Letter

Hydrodefluorination of Fluoroarenes Using Hydrogen Transfer Catalysts with a Bifunctional Iridium/NH Moiety

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Hydrodefluorination of Fluoroarenes Using Hydrogen Transfer Catalysts with a Bifunctional Iridium/NH Moiety

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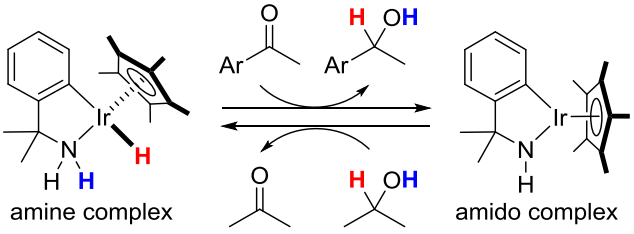
ABSTRACT: The hydrodefluorination of fluoroarenes with transfer hydrogenation catalysts using 2-propanol or potassium formate is described. With the aid of metal/NH cooperation, the C–N chelating Ir complexes derived from benzylic amines can efficiently promote the reduction involving the C–F bond cleavage under ambient conditions even in the absence of hydrosilanes or H_2 gas, leading to the partially fluorinated products in good yields and with high selectivity.

KEYWORDS: *Iridium catalysis, transfer hydrogenation, hydrodefluorination, fluoroarenes, formate salts*

Due to the growing demands for organofluorine molecules possessing unique and value-added properties, transformation of perfluorinated compounds has been extensively studied as a promising synthetic approach for obtaining partially fluorinated skeletons that allows fine tuning of the functional features as well as further derivatization.[1] In particular, much attention has been directed to the catalytic conversion of a carbon–fluorine bond into a carbon–hydrogen bond, referred to as hydrodefluorination.[2] Since the seminal report of Milstein on a homogeneous catalysis of hydrodefluorination based on the carbon-fluorine bond cleavage of hexafluorobenzene by a silylrhodium(I) complex in 1994,[3] various transition metal complexes have emerged as potential catalysts. Most of these systems employed fluorophilic reducing agents including hydrosilanes[4] and aluminum hydrides[5] to facilitate the hydride substitution, but were inevitably accompanied by formation of undesirable reaction side products. Other catalysts applied for the H_2-hydrogenation of fluoroarenes required pressurized hydrogen or resulted in modest activity under mild conditions.[6] Transfer hydrogenation using H_2 equivalents such as alcohols and formic acid has been recognized as a beneficial alternative process[7] that overcomes these shortcomings. Recently, transfer hydrogenation of perfluoroarenes was executed in CH_3CN at 80 °C by using sodium formate in the presence of $[Co(PMe_3)_4]$ albeit with a limited turnover number up to 8.57.[8] Weaver et al. reported a photocatalytic approach to the hydrodefluorination with 2-phenylpyridine-Ir complex in the presence of amines as sacrificial reagents.[9]

Metal-ligand cooperation in protic amine complexes has been exploited for the redox catalysis in which interconversion between NH(amido) and NH_2(amine) ligands on the metal center proceeds concurrently with a smooth hydrogen transfer from the primary and secondary alcohols to the carbonyl compounds (Scheme 1).[10] Significant progress in the applications of this bifunctional catalysis has been made by structural modification of the prototype *N*-sulfonylated diamine complexes. For example, we have found that a family of half-sandwich Ru, Rh, and Ir complexes with a C–N chelating benzylic amine moiety behave as highly efficient hydrogen transfer promoters.[11,12] The enhancement of hydrogen delivery is possibly induced by the nucleophilicity of the hydrido ligand, originating from the pronounced σ-donor nature of the chelating carbon atom. As a part of our ongoing efforts to extend the utility of the privileged hydrogen transfer catalyst, we disclose here the selective hydrodefluorination of perfluoroarenes under transfer hydrogenation conditions using 2-propanol or formate salts.

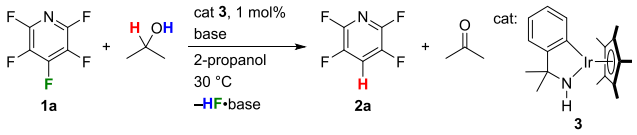


Scheme 1. Hydrogen Transfer to Ketones Based on the Amine/Amido Interconversion

We initially investigated the reaction of pentafluoropyridine (**1a**) as a benchmark substrate in the presence of a bifunctional C–N chelating amido complex (**3**) derived from cumylamine with a substrate/catalyst ratio of 100 in 2-propanol at 30 °C. As summarized in Table 1, a smooth hydrodefluorination proceeded to afford 2,3,5,6-tetrafluoropyridine (**2a**) in 30% yield after 5 h (entry 1). Addition of a base to abstract the releasing hydrogen fluoride proved to be effective for accelerating the reaction. Among the tested carbonate salts (entries 2-5), K_2CO_3 significantly improved the product yield to 87% with a perfect selectivity (entry 4). A favorable result with CaO rather than with $CaCO_3$ (entries 5 and 6) also indicated that a higher catalytic activity is presumably obtained with increasing the basicity of the additive; however, the addition of KOH gave rise to competitive formation of 4-hydroxy-2,3,5,6-tetrafluoropyridine in 62% yield via nucleophilic substitution with OH^- (entry 7). Triethylamine also contributed to promoting the reaction in 90% yield within 1 h (entry 8). It is note-

worthy that further improvement was achieved with HCOOK to furnish **2a** in 94% yield (entry 9).

Table 1. Catalytic Hydrodefluorination of 1a in 2-Propanol Using Ir Catalysts[a]



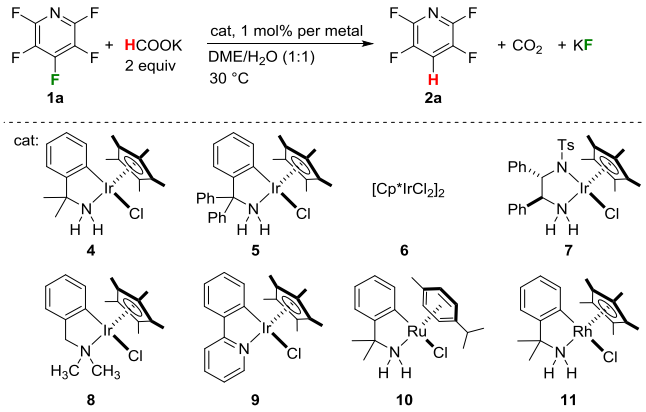
entry	base	time, h	% yield[b]
1	—	5	30
2	Li_2CO_3[c]	1	56
3	Na_2CO_3[c]	1	84
4	K_2CO_3[c]	1	87
5	$CaCO_3$[c]	1	43
6	CaO[c]	1	66
7	KOH[d]	1	38 (62[e])
8	NEt_3[d]	1	90
9	HCOOK[d]	1	94

[a]Reaction conditions: The reaction was carried out with **1a** (0.5 mmol) and catalyst **3** (0.005 mmol) in 2-propanol (5.0 mL) at 30 °C. [b]Determined by ^{19}F NMR using trifluoromethylbenzene as an internal standard. [c]A half molar amount (0.25 mmol) of base was used. [d]An equimolar amount (0.5 mmol) of base was used. [e]The yield of a side product (4-hydroxy-2,3,5,6-tetrafluoropyridine).

The fascinating outcome for the reaction with the formate salt prompted us to explore the hydrogen transfer without 2-propanol. When we submitted **1a** to the transfer hydrogenation using HCOOK, an optimum result was obtained in a 1:1 mixed solvent of DME and water (see Supporting Information, Table S1). The precursory C–N chelating chloroiridium complexes, [Cp*Ir(Cl){κ^2(*N,C*)-NH_2CR_2-2-C_6H_4}] (R = CH_3, **4**; R = C_6H_5, **5**), could promote the hydrodefluorination as well[13], as shown in entries 1 and 2 of Table 2. The reaction was completed with 1 mol% of **4** in the presence of 2 equiv of HCOOK at 30 °C within 1 h. The positive effect of the C–N chelating skeleton was confirmed by the fact that [IrCl(μ-Cl)Cp*]$_2$ (**6**, entry 3) and a N–N chelating iridium complex (**7**, entry 4) did not catalyze the hydrodefluorination. The C–N chelating complexes derived from *N*,*N*-dimethylbenzylamine and 2-phenylpyridine (**8** and **9**) contributed little to the catalysis, supporting the important role of the metal/NH moiety in the acceleration of the hydrogen transfer (entries 5, 6). The Ru and Rh analogues (**10** and **11**) exhibited poor catalytic activity (entries 7 and 8). Notably, the turnover number (TON) for the hydrodefluorination of **1a** exceeded 250 at the catalyst loadings of 0.2 mol% after 1 h.

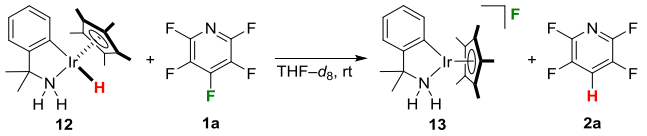
In a separate NMR experiment, treatment of a catalytic intermediate model, [Cp*Ir(H){κ^2(*N,C*)-$NH_2C(CH_3)_2$-2-C_6H_4}] (**12**), with a slight excess amount of **1a** in the absence of base in THF-d_8 at room temperature resulted in prompt formation of **2a**, which was characterized by ^{1}H and ^{19}F NMR spectra. In conjunction with disappearance of the hydride species, the ^{19}F NMR spectrum displayed a new singlet peak at –100.6 ppm that is presumably ascribed to the fluoride anion released from **1a**, implying the simultaneous formation of a cationic species **13** or a neutral fluoride complex (Scheme 2 and Figure S1). Under the catalytic conditions, the added base smoothly abstracts HF to drive the catalytic cycle with forming the catalytically active amidoiridium intermediate.

Table 2. Catalytic Hydrodefluorination of 1a with Formate Salts [a]



entry	catalyst	time, h	% yield[b]
1	**4**	1	100
2	**5**	1	97
3	**6**	5	0
4	**7**	5	1
5	**8**	5	10
6	**9**	5	10
7	**10**	5	4
8	**11**	5	6

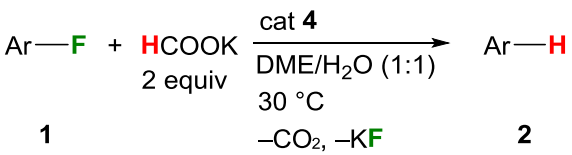
[a]Reaction conditions: **1a** (0.5 mmol), catalyst (0.005 mmol per metal), and sodium formate (1.0 mmol) in DME (2.5 mL) and water (2.5 mL) at 30 °C. [b]Determined by ^{19}F NMR using trifluoromethylbenzene as an internal standard.

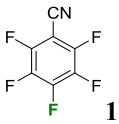
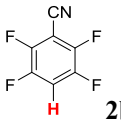
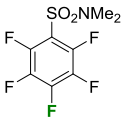
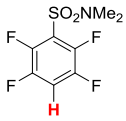
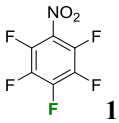
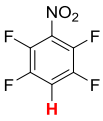
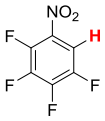
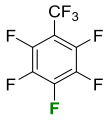
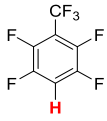
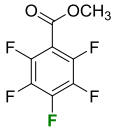
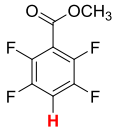
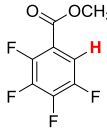
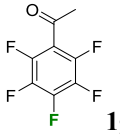
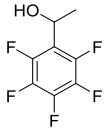
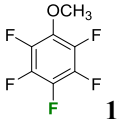
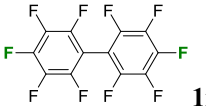
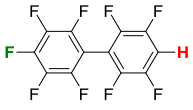
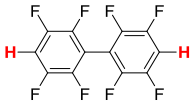
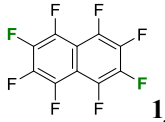
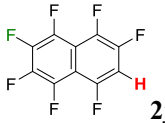
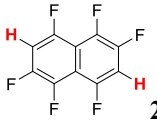
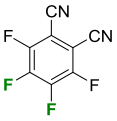
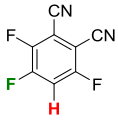
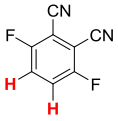
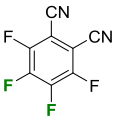
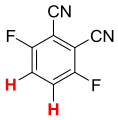


Scheme 2. Stoichiometric Reaction of Hydrido Complex 12 and Pentafluoropyridine 1a

Having obtained the optimal catalyst, we explored the substrate scope of this hydrodefluorination with a variety of highly electron-deficient perfluoroarenes as shown in Table 3. Similar to **1a** listed in entry 1 of Table 2, pentafluorobenzonitrile (**1b**) was transformed into 2,3,5,6-tetrafluorobenzonitrile (**2b**) within 1 h as a sole product (entry 1). The reduction of *N*,*N*-dimethyl pentafluorobenzenesulfonamide (**1c**) afforded the corresponding 2,3,5,6-tetrafluorobenzenesulfonamide (**2c**) in 92% yield (entry 2). In contrast, pentafluoronitrobenzene (**1d**) reacted at the 4- and 2-positions to give a mixture of monohydrodefluorinated products (*p*- and *o*-**2d**) in 61% and 20% respectively, along with a slight amount of dihydrodefluorinated products of 2,3,5-trifluoronitrobenzene and 3,4,5-trifluoronitrobenzene (entry 3). Although the reaction of octafluorotoluene (**1e**) and methyl pentafluorobenzoate (**1f**) required a higher catalyst loading to 2 mol% and a prolonged reaction time to 2 h, the hydrodefluo-

Table 3. Catalytic Hydrodefluorination of Perfluoroarenes Using Potassium Formate

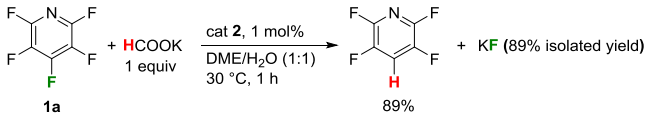


entry	substrate	catalyst, mol%	time, h	products, % yield[b,c]	
1	 **1b**	1	1	 **2b**, 100	
2	 **1c**	1	1	 **2c**, 92	
3	 **1d**	1	1	 *p*-**2d**, 61	 *o*-**2d**, 20
4	 **1e**	2	2	 **2e**, 97	
5	 **1f**	2	2	 *p*-**2f**, 88	 *o*-**2d**, 2
6	 **1g**	1	1	 100	
7	 **1h**	1	12	0	
8	 **1i**	10	12	 **2i**, 64	 **2i'**, 21
9	 **1j**	10	12	 **2j**, 66	 **2j'**, 24
10[d]	 **1k**	1	1	 **2k**, 91(88)	 **2k'**, 2
11[e]	 **1k**	1	1	 **2k'**, 100(86)	

[a]Reaction conditions: **1** (0.5 mmol), catalyst (0.005 mmol), and sodium formate (1.0 mmol) in DME (2.5 mL) and water (2.5 mL) at 30 °C. [b]Determined by ^{19}F NMR using trifluoromethylbenzene as an internal standard. [c]Isolated yield in parenthesis. [d]HCOOK (0.5 mmol). [e]HCOOK (1.5 mmol).

rination at the 4-position proceeded with a considerably high selectivity (entries 4 and 5). The cyano, nitro and ester groups were tolerated under these hydrogen transfer conditions, whereas the ketonic carbonyl group in 2,3,4,5,6-pentafluoroacetophenone (**1g**) was reduced in preference to the hydrodefluorination to form the corresponding alcoholic product (entry 6). A substrate (**1h**) containing electron-donating OCH_3 group remained intact after the reaction under the identical conditions (entry 7). Based on these results, it is clear that the attachment of electron deficient substituents is effective for facilitating the nucleophilic attack of the iridium hydride. Decafluorobiphenyl (**1i**) was also reducible at a relatively high catalyst concentration (10 mol%) to give 4-hydrononafluorobiphenyl (**2i**, 64% yield) accompanied with 4,4'-dihydrooctafluorobiphenyl (**2i'**, 21% yield) as a doubly-hydrodefluorinated product (entry 8). Notably, in the reaction of octafluoronaphthalene (**1j**), the C–F bond cleavage took place selectively at the β-position, yielding 2-hydroheptafluoronaphthalene (**2j**) and 2,6-dihydrohexafluoronaphthalene (**2j'**) in 66% and 24% (entry 9). Such a consecutive hydride substitution could be controlled in the reaction of tetrafluorophthalonitrile (**1k**). The mono defluorinated product (**2k**) was obtained in 91% yield by using an equimolar amount (0.5 mmol) of potassium formate (entry 10). Addition of three molar amounts of the formate salt led to further hydrodefluorination to provide 3,6-difluorophthalonitrile (**2k'**) with perfect selectivity (entry 11). These products (**2k** and **2k'**) could be isolated in 88% and 86% respectively after purification by silica gel column chromatography.

It should be noted that the released fluoride in the transfer hydrogenation using formate salts could be retrieved from the reaction mixture in Scheme 3. After filtering the aqueous extract over the activated carbon, evaporation of the filtrate under reduced pressure to dryness gave a white powder of pure potassium fluoride in 89% isolated yield. As contrasted with the reduction with hydrosilanes, the fluoride salt obtainable in this protocol is potentially reusable in fluorination reactions that should be highly beneficial for recycling fluorine resources.



Scheme 3. Recovery of Potassium Fluoride

In conclusion, we achieved the efficient hydrodefluorination of perfluoroarenes by transfer hydrogenation catalysts possessing metal/NH cooperating functions. These findings have significant implications for the design of practical hydrodefluorination catalysts without using hydrosilanes or hydrogen gas. The transfer hydrogenation system is characterized by excellent catalytic performance even at the ambient temperature and offers advantages in terms of operational simplicity using mild reducing agents. The strong σ-donating nature of the C–N chelating ligands should play a pivotal part in the catalysis, giving rise to the smooth hydride transfer from the nucleophilic hydrido complexes to the fluoroarene substrate. Further studies directed towards elucidating the mechanistic aspects of this catalysis, expanding the substrate scope, and applications to other challenging substrates are ongoing.

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Notes

The authors declare no competing financial interest.

ASSOCIATED CONTENT

Supporting Information.

Experimental details and characterization data, and NMR spectra of the products.Supporting Information is available free of charge on the ACS Publications website at http://pubs.acs.org.

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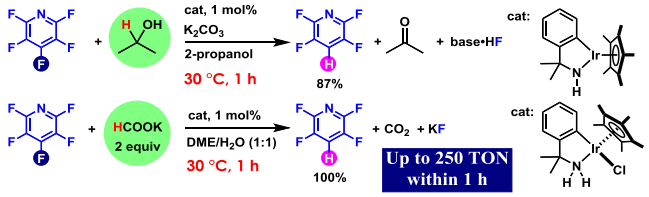
(13) The activity of **4** was comparable to that of **3** in the hydrodefluorination using potassium formate.


cat, 1 mol%
K2CO3
2-propanol
30 °C, 1 h
87%
+ base•HF
cat:
cat, 1 mol%
DME/H2O (1:1)
30 °C, 1 h
100%
+ CO2 + KF
Up to 250 TON
within 1 h
cat: