Nickel-catalyzed exhaustive hydrodefluorination of perfluoroalkyl arenes

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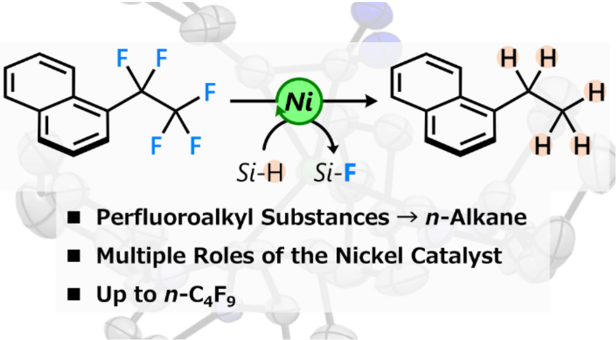
Abstract



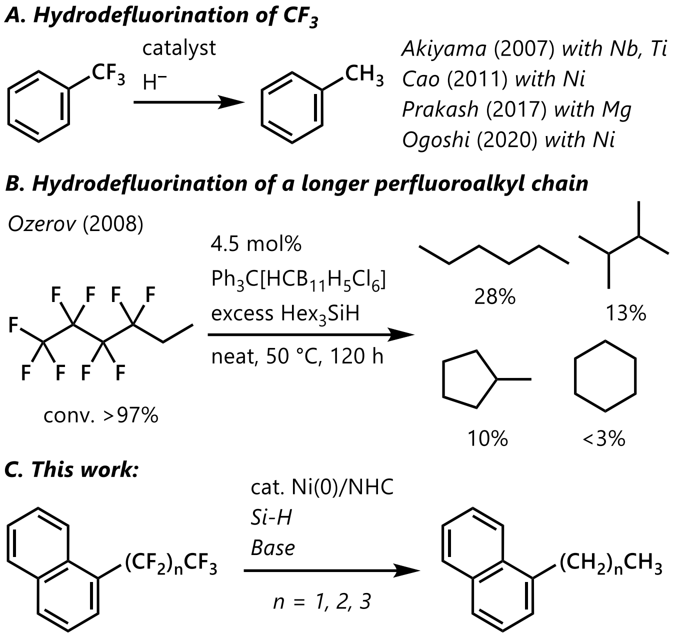
Perfluoroalkyl compounds are persistent environmental pollutants due to their strong $C(sp^3)-F$ bonds. Hydrodefluorination has emerged as a potential alternative disposal method for perfluoroalkyl compounds. Although the transformation of trifluoromethyl arenes into the corresponding methyl arenes has been studied by several research groups, hydrodefluorination reactions of longer perfluoroalkyl chains remain rare. Herein, we report exhaustive hydrodefluorination reactions of pentafluoroethyl arenes and longer-chain analogues using molecular nickel catalysis. Despite the cleavage of multiple $C(sp^3)-F$ bonds, the reaction already proceeds upon gentle heating (60 °C). A mechanistic investigation indicated that the reaction proceeds via benzylic hydrodefluorination reactions followed by homobenzylic ones. We reveal the multiple roles of the Ni catalyst,

which include C−F bond cleavage, promotion of HF elimination, and hydrosilylation.

Introduction

Perfluoroalkyl compounds that contain at least one CF_3 or difluoromethylene group are recognized as persistent environmental pollutants. Many organofluorine compounds have been produced in the chemical industry, as their unique chemical, physical, and physiological properties have found various applications in pharmaceuticals, agrochemicals, surfactants, refrigerants, and polymers.[1,2] One of the most remarkable properties of perfluoroalkyl substances is their chemical and thermal stability, which is derived from the strong $C(sp^3)-F$ bonds. However, the inertness of these materials hampers their destruction. The continuous environmental release of perfluoroalkyl substances has resulted in their ubiquity as persistent pollutants in air, water, and soil.[3] Some perfluoroalkyl gases show high global warming potentials,[4] while others have been reported to accumulate in living organisms, including human beings.[5] Therefore, the development of efficient decomposition methods is in urgent demand. The incineration of perfluoroalkyl substances requires very high temperatures and has the potential to produce volatile organofluorine waste.[6] Other disposal methods are currently under intense investigation.[7] For instance, recently, a mild homogeneous mineralization of perfluoroalkanoic acids with sodium hydroxide in DMSO has been developed.[8]

Hydrodefluorination is a potential alternative disposal method for perfluoroalkyl compounds. The replacement of all the fluorine atoms of a perfluoroalkyl substance with hydrogen atoms produces a hydrocarbon, which can be disposed of using common methods such as burning or biodegradation. A large number of hydrodefluorination reactions have been developed following the seminal paper of Milstein using homogeneous catalysis.[9–11] However, it should be noted here that most of the hydrodefluorination reactions reported to date involve the conversion of $C(sp^2)-F$ bonds, and that the $C(sp^3)-F$ bonds of perfluoroalkyl groups are more stable than those of monofluoroalkanes.[12] The occurrence of dipolar resonance structures as well as steric shielding of carbon centers by fluorine atom(s) are obstacles to the ready transformation of C−F bonds in perfluoroalkyl groups. One example of such a hydrodefluorination of aliphatic C−F bonds is that reported by Jones using a stoichiometric amount of a Zr hydride complex, in which the reduction of CF_3 was sluggish.[13,14]



Scheme 1. Hydrodefluorination reactions. A. Hydrodefluorination of CF_3. B. Hydrodefluorination of a longer perfluoroalkyl chain reported by Ozerov. C. This work: Hydrodefluorination of a longer perfluoroalkyl arene using a nickel catalyst.

Nonetheless, chemists have succeeded in developing some reactions for the hydrodefluorination of trifluoromethyl arenes into methyl arenes (Scheme 1). Some metal salts, such as $NbCl_5$,[15,16] $TiCl_4$,[17,18] and $NiCl_2$,[19] are efficient catalysts for the hydrodefluorination of benzotrifluorides in the presence of metal hydride sources. Prakash has demonstrated that Mg powder suspended in water, acetic acid, and DMSO is an efficient reductant for benzotrifluoride carrying a nitrile group.[20] Our group has discovered that a low-valent nickel complex is an active catalyst for the hydrodefluorination of 1-trifluoromethyl naphthalene using hydrosilane as a hydride source.[21] We have revealed that the low-valent nickel complex directly cleaves a $C(sp^3)$–F bond of the benzotrifluorides via oxidative addition, which was studied by stoichiometric reactions and density-functional-theory (DFT) calculations.

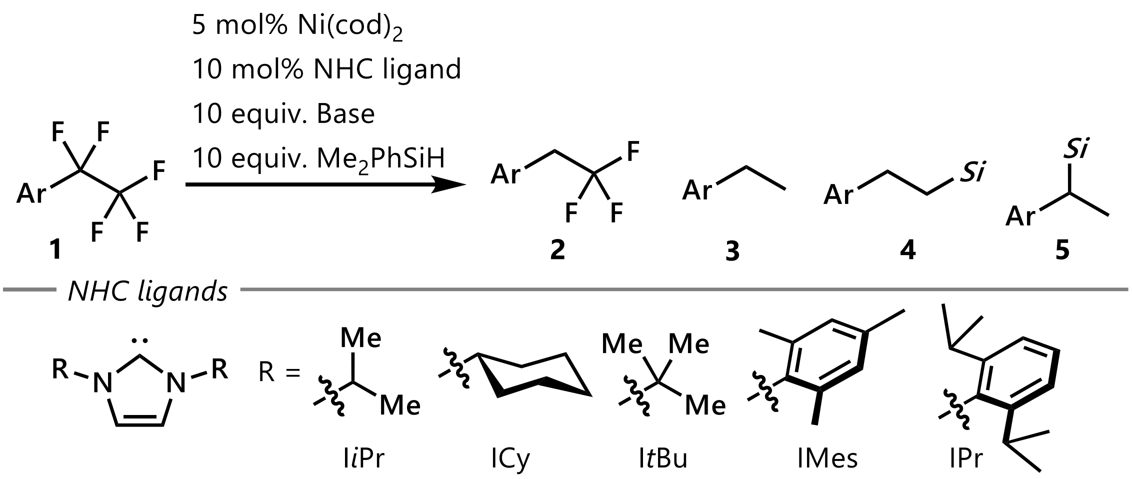
Compared to exhaustive hydrodefluorination reactions of trifluoromethyl groups, those of longer perfluoroalkyl chains are scarce. Ozerov has disclosed that a hydrodefluorination reaction of 1,1,1,2,2,3,3,4,4-nonafluorohexane with trihexylsilane proceeds under mild conditions (50 °C) using $Ph_3C[HCB_{11}H_5Cl_6]$ as a catalyst.[22] The carborane counter cation is essential to achieve the high turnover number (TON) through stabilization of the active cationic silyl species. The substrate scope for the perfluoroalkyl group, which was limited to this single example, prompted us to investigate the possibility of using a nickel catalyst for the hydrodefluorination of longer perfluoroalkyl chains. Herein, we report exhaustive hydrodefluorination reactions of pentafluoroethylarenes and longer-chain analogues using molecular nickel catalysis.

Reaction-Condition Screening

We commenced our investigation by applying our previously reported protocol to 1-pentafluoroethylnaphthalene (**1**; Table 1, entry 1).[21] However, the reaction of **1** with 10 equiv. of Me_2PhSiH (2 equiv. of Si−H relative to the amount of C−F bonds) in the presence of CsF and a catalytic amount of $Ni(cod)_2$ and 1,3-diisopropylimidazol-2-

ylidene (I*i*Pr) did not give 1-(2,2,2-trifluoroethyl)naphthalene (**2**), but instead produced the exhaustive hydrodefluorination product 1-ethylnaphthalene (**3**) in 37% yield. We also observed the formation of small amounts of alkyl silanes **4** and **5** in the reaction mixture. We then tested other *N*-heterocyclic (NHC) ligands (entries 2–5) and identified 1,3-dicyclohexyllimidazol-2-ylidene (ICy) as the ligand that produced **3** in the highest yield. Next, we investigated the effect of varying the base on the reaction outcome. While the reaction using KF gave a similar result (entry 6), the addition of K_3PO_4 increased the yield of **3** to 86% (entry 7). Under these reaction conditions, we observed the formation of 83% $PhMe_2SiF$ (**6**) relative to the amount of C−F bonds. When the amount of K_3PO_4 was reduced to 1 equiv., the yield of **3** decreased by 32% with concomitant production of silane **5** in 35% yield (entry 8). This result implies that silane **5** was transformed into hydrocarbon **3** upon addition of excess hygroscopic K_3PO_4, which introduces a certain amount of water. In the absence of a base, the yield of hydrocarbon **3** decreased (entry 9). In this case, we observed benzylic hydrodefluorination product **2**, indicating that the addition of a base accelerates the transformation of **2** into **3**. When we performed the reaction with a reduced amount of silane (entry 10), for a shorter time (entry 11), or at a lower temperature (entry 12), a non-negligible amount of **2** was observed in each case. This observation supports the conclusion that **2** is a reaction intermediate to produce **3** (*vide infra*). Control experiments showed that the reaction is promoted by a nickel complex, albeit that a small quantity of the hydrodefluorination product was obtained without adding an NHC ligand (entries 13, 14).

Table 1. Screening of the reaction conditions [a]

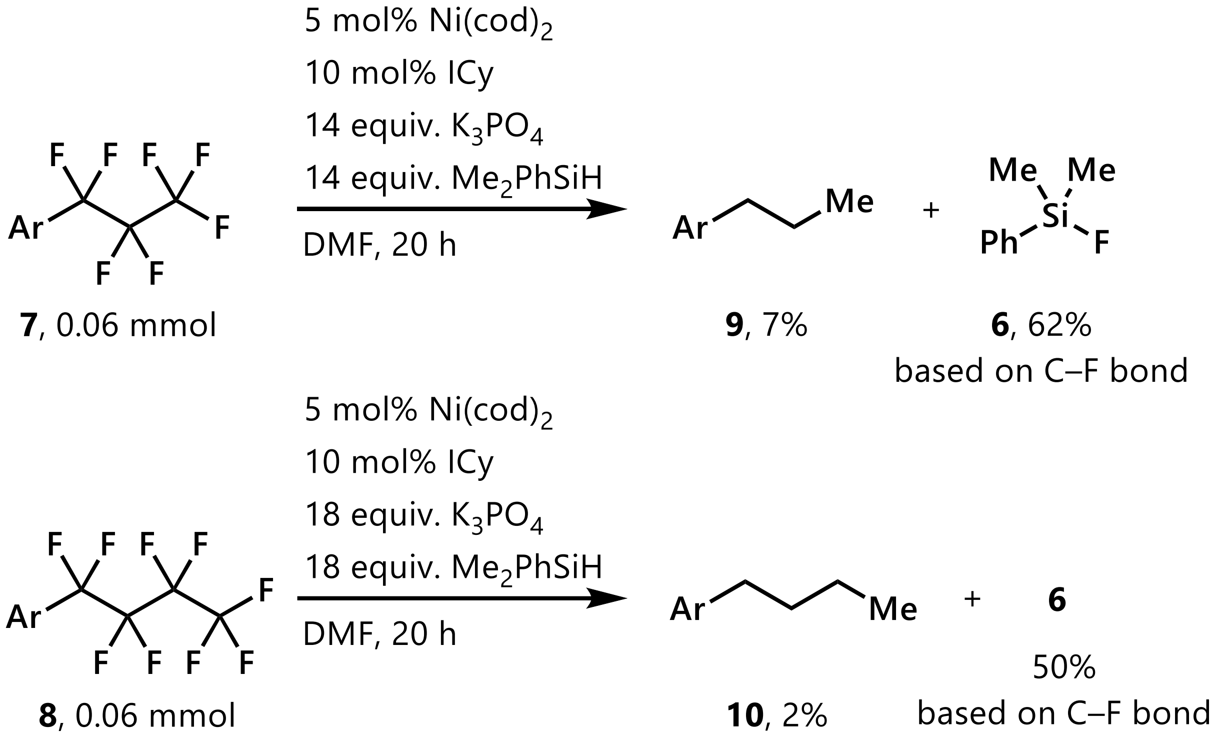


Entry	Ligand	Base	Solvent	GC Yield			
				2	**3**	**4**	**5**
1	I*i*Pr	CsF	DMF	n.d.	37%	9%	1%
2	ICy	CsF	DMF	n.d.	58%	12%	trace
3	I*t*Bu	CsF	DMF	n.d.	30%	19%	n.d.
4	IMes	CsF	DMF	3%	18%	8%	2%
5	IPr	CsF	DMF	4%	2%	3%	2%
6	ICy	KF	DMF	n.d.	51%	6%	31%
7	ICy	K_3PO_4	DMF	n.d.	86%	10%	trace
8[b]	ICy	K_3PO_4	DMF	n.d.	54%	9%	35%
9	ICy	-	DMF	37%	15%	5%	33%
10[c]	ICy	K_3PO_4	DMF	9%	83%	8%	trace
11[d]	ICy	K_3PO_4	DMF	31%	42%	8%	8%
12[e]	ICy	K_3PO_4	DMF	22%	47%	6%	22%
13[f]	ICy	K_3PO_4	DMF	n.d.	n.d.	n.d.	n.d.
14	-	K_3PO_4	DMF	8%	1%	5%	trace

[a] Ar = 1-naphthyl; *Si* = Me$_2$PhSi; n.d. = not detected. Yields were determined by GC analysis of the reaction mixture after 20 h of stirring using dodecane as an internal standard. [b] 1 equiv. of base. [c] 0.7 equiv. of silane. [d] 6 h. [e] 40 °C. [f] In the absence of any nickel source.

Reactions of Longer Perfluoroalkyls

Our discovery of homobenzylic C−F bond cleavage posed the question of how long a perfluoroalkyl chain could be exhaustively hydrodefluorinated by this nickel catalysis. For this purpose, we synthesized 1-heptafluoropropylnaphthalene (**7**) and 1-nonafluorobutylnaphthalene (**8**) and tested their reactivity. The reaction of **7** with 14 equivalents of hydrosilane and K_3PO_4 resulted in poor conversion of the starting material (~30%), which prompted us to test the reaction at a higher temperature. At 120 °C, **7** was fully converted and a small amount of fully hydrodefluorinated product **9** was detected. Under these conditions, fluorosilane **6** was detected in 62% yield. Furthermore, the reaction of **8** with 18 equivalents of hydrosilane gave a small quantity of the exhaustively hydrodefluorinated product **10** together with fluorosilane **6** in 50% yield.



Scheme 2. Hydrodefluorination of longer perfluoroalkanes. Yields of **9** and **10** were determined via GC analysis using dodecane as an internal standard. Yields of **6** were determined via ^{19}F NMR analysis of the crude reaction mixture using $CyCF_3$ as an internal standard.

Mechanistic Study 1: Overview

Our optimization experiments (Table 1) suggested that the reaction proceeds via the cleavage of benzylic C(sp^3)–F bonds followed by homobenzylic bond cleavage. An analysis of the reaction mixture via periodic sampling revealed that **2** and **5** are initially formed and ultimately consumed, whereas the concentrations of **3** and **4** continue to increase (Figure 1). This result suggests that **2** and **5** are reaction intermediates to produce **3**. Especially **2** is a reasonable reaction intermediate given that our previous work suggests that the coordination of Ni(0) to a trifluoromethyl arene leads to the oxidative addition of a proximal benzylic C(sp^3)−F bond.

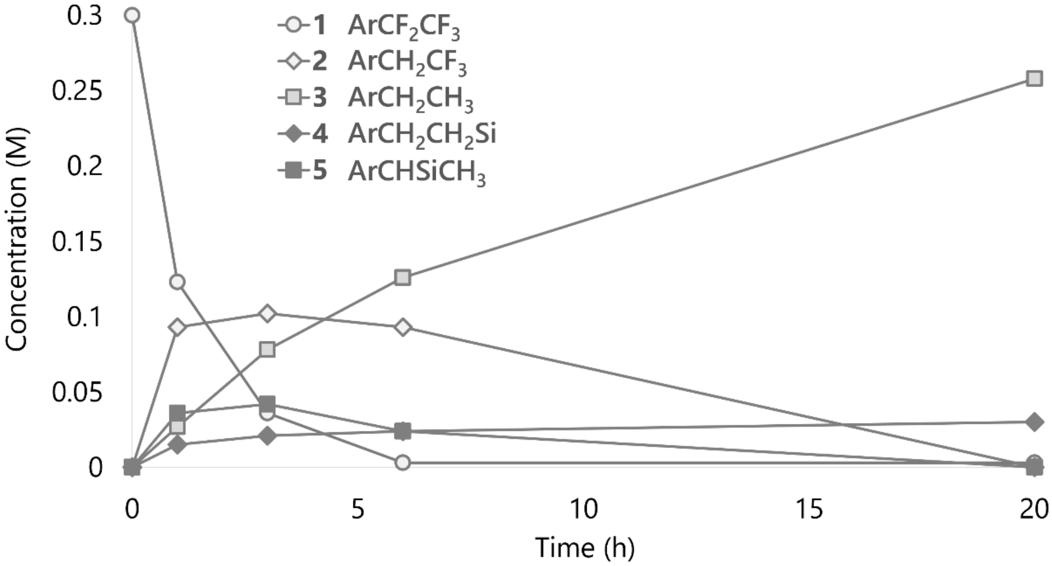
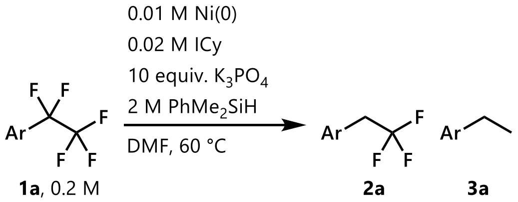


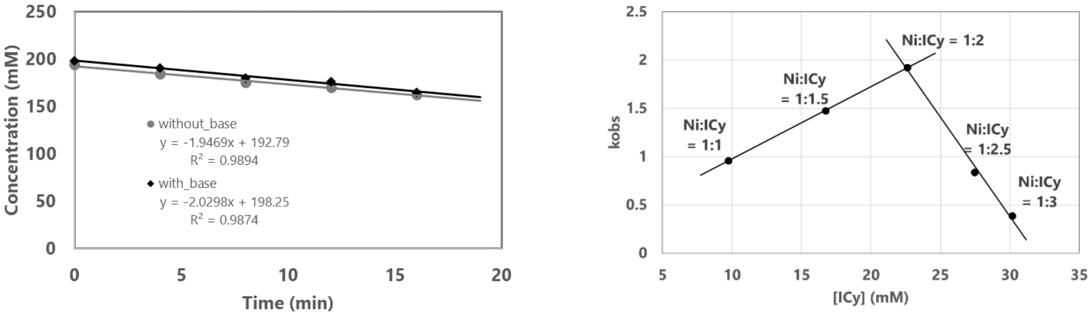
Figure 1. Analysis of the reaction profile. Conditions: **1** (0.03 mmol), K_3PO_4 (0.3 mmol), Me_2PhSiH (0.3 mmol), Ni(cod)$_2$ (1.5 μmol), ICy (1.5 μmol), DMF (0.2 M), 60 °C.

Mechanistic Study 2: Hydrodefluorination of Benzylic C−F Bonds



a) k_{obs} with or without K_3PO_4

b) k_{obs} vs [ICy]



c) Calculated reaction paths

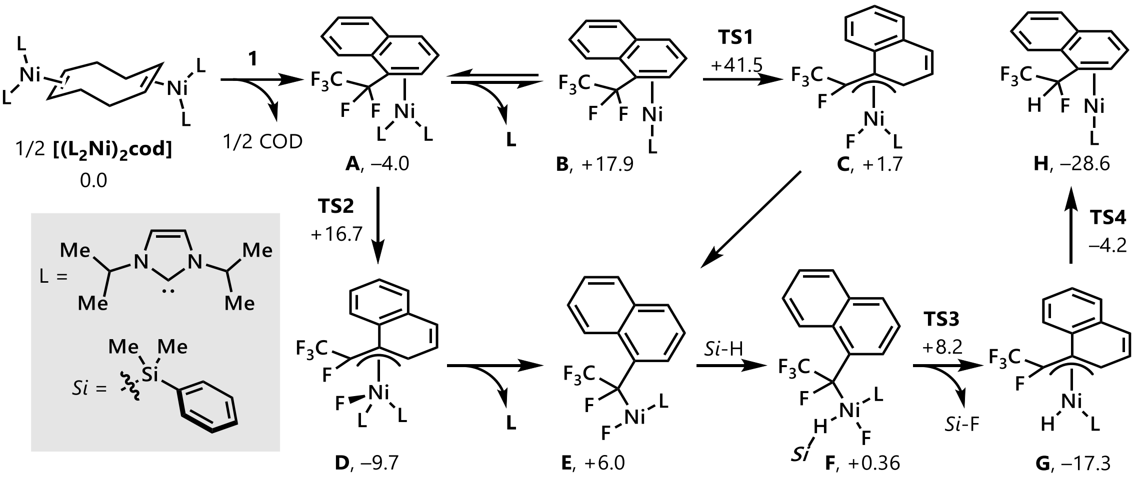


Figure 2. Mechanistic studies of the hydrodefluorination of benzylic C−F bonds. a) Plots of the concentration of **1a** versus time (min) with or without K_3PO_4. b) Plot of k_{obs} versus [ICy]. The ratio of [Ni]/[ICy] is labeled at each data point. c) Relative energies (kcal/mol) and transition-state (TS) activation barriers based on 1/2[(L_2Ni)cod] are described with symbols for intermediates (**A**–**H**) or TSs.

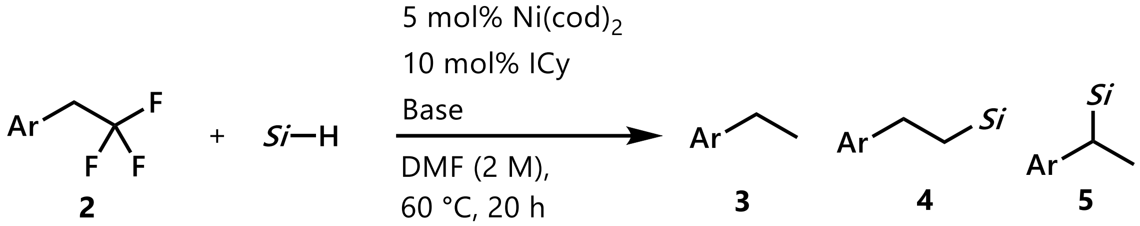
We then investigated the effect of the base on the benzylic C−F bond cleavage process. We periodically analyzed reaction mixtures containing 0.2 M of **1a**, a catalytic amount of Ni(0) and ICy, and a tenfold excess of $PhMe_2SiH$ with or without K_3PO_4. The initial reaction rates k_{obs} (~25% conversion) were obtained by plotting the concentration (mM) of **1a** as a function of time (min) (Figure 2a). When we performed the reaction without K_3PO_4, the reaction rate was not influenced. This result indicates that the base does not participate in the rate-determining step at this stage. We then measured k_{obs} for different Ni/ICy ratios using $Ni(cod)_2$ and ICy (Figure 2b). When the ratio Ni/ICy was greater than 2, the reaction rate was proportional to the amount of ICy. In contrast, when more than two equivalents of ICy were added relative to Ni, the reaction slowed down. These results indicate that the reaction includes a ligand-dissociation step.

To gain further insight, we performed DFT calculations (Figure 2c), whereby I*i*Pr (**L**) was employed instead of ICy to reduce calculation costs. The reaction is initiated by the replacement of 1,4-cyclooctadiene (cod) of $[(L_2Ni)_2cod]$ with **1a** to form arene complex **A**, which is energetically slightly favored. We then examined two possible scenarios: (1) dissociation of a ligand from **A** followed by oxidative addition and transmetalation with the hydrosilane, and (2) oxidative addition followed by ligand exchange between **L** and hydrosilane. The dissociation of free **L** from **A** is energetically unfavorable by +17.9 kcal/mol. Furthermore, the oxidative addition of a C−F bond to give η^3-benzyl complex **C** requires +41.5 kcal/mol. Importantly, the relatively high TS barrier for **TS1** is inconsistent with the experimental results. In contrast, the oxidative addition of **A** to give Ni fluoride complex **D** requires only +20.7 kcal/mol and is thus thermodynamically more favorable. The dissociation of **L** from **D** followed by the coordination of hydrosilane is energetically unfavorable, albeit that the subsequent transmetalation with hydrosilane is a thermodynamically favorable process due to the formation of a stable Si–F bond. The reductive elimination of complex **G** to give complex **H** can be expected to be fast according to the calculated TS energy.

Mechanistic Study 3: Hydrodefluorination of Homobenzylic C–F Bonds

Upon treating **2** using the optimized reaction conditions (Table 2), the reaction furnished **3**, indicating that **2** is a possible reaction intermediate. We also found that in the absence of a base, the conversion of **2** was only 27%. This low conversion stands in stark contrast to the reaction of **1** in the absence of a base (Table 1, entry 9), which led to the complete consumption of the starting material. In their entirety, these results indicate that K_3PO_4 plays a pivotal role in the homobenzylic hydrodefluorination of **2**.

Table 2. Hydrodefluorination of **2**



Base (equiv.)	GC Yields		
	3	**4**	**5**
K_3PO_4 (10)	47%	3%	1%
none	8%	trace	18%

There are two possible scenarios for the transformation of homobenzylic C(sp^3)−F bonds starting from **2** (Figure 3). Path A is a stepwise process via alkene intermediates. First, the base-promoted elimination of HF affords a difluoroalkene. Then, hydrodefluorination of the C(sp^2)−F bonds delivers a vinyl arene. Finally, hydrogenation or hydrosilylation gives the corresponding alkane and hydrosilylation by-products. Path B is the direct hydrodefluorination of the C(sp^3)−F bonds with nickel hydride species. Newman and co-workers have reported the hydrogenation of the C(sp^3)−O bond at the homobenzylic position using hydrosilane and a Ni/ICy catalyst.[23] They suggested direct cleavage of the C(sp^3)−O bond by nickel hydride with the aid of the arene moiety as a directing group, although no mechanistic picture was provided. Thus, we decided to evaluate path B, even though direct substitution at CF_3 is an uncommon event.

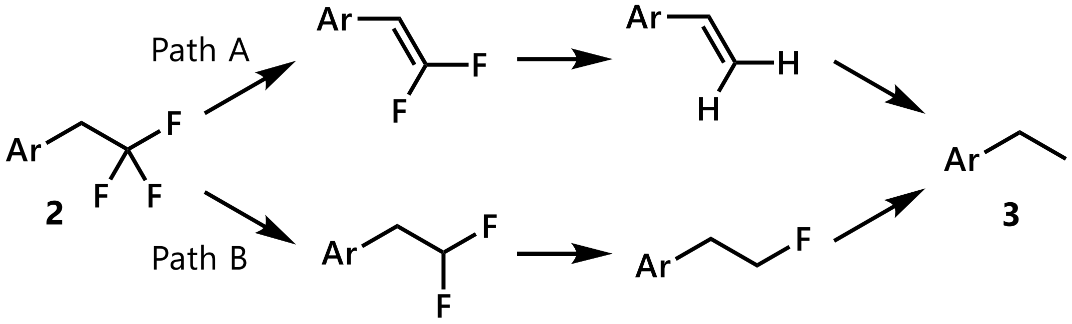
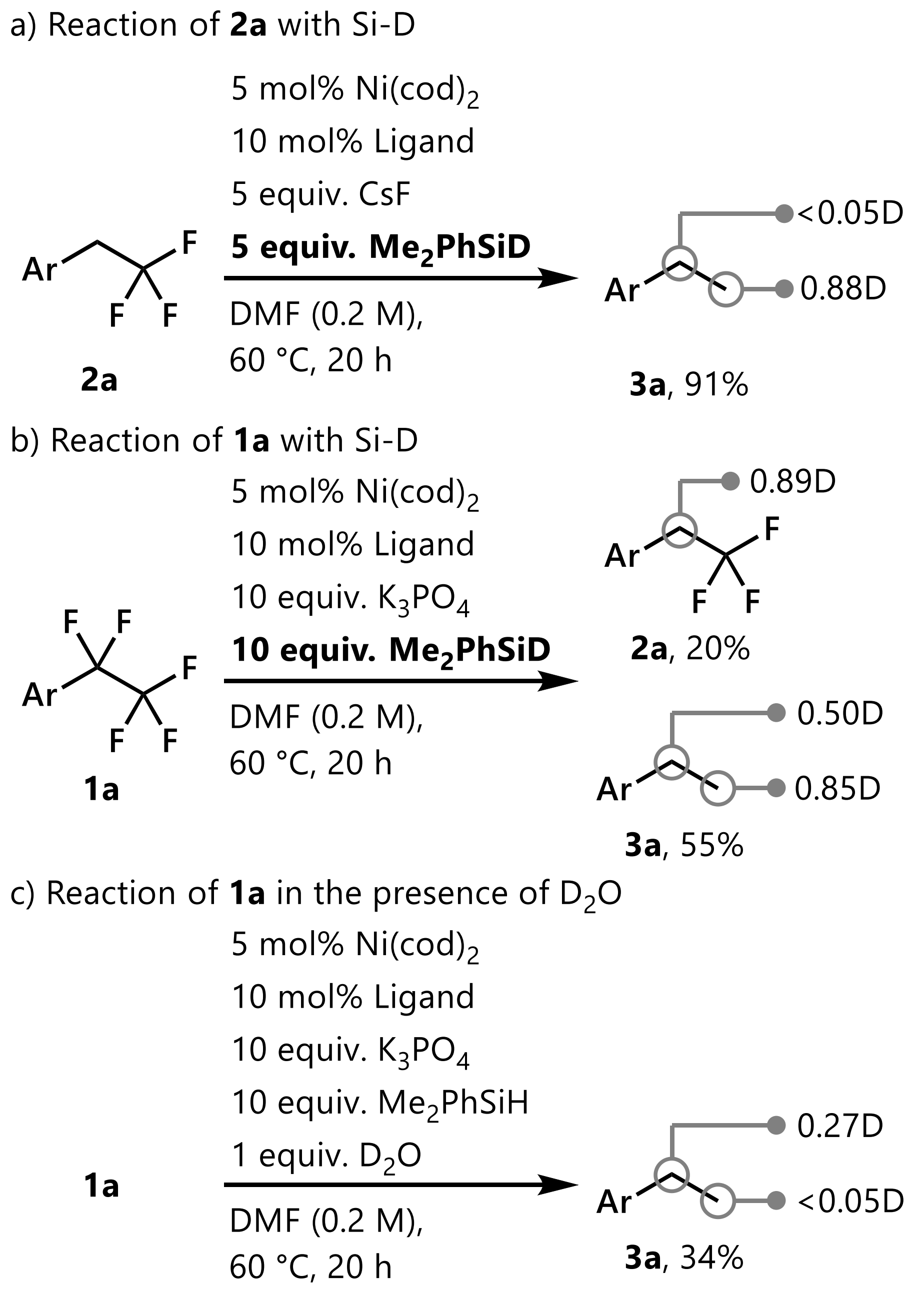


Figure 3. Possible reaction paths A and B.

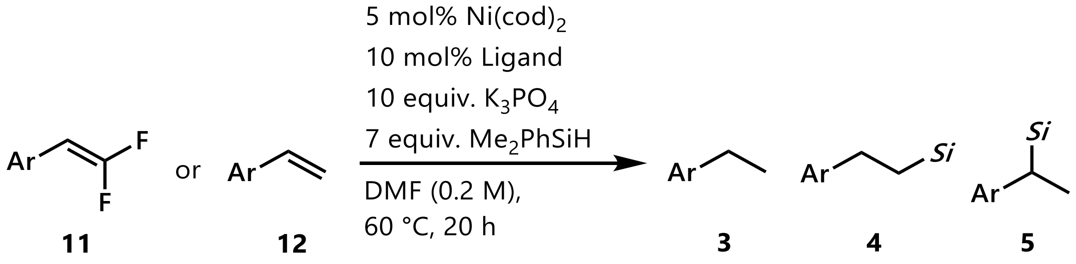
A mechanistic study using a deuteriosilane agreed with path A. We tested the reaction of **2** with the deuteriosilane to clarify the hydrogen source (Scheme 3a). We observed deuterium incorporation not at the benzylic, but at the homobenzylic positions (88% D incorporation). Although this result agrees with path B, the possibility that the reaction could proceed via path A cannot be dismissed due to the possible existence of other proton sources for the benzylic position. We then conducted the reaction of **1a** with the deuteriosilane (Scheme 3b). In this case, deuterated **2a** and **3a** were obtained in 20% and 50% yield, respectively. While the deuterium-incorporation rate at the benzylic position of **2a** was high (89%), that of **3a** was 50%. Taking into account the conclusion that **2a** is a reaction intermediate of **3a**, one benzylic deuterium atom of **2a** would be converted to a hydrogen atom during the transformation of **2a** into **3a**. This would speak in favor of path A, in which a benzylic hydrogen is eliminated to form a difluoroalkene intermediate. The proton source would then most likely be water provided by hygroscopic potassium salts. In fact, when we performed the reaction of **2a** in the presence of 1 equiv. of D_2O, we obtained **3a** with 27% deuterium incorporation at the benzylic position (Scheme 3c).



Scheme 3. Reactions using deuteriosilane Me_2PhSiD.

We then conducted reactions of difluoroalkene **11** and vinyl arene **12** with a hydrosilane to judge whether they were possible reaction intermediates, as would be expected for path A (Table 3). Interestingly, **11** and **12** were not detected in the reaction mixture of pentafluoroethyl arene **1** and the hydrosilane. The reactions of both **11** and **12** gave target product **3** and silanes **4** and **5**. The poor mass balance for the reaction of **6** is probably due to the low stability of difluoroalkene **11**.

Table 3. Reactions of alkenes with a hydrosilane



Substrate	Yield		
	3	**4**	**5**
11	43%	2%	1%
12	45%	2%	41%

[a] Yields were determined by GC analysis. 0.03 mmol of **11** or **12** was used.

We subsequently asked ourselves: “Is the elimination of HF so easy?” Indeed, the E2 elimination of β-fluoroethyl arene usually requires strong bases such as alkoxides.[24]

To answer this question, we treated **2** with K_3PO_4 in DMF (Figure 4). However, **2** remained intact after heating at 60 °C. We then attempted the elimination reaction in the presence of $Ni(cod)_2$ and ICy. The η^2-complex **13**, which is also accessible through the reaction of difluoroalkene **11** and $[(ICy)_2Ni]_2(cod)$, was observed via ^{19}F NMR analysis. The structure of **13** was determined using NMR spectroscopy as well as X-ray crystallography. Complex **13** was not observed in the absence of K_3PO_4. These results suggest that Ni/ICy promoted the elimination of HF by K_3PO_4.

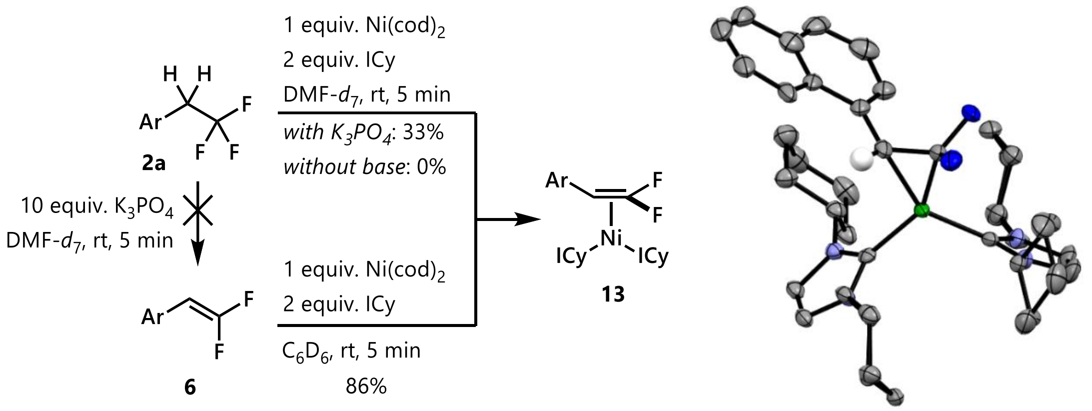


Figure 4. Elimination of HF from **2a** (left) and the crystal structure of **8** with thermal ellipsoids at 30% probability (right); hydrogen atoms, except for the vinylic one, are omitted for clarity.

Discussion

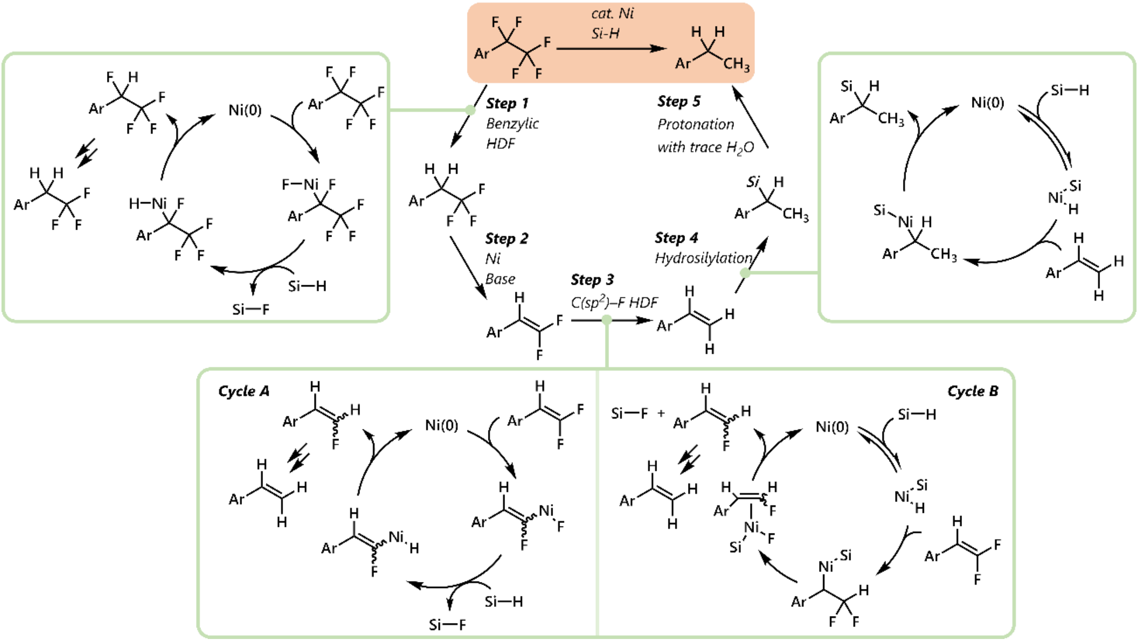


Figure 5. A plausible reaction mechanism.

Based on the experimental results, we would like to propose the reaction mechanism shown in Figure 5. Although multiple reaction pathways can be expected to be in operation, we considered, based on the reaction monitoring, one possible pathway in which hydrodefluorination at the benzylic position is followed by homobenzylic hydrodefluorination. In step 1, oxidative addition of the C−F bond affords a benzyl nickel intermediate. Transmetalation with the hydrosilane and reductive elimination give a hydrodefluorination product. In this step, K_3PO_4 does not influence the reaction rate. Next, the elimination of HF from intermediate **2** gives rise to the formation of difluoroalkene **11**. It should be noted here that we did not employ a strong base such as an alkoxide, which typically promotes E2 elimination. Our mechanistic study suggested that this step is promoted by Ni/ICy, although the reason for this remains unclear at this stage. Subsequently, the difluoroalkene is rapidly transformed into the vinyl arene via the cleavage of the C(sp^2)−F bonds. In this step, two possible catalytic cycles were considered. One possible cycle is initiated by the direct oxidative addition of a C(sp^2)−F bond to Ni(0) (left, cycle A).[25] Transmetalation with the hydrosilane and reductive elimination then furnish the monofluoroalkene. The same catalytic cycle gives the vinyl arene. Another possible cycle is mediated by Ni–H species generated via the oxidative addition of the hydrosilane.[26-28] The coordination and insertion of difluoroalkene generate a benzyl nickel intermediate, which gives the monofluoroalkene via β-fluorine elimination. Again, the same catalytic reaction furnishes the alkene. The Ni(0) species is subsequently regenerated by the reductive elimination of the fluorosilane. Finally, hydrosilylation catalyzed by Ni/ICy occurs to give alkylsilanes **4** and **5**. A related Ni/NHC catalysis for the hydrosilylation of alkenes, including vinyl arenes, has been developed by Cook and co-workers.[29] According to their mechanistic proposal, the hydrosilylation proceeds via the Chalk–Harrod mechanism: Oxidative addition of the Si−H bond to Ni(0), insertion of the alkene, and reductive elimination to give alkyl silanes. Thehydrosilylation gave a mixture of silanes **4** and **5** due to the two possible insertion modes of an alkene to a Ni−H bond. Alkyl silane **4** is prone to protonation, releasing the desired product **3**, whereas alkylsilane **5** remains intact in our process. In our reaction, Ni/ICy plays at least four distinguished roles in the reaction mixture: benzylic C(sp^3)−F bond hydrodefluorination, promotion of HF elimination, C(sp^2)−F bond hydrodefluorination of the difluoroalkene intermediate, and hydrosilylation of the vinyl arene.

Conclusions

In conclusion, we have developed a Ni-catalyzed exhaustive hydrodefluorination of perfluoroalkyl arenes using hydrosilanes as reductants. Mechanistic studies revealed that the reaction proceeds via benzylic hydrodefluorination, nickel-promoted elimination of HF, C(sp^2)−F bond hydrodefluorination, hydrosilylation of the alkene, and protonation of the benzylsilane with trace amounts of water. The Ni(0)/ICy catalyst plays multiple roles in the reaction, enabling the unprecedented hydrodefluorination of non-benzylic C−F bonds mediated by a transition-metal complex.

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was performed through the use of SQUID at the Cybermedia Center of Osaka University.

Competing Interests

The authors declare no competing interests.

Author Contributions

R.D. and S.O. conceived and directed this project. M.Y., N.K., and K.K. performed the experiments. R.D. performed theoretical calculations. R.D. prepared the manuscript with feedbacks from M.Y., N.K., K.K., and S.O.

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