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Selectively catalytic hydrodefluorination of perfluoroarenes by Co(PMe₃)₄ with sodium formate as reducing agent and mechanism study[†]

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Successful selective hydrodefluorinations of aryl fluorides were carried out in the presence of a cobalt catalyst supported by trimethylphosphine and with sodium formate as a reducing agent in acetonitrile or DMSO. Octafluorotoluene (1), pentafluoropyridine (2), hexafluorobenzene (3), pentafluorobenzene (3a) and perfluorobiphenyl (4) were studied to investigate the scope of this catalytic system. It was found that the fluorinated compounds 1, 2 and 4 with electron-withdrawing groups are more active than 3 and 3a. The catalytic hydrodefluorination mechanism is proposed and discussed with the support of the experimental results of the stoichiometric reactions and the *in situ* IR and NMR data.

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1. Introduction

C-F bond activation has attracted more and more attention owing to the growth of the application of fluoro compounds in advanced materials, pharmaceuticals, agricultural chemicals and some other fields,¹⁻¹⁵ but catalytic C-F bond activation and functionalization with transition metal complexes as catalysts are still rare.¹⁶⁻²⁴ The first example of homogeneously catalytic C-F bond activation by transition metal complexes was the catalytic reaction between polyfluorobenzenes and hydrosilanes with Rh(1) silyl coordination compounds as catalysts by Milstein.²⁵ C-F bonds of C₆F₆ and C₆F₅H can be selectively hydrogenolyzed in a simple reaction with H₂ by trimethylphosphine complexes of rhodium as catalysts in the presence of a base.¹⁶ Aqueous ammonia as the reaction medium was used in the reductive defluorination of polyfluoroarenes by zinc in a highly selective manner.¹⁷ Rhodium hydrides with a pentamethylcyclopentadienyl ligand were used as potential catalysts in C-F bond activation of polyfluoroaromatics.¹⁸ With a ketone carbonyl group as the directing group, rhodium-catalyzed C-F bond activation via a Si-F exchange reaction between fluorobenzenes and a disilane was reported by Murai.¹⁹ Grushin disclosed his study results on the catalytic hydrogenolysis of a

C-F bond in unreactive monofluoroarenes with rhodium complexes.²⁰ Braun showed the first activation of an aromatic C-F bond at a metal center in the presence of a C-Cl bond in the same aromatic ring.²¹ The hydrodefluorination of fluorinated alkenes proceeded at the rhodium center.²² Braun also realized a stoichiometric and catalytic route to fluorinated pyridine derivatives based on C-F bond activation reactions of pentafluoropyridine at palladium.²³ The *N*-heterocyclic carbene complexes of ruthenium have shown to be precursors for the catalytic hydrodefluorination of aromatic fluorocarbons in the presence of alkyl silanes.²⁶ Hydrodefluorination of perfluorinated aromatic compounds with silane is catalyzed by the addition of iron(II) fluoride complexes, giving mainly the singly hydrodefluorinated products.²⁷ Zhang and co-workers have found that gold(1) complexes and copper(1) salts have good catalytic reactivity towards the hydrodefluorination of fluoroarenes using silanes as a hydrogen source.²⁸ However, in most of the studies, either noble metals or high pressure hydrogen were used. In some cases, more expensive silanes were added as reducing agents.

Recently, we have reported the selective C–F/C–H bond activation of fluoroarenes by a cobalt complex supported with phosphine ligands.²⁹ The C–H bond activation product, (C_6F_5) Co(PMe₃)₄, was obtained as the main product through the reaction of Co(PMe₃)₄ with pentafluorobenzene. The hydro-defluorination products, 1,2,4,5-C₆F₄H₂ and F₂PMe₃, were also observed as the byproducts. The reaction mechanism including a hydrido cobalt(π) intermediate (**A**) and ligand exchange intermediate, tris(trimethylphosphine)pentafluorophenylcobalt(π) fluoride (**B**), was proposed and partly-experimentally verified (Scheme 1).

Based on the above research on the stoichiometric reactions and mechanism study, we selected $Co(PMe_3)_4$ as the catalyst

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for the catalytic hydrodefluorination of aryl fluorides. The reaction of the arvl fluorides (compounds 1, 2, 3, 3a and 4) with sodium formate in the presence of the cobalt catalyst selectively leads to hydrodefluorination products at parapositions (exception of 3). In the case of 3, the conversion to pentafluorobenzene was poor, while 1,2,4,5-tetrafluorobenzene (3b) was obtained from 3a in a high yield. From compound 4, 2,3,5,6,2',3',4',5',6'-nonafluorobiphenyl (4a) or 2,3,5,6,2',3',5',6'-octafluorobiphenyl (4b) could be selectively obtained depending on the different reaction conditions. A reaction mechanism of this hydrodefluorination process is proposed and supported by in situ IR experiments. At the present time, the hydrodefluorination reaction is one of the important synthetic tools for the generation of partiallyfluorinated building blocks from readily available perfluorinated bulk chemicals.³⁰ Until now, there has been only one example of a cobalt mediated hydrodefluorination reaction, reported by Holland.¹⁴ In this paper, several derivatives of polyfluoroarenes were selectively obtained through cobalt-catalyzed hydrodefluorination under mild conditions. It is not easy to prepare some of these products directly with classic routes of organic synthesis.³¹

2. Experimental

2.1. General procedures and materials

Standard vacuum techniques were used in the manipulations of volatile and air sensitive materials. Solvents were dried by known procedures and distilled under nitrogen before use. Literature methods were used in the preparation of $Co(PMe_3)_4$.³² Aryl fluorides **1**, **2**, **3**, **3a** and **4** were obtained from ABCR. All other chemicals were used as purchased. The *in situ* IR analysis was carried out on a METTLER TOLEDO React IR IC 15. ¹H, ¹³C and ¹⁹F NMR spectra (300, 75 and 282 MHz, respectively) were recorded on a Bruker Avance 300 spectrometer. ¹³C NMR resonances were obtained with broadband proton decoupling. The melting points were measured in capillaries sealed

under nitrogen and are uncorrected. GC-MS were recorded on a TRACE-DSQ.

2.2. Catalytic study

In a typical reaction, the substrate (0.5 mmol) was dissolved in dried DMSO or CH_3CN (3 mL) together with HCOONa (0.75 mmol), stirring for 1 minute. After the addition of $Co(PMe_3)_4$ (0.05 mmol), the suspension was stirred for 3 h at the given temperature under oxygen-free nitrogen. The solution turned to orange from brown. The products and their yields were determined from the catalytic solutions by ¹⁹F NMR spectra. The ¹⁹F NMR was measured with trifluoromethyl-toluene as the external standard.

2.2.1. Isolation of 1a. The reaction mixture was quenched with dilute HCl (1 M) and extracted by diethyl ether, dried over MgSO₄ and filtered. Compound 1a as a colorless liquid was obtained by distillation (boiling range 110–115 °C). Yield: 0.076 g (69.7%). ¹H NMR (CDCl₃, 300 MHz): δ 7.12–7.42 (m, Aryl-*H*). ¹⁹F NMR (CDCl₃, 282 MHz): δ –56.62 (t, 3F, ⁴J_{FF} = 22.5 Hz), –136.3 (m, 2F), –140.2 (m, 2F). GC-MS (*m*/*z*): M⁺: 217.9.

2.2.2. Isolation of 2a. A similar method as that for 1a was used to isolate 2a (boiling range 98–105 °C). Yield: 0.046 g (61.3%). ¹H NMR (CDCl₃, 300 MHz): δ 7.63 (m). ¹⁹F NMR (CDCl₃, 282 MHz): δ –90.7 (m, 2F), –139.7 (m, 2F). ¹³C NMR (CDCl₃, 75.5 MHz): δ 143.7 (m, ¹*J*_{CF} = 215.1 Hz, ²*J*_{CF} = 15.1 Hz), 141.7 (m, ¹*J*_{CF} = 264.2 Hz), 119.1 (tt, ²*J*_{CF} = 20.3 Hz, ³*J*_{CF} = 2.64 Hz). GC-MS (*m*/*z*): M⁺: 150.9.

2.2.3. Confirmation of 3a. Compound 3a could not be isolated due to the low yield. ¹⁹F NMR: δ –139.0 (m, 2F), –153.8 (t, 1F), –162.7 (m, 2F). GC-MS (*m*/*z*): M⁺: 167.9.

2.2.4. Confirmation of 3b. Compound 3b could not be isolated due to the low yield. ¹⁹F NMR: δ –140.1 (m). GC-MS (*m*/*z*): M⁺: 150.1.

2.2.5. Isolation of 4a. The reaction mixture was quenched with dilute HCl (1 M), extracted by diethyl ether, dried over MgSO₄ and filtered. 4a as a white solid was obtained by column chromatography (silica) using petroleum ether (60–90 °C) as an eluent. Yield: 0.12 g (75.9%). ¹H NMR (CDCl₃, 300 MHz): δ 7.13–7.02 (m). ¹⁹F NMR (CDCl₃, 282 MHz): δ –137.4 (m, 4F), –138.2 (m, 2F), –150.2 (t, 1F), –160.5 (m, 2F). ¹³C NMR (CDCl₃, 75.5 MHz): δ 147.6 (m), 145.8 (m), 144.3 (m), 142.3 (m), 139.5 (m), 108.1 (tt, ²_{JCF} = 97.3 Hz, ³_{JCF} = 5.2 Hz). GC-MS (*m/z*): M⁺: 316.0. M.p.: 80 °C.

2.2.6. Isolation of 4b. A similar method as that for 4a was used to isolate 4b. Yield: 0.12 g (80.5%). ¹H NMR (CDCl₃, 300 MHz): δ 7.20–7.31 (m). ¹⁹F NMR (CDCl₃, 282 MHz): δ –137.7 (m, 4F), –138.2 (m, 4F). ¹³C NMR (CDCl₃, 75.5 MHz): δ 146.2 (m, ¹_{J_{CF}} = 272.5 Hz), 144.4 (m, ¹_{J_{CF}} = 236.3 Hz), 107.8 (m, ²_{J_{CF}} = 22.6 Hz). GC-MS (*m*/z): M⁺: 298.0. M.p.: 84 °C.

3. Results and discussion

3.1. Cobalt-catalyzed selective C–F bond activation and hydrodefluorination of perfluoroarenes

In this cobalt-catalyzed C-F bond activation system, the hydrodefluorination of 1, 2, 3, 3a and 4 as substrates was

	$F + F + HCOONa \xrightarrow{10 \text{ mol}\% \text{ Co}(\text{PMe}_3)_4}_{80^\circ\text{C}, 3h} + F + \text{NaF} + \text{CO}_2$					(2)
Solvents	DMSO	NMP	DMF	CH ₃ CN	Toluene	Dioxane
Conversion (%)	100	100	100	100	70.0	61.4
Yield ^a (%)	46.5	53.7	68.5	85.6	34.9	37.7
^{<i>a</i>} The yields were deter	mined by ¹⁹ F NMR sp	ectroscopy with trifl	uoromethyltoluene a	as the external standar	d.	

investigated with tetrakis(trimethylphosphine)cobalt(0) as a catalyst and sodium formate as a reducing agent (eqn (1)).

Table 1 Hydrodefluorination of 1 in different solvents

Initially, compound 1 was selected as a model substrate to scan the catalytic conditions (eqn (2)). The experimental results are summarized in Tables 1 and 2. From Table 1 it can be concluded that the best solvent among the five tested solvents for this catalysis is acetonitrile. Although the conversions in some other solvents can also reach 100%, the selectivity is poor. We considered two reasons for the results. For DMSO, NMP and DMF, which have a larger polarity than that of CH₃CN, the catalytic reactions are very fast and more side reactions occur. For 1,4-dioxane and toluene, which have a smaller polarity than that of CH₃CN, the catalytic reactions are slow. It is suggested that a strong polarity of the reaction medium would be beneficial for increasing the reaction rate. It is important for this catalytic system to have a solvent with a suitable polarity, like acetonitrile. Table 2 shows that the reaction yield increases from 35.6% to 85.6% when raising the temperature from 30 °C to 80 °C with CH3CN as the solvent (entries 1-3). At 80 °C, the reaction yield increases from 82.2% to 85.6% when the reaction time is prolonged from 0.5 h to 3 h (entries 5-3).

 $\label{eq:table_state} \begin{array}{l} \textbf{Table 2} & \text{Hydrodefluorination of 1 in CH}_3\text{CN at different temperatures and in different times} \end{array}$

Entry	Time (h)	Temperature (°C)	Conversion (%)	Yield ^a (%)
1	3	30	42.5	35.6
2	3	50	52.7	36.3
3	3	80	100	85.6
4	1.5	80	95.1	83.3
5	0.5	80	90.1	82.2
6	3	80	8.0	0^b

1 mmol substrate, 10 mol% $Co(PMe_3)_4$, 1.5 eq. HCOONa.^{*a*} The yields were determined by ¹⁹F NMR spectroscopy with trifluoromethyltoluene as the external standard. ^{*b*} The experiment was carried out without the catalyst, 1.5 eq. HCOONa.

The catalytic mono-hydrodefluorinations of the other fluorinated arenes with $Co(PMe_3)_4$ are listed in Table 3. All of these transformations have good chemo- and regioselectivity. The hydrodefluorination of 1 took place selectively at position 3. Therefore, 1,2,4,5-tetrafluoro-3-(trifluoromethyl)benzene (1a) was obtained in a yield of 85.6%. Under the same conditions the hydrodefluorination of 2 proceeds rapidly, affording 2,3,5,6-tetrafluoropyridine (2a) in a yield of 72.7%. With perfluorobiphenyl (4) as the substrate, the catalytic reaction leads to the mono-hydrodefluorinated product, 2,3,5,6,2',3',4',5',6'nonafluorobiphenyl (4a), with a conversion of 100% in a yield of 82.6%. When the reaction time was increased from 3 h to 8 h, with a catalyst loading of 20% and 3 eq. of HCOONa, the selective hydrodefluorination in DMSO took place to give rise to the di-hydrodefluorinated product, 2,3,5,6,2',3',5',6'-octafluorobiphenyl (4b), in a yield of 85.7% and with a conversion of 100%. In contrast to the above results, the catalytic transformation of 3 was poor, with a yield of only 9.2% for 3a. Even in DMSO, the yield is 11%, although the selectivity is 100%. However, 3b was obtained in a yield of 51.2% when using 3a as a substrate in DMSO. The para-(C-F) bond to the C-H bond in pentafluorobenzene 3a was exclusively activated.

3.2. Mechanistic study of the catalytic hydrodefluorination reaction

According to the results of the hydrodefluorination of perfluoroarenes and the reported experimental results of the stoichiometric reactions of the selective C-F/C-H bond activation of fluoroarenes and the mechanism study in Scheme 1,²⁹ a mechanism of the catalytic hydrodefluorination is proposed in Scheme 2. The first step is the oxidative addition of the C-F bond of the aryl fluoride at the cobalt(0) center to afford a Co(II)fluoride a. A similar complex to complex a was isolated in our previous work.³³ F^- ligand substitution of intermediate *a* by a formate anion delivers intermediate b with the coordinated carboxyl group. Decarboxylation of intermediate b gives rise to the hydrido cobalt(n) intermediate, c, with the escape of CO_2 . The subsequent ligand exchange of the hydrido H atom by the F atom of the perfluoroarenes yields the hydrodefluorination product along with the recovery of the staring $Co(\pi)$ fluoride *a* to complete this catalytic cycle.

 Table 3
 Cobalt-catalyzed hydrodefluorination of polyfluoroarenes

Substrate	Product	Solvent	Time (h)	Conversion (%)	Yield ^{<i>a</i>} (isolated) (%)	TON ^a
F CF3		CH ₃ CN	3	100	85.6 (69.7)	8.56
		CH ₃ CN	3	84.6	72.7 (61.3)	7.27
F F 2	F F 2a					
F F	FF	CH_3CN	3	19.0	9.2	0.09
F F F	F F 3 9	DMSO	3	11.1	11.1	1.11
F F	E F		2	10 -		
FH	н	CH ₃ CN DMSO	3 3	12.7 73.3	7.3 51.2	1.27 5.12
F F 3a	F F 3b					
	F F F F 4a	$\rm CH_3CN$	3	100	82.6 (75.9)	8.26
		DMSO	8	100	$85.7^{b}(80.5)$	8.57
ŕřŕŕ 4	FFFF 4D					

1 mmol substrate, 10 mol% cat. Co(PMe₃)₄, 1.5 eq. HCOONa, 80 °C.^{*a*} The data were determined by ¹⁹F NMR spectroscopy with trifluoromethyl toluene as the external standard. ^{*b*} 1 mmol substrate, 20 mol% cat. Co(PMe₃)₄, 3.0 eq. HCOONa, 80 °C.



Scheme 2 Proposed mechanism of the catalytic hydrodefluorination.

This mechanism was also supported by the experimental *in situ* IR and ¹H NMR spectroscopy. In the *in situ* IR spectroscopy, the model reaction of the hydrodefluorination of compound **1** was taken to track the reaction process. The substrate **1** was dissolved in dried CH_3CN together with HCOONa. After the addition of $Co(PMe_3)_4$, the suspension was stirred for 5 minutes at room temperature under oxygen-free nitrogen



Scheme 3 The *in situ* IR spectra of the hydrodefluorination of **1** (all the IR spectra of the reaction with CH_3CN as background).

and then the temperature was increased to 80 $^{\circ}\mathrm{C}.$ The color of the reaction solution turned to orange from brown.

According to the results from the *in situ* IR spectra (Schemes 3 and 4), the peak at 1606 cm⁻¹ indicates the presence of intermediate **b** with a coordinated carboxyl group, while this peak is at 1595 cm⁻¹ for the free formate.³⁴ The Co–H bond vibration of the hydrido intermediate **c** appears at 1906 cm⁻¹. The hydrido resonance of the Co–H bond in the ¹H NMR spectra in DMSO-D₆ was observed at –15.1 ppm as a broad peak with the reaction of compound **4** and a stoichiometric amount of Co(PMe₃)₄ as well as 3.0 eq. of HCOONa. In Scheme 4, the developing trends of the specific peak intensity



Scheme 4 The peak intensity trend of the characteristic peaks

are illustrated. In addition, the peak from the C–H bond at 1031 cm⁻¹ gradually appeared with a decrease in the intensity of the peak at 1002 cm⁻¹ from the C–F bond of the substrate. The formation of a white precipitate of NaF, confirmed by the ¹⁹F NMR spectra (δ : –114 ppm), in the solution also supports this putative reaction mechanism.

4. Conclusions

In summary, the successful selective hydrodefluorination of aryl fluorides was carried out in the presence of a $Co(PMe_3)_4$ catalyst and with sodium formate as a reducing agent. Aryl fluorides **1**, **2**, **3**, **3a** and **4** as substrates were studied to investigate the scope of this catalytic system. It was found that the fluorinated compounds **1**, **2** and **4** with electron-withdrawing groups are more active than **3** and **3a**. The catalytic hydrodefluorination mechanism is proposed and discussed with the support of the experimental results of the stoichiometric reactions and the *in situ* IR and NMR data.

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