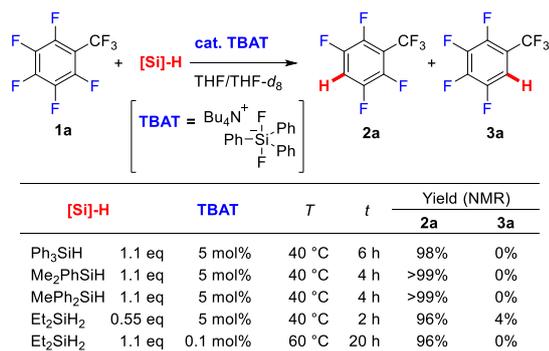
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        and specially appointed Prof. at Osaka University 2016–2017.

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a) TM-catalyzed HDF of polyfluoroarenes

key step:
C-F bond activation

b) TM-free catalytic HDF of fluoroalkanes

key step:
abstraction of fluoride

c) *This work:* TM-free catalytic HDF of polyfluoroarenes

key step:
hydride transfer from hydrosilicate

Figure 1. Various Catalytic HDF Reactions.

usually increases costs significantly and inevitably leads to a contamination of the obtained products with metal traces. Moreover, transition-metal catalysts usually suffer from the strong affinity between the metal and fluorine atoms, which leads in many cases to catalyst deactivation. To accomplish catalytic HDF reactions, the combination of electron-rich late transition metals and fluorophilic reductants such as hydrosilanes has been employed. Recently, photocatalytic HDF reactions using an Ir complex[9] or a pyrene derivative[10] with diisopropylethylamine as the hydride source have been reported, wherein high catalytic turnover numbers (TONs) were achieved due to the low propensity to form deactivating M-F bonds. The reaction with triethylphosphine has also been reported, albeit that the required high temperatures and long reaction times.[11] For aliphatic C-F bonds, catalytic HDF reactions have been achieved by using silylium cations, wherein the abstraction of fluorides from the alkyl fluorides is the key step (Figure 1b).[12] However, substrates were limited in this case to alkyl fluorides, and uncontrollable multi-HDF reactions occurred in the case of polyfluoroalkenes. Given these circumstances, the development of more economical and practical methods for the HDF of polyfluoroarenes in the absence of transition-metal catalysts represents an eagerly anticipated milestone on the road to effective and efficient syntheses of functionalized polyfluoroarenes.

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Scheme 1. HDF reaction of octafluorotoluene using a catalytic amount of TBAT with various hydrosilanes. General conditions: **1a** (0.12 mmol), hydrosilane, TBAT (5 mol%), and THF/THF-d_8 (0.50 mL) were mixed in J. Young NMR tube. Yields were determined by ^{19}F NMR.

To develop such transition-metal-free HDF reactions, we have focused on pentacoordinated hydrosilicates, which exhibit enhanced nucleophilicity of the hydride on the silicon center.[13–15] In fact, facile catalytic hydrosilylations of aldehydes and ketones have been achieved by a hydride transfer from hydrosilicates generated from hydrosilanes and fluoride salts.[13] Moreover, the copolymerization of perfluoroarene with disilylacetylenes in the presence of a catalytic amount of fluoride salts through the nucleophilic attack of alkynyl groups to perfluoroarenes have been reported.[16] In both reactions, the key to successful catalytic reactions is the reactivation of the silanes by coordination of anionic species such as alkoxides or fluorides to the silicon center in order to regenerate the pentacoordinated silicates. These reactions prompted us to investigate the possibility of a hydrosilicate that could act as a highly reactive catalyst for the HDF of polyfluoroarenes via a hydride transfer, wherein the eliminated fluoride could regenerate the hydrosilicate to complete the catalytic cycle (Figure 1c). Herein, we describe the first example of a transition-metal-free catalytic HDF of polyfluoro-arenes using pentacoordinated hydrosilicates. The underlying reaction mechanism was elucidated by stoichiometric reactions and density functional theory (DFT) calculations.

Initially, we optimized the HDF of octafluorotoluene (**1a**) as a model substrate (Scheme 1 and Supplementary Information). In the presence of 5 mol% of tetrabutylammonium difluorotriphenyl-silicate (TBAT), the reaction with Ph$_3$SiH, Me$_2$PhSiH, or MePh$_2$SiH furnished 1-trifluoromethyl-2,3,5,6-tetrafluorobenzene (**2a**) quantitatively as the sole product. Using Et$_2$SiH$_2$, the reaction reached completion faster to afford **2a** (96%) together with a small amount of **3a** (4%). The combination of TBAT and Et$_2$SiH$_2$ was highly efficient, i.e., 0.1 mol% of catalyst afforded **2a** in 96% yield.
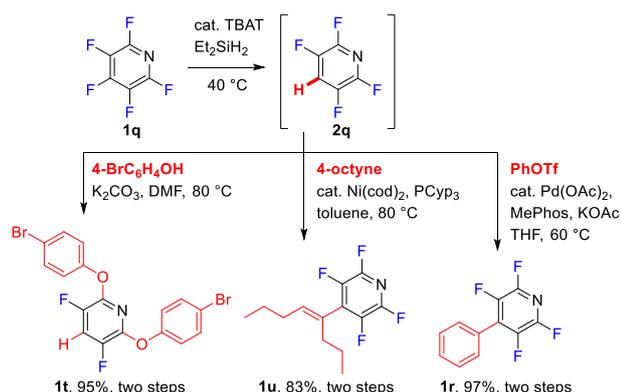
This catalytic HDF reaction can be applied to a variety of polyfluoroarenes (Scheme 2). The reaction of hexafluorobenzene (**1b**) with 1.08 eq of Et$_2$SiH$_2$ afforded pentafluorobenzene (**2b**) together with tetrafluorobenzenes (**3–5b**) via a twofold HDF. Employing **2b** furnished 1,2,4,5-tetrafluorobenzene (**3b**) in 90% yield with high regioselectivity, which is consistent with the ratio of twofold HDF products starting from **1b**. The HDF of **3b** was sluggish, even at 100 °C. Decafluorobiphenyl (**1c**) reacted with 1.08 eq of Et$_2$SiH$_2$ to afford the twofold HDF product **2c**, wherein a single HDF occurred on each ring. Ocatafluoronaphthalene (**1d**)
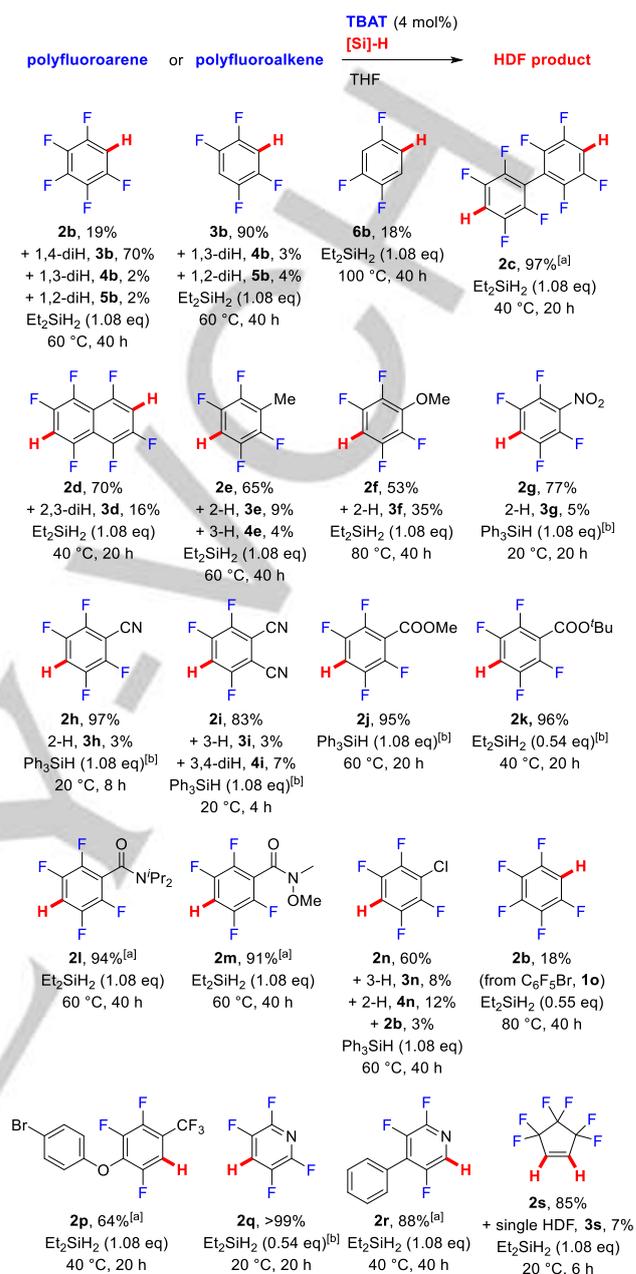
Scheme 2. Hydrosilicate-catalyzed HDF reaction of various polyfluoroarenes and octafluorocyclopentene. General conditions: **1** (0.50 mmol), hydrosilane, TBAT (4 mol%), and THF (0.50 mL) were mixed in J. Young NMR tube. Yields of the products with high volatility were determined by ^{19}F NMR. [a] Isolated yield. [b] With 1 mol% TBAT.

also underwent the twofold HDF to afford the mixture of **2d** and **3d**. The reactions of 2,3,4,5,6-pentafluorotoluene (**1e**) and 2,3,4,5,6-pentafluoroanisole (**1f**) afforded the corresponding products (**2–4e**, **2f**, and **3f**), albeit with decreased reactivity due to the relatively high electron density. This HDF reaction tolerates various functional groups including multiple bonds. Polyfluoro-benzenes bearing nitro (**1g**) and cyano group (**1h** and **1i**) afforded the corresponding HDF products in high yields even when Ph$_3$SiH and 1 mol% of TBAT were used at 20 °C. In the case of
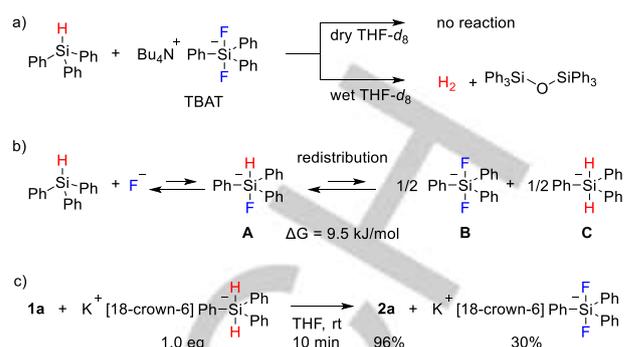
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**Scheme 3.** One-pot synthesis of polyfluoroarenes using the present HDF.

Scheme 4. a) Stoichiometric reactions between Ph₃SiH and TBAT. b) Redistribution reaction of fluorohydrosilicate. The DFT calculations were carried out using the B3PW91 functional in combination with the 6-311++G** basis set and Grimme's DFT-D3 London-dispersion correction with Becke-Johnson damping (D3BJ). c) Stoichiometric reactions of octafluorotoluene with dihydrosilicate. Yields were determined by ^{19}F NMR.

pentafluorobenzoic acid esters (**1j** and **1k**) or amides (**1l** and **1m**), the HDF reaction proceeded exclusively at the 4-position. Chloropentafluoro-benzene (**1n**) produced a mixture of HDF products (**2–4n**) and a small amount of hydrodechlorination product **2b**. In contrast, Bromopentafluorobenzene (**1o**) underwent only hydridebromina-tion to afford **2b**. Conversely, in the reaction of **1p**, the bromine atom bound to the non-fluorinated phenoxy group remained intact and HDF product **2p** was obtained as the sole product. Polyfluoro-pyridines (**1q** and **1r**) were also converted into the corresponding products (**2q** and **2r**) in high yields. Furthermore, octafluoro-cyclopentene **1s** could be transformed, whereby only the HDF of the alkenyl fluoride proceeded to afford **2s** and **3s**. In the present HDF reaction, various solvents can be used and the only by-products are fluorosilanes that should be innocent regarding further transformations. Thus, we subsequently examined one-pot procedures without purifications (Scheme 3). For example, tetrafluoropyridine (**2p**), prepared by the present HDF in DMF, was directly treated with 4-bromophenol in the presence of K₂CO₃ to afford fluorine-containing polyarylether (**1s**). This one-pot procedure could be applied to the synthesis of 4-substituted 2,3,5,6-tetrafluoropyridines (**1u** and **1r**) via the HDF reaction, followed by nickel- or palladium-catalyzed coupling reactions.

To gain deeper insight into the reaction mechanism involving the pentacoordinated fluorohydrosilicate,[13b,14a,15] we conducted stoichiometric reactions between hydrosilanes and fluoride salts (Scheme 4 and Supplementary Information). A mixture of Ph₃SiH and TBAT in THF-d_8 at room temperature did not show any evidence for the formation of either fluorohydrosilicate or dihydrosilicate on NMR due to their instability (Scheme 4a, top). On the other hand, the same reaction in the presence of a small amount of water afforded hydrogen and Ph₃SiOSiPh₃ (Scheme 4a, bottom),[14a] which was not observed in the absence of TBAT. These results suggest that the combination of Ph₃SiH and TBAT generates highly reactive hydrosilicates (Scheme 4b). Fluorohydrosilicate **A** can generate difluorosilicate **B** and dihydrosilicate **C** via a redistribution.[15,17] DFT calculations using Grimme's DFT-D3 London-dispersion correction Becke-Johnson damping (D3BJ)[18] indicates in a qualitative trend that equilibrium is possible between the different forms (estimated ΔG = 9.5 kJ/mol at 298 K). We next examined a stoichiometric reaction of **1a** with 1.0 eq of dihydrosilicate (K⁺[18-crown-6]Ph₃SiH₂⁻)

(Scheme 4c).[15] The HDF proceeded smoothly to afford **2a** (96%) and difluorosilicate (K⁺[18-crown-6]Ph₃SiF₂⁻) along with Ph₃SiH and probably KF. These results suggest that the present HDF reaction involves the generation of hydrosilicates.

The proposed catalytic cycles, which involve a hydride transfer from either fluorohydrosilicate **A** or dihydrosilicate **C**, are shown in Figure 2. Initially, **A** should be generated by the reaction of the hydrosilane with TBAT (**B**). In **cycle I** (Figure 2a, left), the polyfluoroarene could coordinate to **A** via π-π stacking,[19] followed by isomerization to **cis-D**, which should undergo a hydride transfer through **TS D-E** to afford intermediate **E** (Video 1). The eliminated fluoride should be trapped intramolecularly by a fluorosilane or a hydrosilane to regenerate **B** or **A**, respectively. **Cycle II** (Figure 2a, right) shows an alternative path that involves dihydrosilicate **C** as a key intermediate, which could be generated through the redistribution of **A**. The hydride transfer from **cis-F** could proceed via **TS F-G** to generate intermediate **G** (Video 2). The eliminated fluoride should be trapped by a hydrosilane to regenerate **A** under concomitant formation of the HDF product. In order to get qualitative trends, the energy profiles based on DFT calculations with D3BJ, carried out at 353.15 K using a polarizable continuum model (PCM) for the solvent (THF), are depicted in Figure 2b. The relative Gibbs energy of **TS F-G** (ΔG = +45.0 kJ/mol) was lower than that of **TS D-E** (ΔG = +79.4 kJ/mol), which suggests that the reaction should proceed more likely via **path II** than **path I**. Furthermore, we calculated the regioselectivity of the HDF reaction using pentafluorobenzene with Ph₃SiH involving **A** or **C**, and compared the results to those of the experimental ratio (Supplementary Information). The HDF reaction of pentafluoro-benzene at 60 °C afforded tetrafluoro-benzene as an isomeric mixture (*p:m:o* = 82:2:16), and the ratio was in better agreement with the calculated values for **B** (*p:m:o* = 84:4:11 with Grimme's DFT-D3 London-dispersion correction on with zero damping (D3); *p:m:o* = 72:4:24 with D3BJ) than with those for **A** (*p:m:o* = 95:2:3 with D3; *p:m:o* = 95:1:4 with D3BJ). These results also support the notion that the present HDF proceeds via a hydride transfer from **B**. It should be noted that the DFT calculations showed single transition states (**TS D-E** and **TS F-G**), while Meisenheimer-type intermediates were not observed on either

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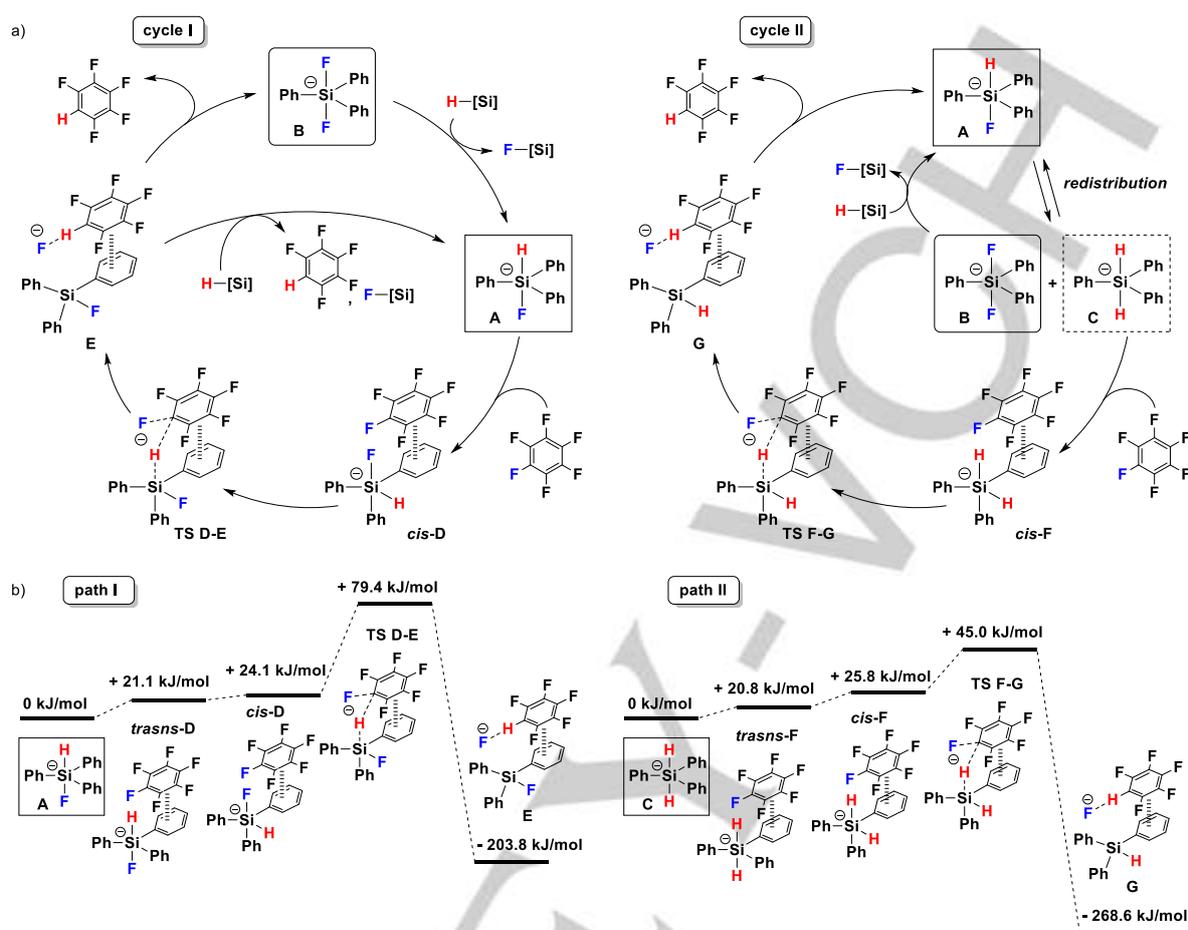
Figure 2. Proposed reaction mechanism and energy profiles for the present HDF reaction. The dotted lines in **TS D-E** and **TS F-G** represent the bonds involved in the transition state, albeit that they are not representative of the degree of the activation. DFT Calculations were carried out using the B3PW91 functional in combination with the 6-311++G** basis set and Grimme's DFT-D3 London-dispersion correction with Becke-Johnson damping (D3BJ). The solvent (THF) was modeled by application of a polarizable continuum model (PCM). The energy profiles represent the relative Gibbs energies.

paths. These results indicate that the present HDF proceeds via a concerted nucleophilic aromatic substitution (CS_NAr) reaction rather than via a classical two-step nucleophilic aromatic substitution (S_NAr) reaction. Similar transition states are thus suggested as a key step for deoxyfluorination or hydro-dehalogenation reactions.[20]

In conclusion, we have demonstrated a HDF reaction of polyfluoroarenes catalyzed by pentacoordinated hydrosilicates. DFT calculations suggests that the reaction should proceed via a concerted nucleophilic aromatic substitution (CS_NAr) reaction, whereby Meisenheimer-type intermediates are not generated. These findings should thus provide an alternative synthetic approach to polyfluoroarenes.

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[19]   The DFT calculations have been conducted using Grimme's dispersion correction in order to take into a better account the possibility of the intermolecular non-covalent interaction. With the optimized structures of intermediates, the polyfluoroarene or the HDF product are close to one of the phenyl group attached to the silicon center. When the combinations of Et_2SiH_2 with tetrabutylammonoum fluoride (TBAF) or tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF) were employed, the reactivity was decreased (see Supplementary Information). These results suggests that the π-π stacking induced by the phenyl group on silicon center may influence the reactivity.

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A simple but artful combination: Transition-metal-free catalytic hydrodefluorination (HDF) of polyfluoroarenes was enabled by hydrosilicate catalyst formed in situ from hydrosilane and fluoride ion. The reaction involves a direct hydride transfer from the hydrosilicate through a nucleophilic aromatic substitution reaction (CS_NAr).

Transition-metal-free hydrodefluorination
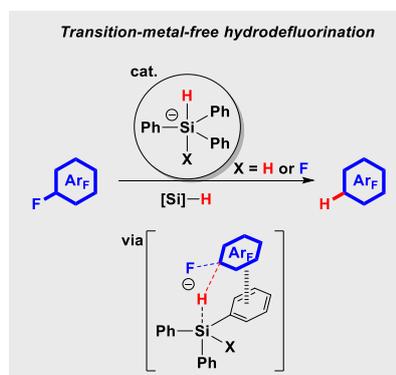
Kotaro Kikushima, Mary Grellier, Masato Ohashi, and Sensuke Ogoshi*

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Transition-metal-free catalytic hydrodefluoronation of polyfluoroarenes via a concerted nucleophilic aromatic substitution with a hydrosilicate

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