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Light induced catalytic hydrodefluorination of perfluoroarenes by porphyrin rhodium†

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Photocatalytic hydrodefluorination of perfluoroarenes by rhodium porphyrin complexes with high tolerance to various functional groups has been developed. Mechanistic studies reveal that the rhodium aryl complex, (por)Rh-C_6F_4R, is the key intermediate.

Fluorine-containing organic compounds are essential building blocks that have been extensively employed in materials chemistry, medicinal chemistry as well as agrochemistry.[1] Simple perfluorinated bulk chemicals are easily accessible on an industrial scale, whereas the selective cleavage of C–F bonds of perfluorinated compounds is regarded as a promising approach to access partially fluorinated compounds.[1d–h] However, this defluorination process has been considered as one of the greatest challenges for synthetic chemistry due to the relative inertness of the C–F bond.[2]

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† Electronic supplementary information (ESI) available: General procedure for stoichiometric and catalytic reactions, and NMR data of typical organometallic compounds and organic products. See DOI: 10.1039/c5qi00269a

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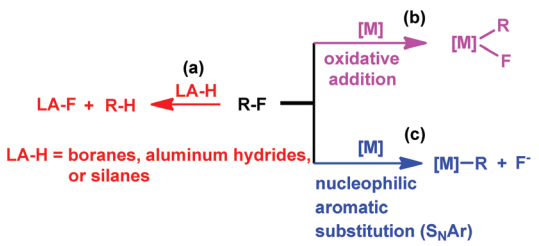
Transition metal complexes have been primarily used in catalyzing C–F bond activation,[3] typical metals include Ti,[4] Zr,[5] Fe,[6] Ru,[7] Rh,[8] Ir,[9] Ni,[10] Pd,[11] Pt,[12] Cu,[13] Au,[14] and Zn.[15] In addition, fluorophilic reagents, such as boranes,[16] aluminum hydrides[17] and silanes,[18] also gave hydrodefluorination products where the fluorine atom is replaced by hydrogen (Scheme 1(a)).

The transition metal catalyzed C–F bond activation through an oxidative addition reaction often led to the formation of strong metal–fluorine bonds which impeded catalyst regeneration (Scheme 1(b)). However, rational design of alternate routes to avoid the formation of the catalyst–fluorine bond would give catalytic C–F bond activation with improved efficiency. Photocatalysis has recently been attracting increasing attention as a unique pathway to overcome high thermal barriers at relatively low energy and environmental costs.[19] Weaver's group previously reported photocatalytic hydrodefluorination of perfluoroarenes mediated by the Ir(ppy)$_3$ complex (tris[2-phenypyridinato-C^2,N]iridium(III)).[9c] The 18 e$^-$, coordination saturated Ir(ppy)$_3$ complex would circumvent the formation of the catalyst–fluorine bond for catalytic turnover.

We recently reported the photocatalytic hydration of Si–C bonds[20] and alkynes[21] using the tetra(*p*-sulfonatophenyl)porphyrin rhodium ((TSPP)Rh) complex. Mechanistic studies indicated that one of the key steps was the visible light triggered hydration of Rh–C bonds to form the corresponding Rh–OH



Scheme 1 Approaches to C–F bond activation.

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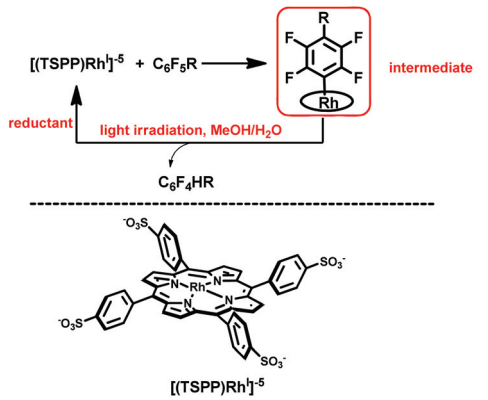

Scheme 2 Hydrodefluorination of perfluoroarenes catalyzed by [(TSPP)Rh^{I}]$^{5-}$.

complex, which afforded a novel strategy to accomplish unusual photo-processes (eqn (1)).

$$[(\mathrm{TSPP})\mathrm{Rh}\text{-}\mathrm{CH_3}]^{4-} + \mathrm{HO-H} \xrightarrow[\text{r.t.}]{\text{visible light}} [(\mathrm{TSPP})\mathrm{Rh}^{\mathrm{III}}\text{-}\mathrm{OH}(\mathrm{H_2O})]^{4-} + \mathrm{CH_3-H} \quad (1)$$

Herein, we report on light promoted catalytic hydrodefluorination of perfluoroarenes catalyzed by a highly reactive nucleophile, [(TSPP)Rh^{I}]$^{5-}$, through a nucleophilic aromatic substitution pathway (S_NAr) with a turnover number (TON) of 880 for octafluorotoluene. The [(TSPP)Rh^{I}]$^{5-}$ attacks the C–F bond in the perfluoroarenes to form the [(TSPP)Rh-C_6F_4R]$^{4-}$ complex (Scheme 1(c)). The polyfluorine-substituted organo–metal bond is quite inert so no facile thermal pathways are available for further transformation to complete the catalytic cycle.[8h,22] However, in this study, a photo-hydration strategy is applied to [(TSPP)Rh-C_6F_4R]$^{4-}$ producing the hydrodefluorinated product and [(TSPP)Rh^{III}-OH]$^{4-}$. The facile reduction of the resulting Rh^{III}-OH species regenerates [(TSPP)Rh^{I}]$^{5-}$ completing the catalytic cycle (Scheme 2).

Stoichiometric hydrodefluorination reaction

Stirring the methanol solution of [(TSPP)Rh^{I}]$^{5-}$ (2.5 mM), sodium borate (0.012 M) and hexafluorobenzene (0.1 mmol) at 25 °C for 2 hours produced [(TSPP)Rh-C_6F_5]$^{4-}$ quantitatively. ESI-MS of [(TSPP)Rh-C_6F_5]$^{4-}$ gave a peak at m/z = 621.95265, corresponding to the anion [(TSPP)Rh-C_6F_5]Na_2^{2-} (Fig. 1S†). In addition, the structure of [(TSPP)Rh-C_6F_5]$^{4-}$ was also verified by ^{1}H NMR and ^{19}F NMR (Fig. 2S and 3S†).

Heating the methanol-d_4 solution of [(TSPP)Rh-C_6F_5]$^{4-}$ at 110 °C for 24 hours only produced a trace amount of pentafluorobenzene detected by GC-MS through the thermal dissociation of the Rh–C bond. However, with irradiation of the methanol solution of [(TSPP)Rh-C_6F_5]$^{4-}$ for 2 hours using a mercury lamp, over 95% conversion was achieved together with the formation of C_6F_5H detected by GC-MS, and [(TSPP)Rh^{III}]$^{3-}$, as evidenced by ^{1}H NMR (eqn (2)–(5)). As expected, irradiation shunted the thermally disfavored reaction to a viable and efficient photo-process for the cleavage of Rh–C bonds. Furthermore, the carbon centered radicals resulting from the photocleavage of Rh–C bonds were trapped by TEMPO (TEMPO = 2,2,6,6-tetramethylpiperidine-1-oxyl) indicating that the reaction occurred through a radical pathway (Fig. 4S†).

$$[(\mathrm{TSPP})\mathrm{Rh}\text{-}\mathrm{C_6F_5}]^{4-} \overset{\text{light}}{\rightleftharpoons} [(\mathrm{TSPP})\mathrm{Rh}^{\bullet\mathrm{II}}]^{4-} + {}^{\bullet}\mathrm{C_6F_5} \quad (2)$$

$$2[(\mathrm{TSPP})\mathrm{Rh}^{\bullet\mathrm{II}}]^{4-} + \mathrm{MeOH} \rightleftharpoons [(\mathrm{TSPP})\mathrm{Rh}\text{-}\mathrm{OMe}]^{4-} + [(\mathrm{TSPP})\mathrm{Rh}\text{-}\mathrm{H}]^{4-} \quad (3)$$

$$[(\mathrm{TSPP})\mathrm{Rh}\text{-}\mathrm{H}]^{4-} + {}^{\bullet}\mathrm{C_6F_5} \rightarrow [(\mathrm{TSPP})\mathrm{Rh}^{\bullet\mathrm{II}}]^{4-} + \mathrm{C_6F_5H} \quad (4)$$

$$[(\mathrm{TSPP})\mathrm{Rh}\text{-}\mathrm{C_6F_5}]^{4-} + \mathrm{MeOH} \xrightarrow{\text{light}} [(\mathrm{TSPP})\mathrm{Rh}\text{-}\mathrm{OMe}]^{4-} + \mathrm{C_6F_5H} \quad (5)$$

Catalytic hydrodefluorination reaction

The [(TSPP)Rh-OMe]$^{4-}$ generated from the photolysis of [(TSPP)Rh-C_6F_5]$^{4-}$ in methanol can be readily reduced to [(TSPP)Rh^{I}]$^{5-}$ by various reductants.[23] Dihydrogen, commonly recognized as one of the cleanest and most environmentally friendly reductants, reduced [(TSPP)Rh^{III}]$^{3-}$ at 25 °C (P_{H_2} ≈ 0.5–0.8 atm).[23b] To our delight, 10 TONs were obtained and detected by GC when irradiating the 0.4 mL methanol-d_4 solution containing hexafluorobenzene (0.1 mmol) and [(TSPP)Rh^{III}]$^{3-}$ (2.5 mM) at 60 °C for 24 hours under one atmosphere of dihydrogen.

$$[(\mathrm{TSPP})\mathrm{Rh}^{\mathrm{III}}]^{3-} + \mathrm{H_2} \rightleftharpoons [(\mathrm{TSPP})\mathrm{Rh}\text{-}\mathrm{H}]^{4-} + \mathrm{H^+} \quad (6)$$

$$[(\mathrm{TSPP})\mathrm{Rh}\text{-}\mathrm{H}]^{4-} \rightleftharpoons [(\mathrm{TSPP})\mathrm{Rh}^{\mathrm{I}}]^{5-} + \mathrm{H^+} \quad (7)$$

$$[(\mathrm{TSPP})\mathrm{Rh}^{\mathrm{III}}]^{3-} + \mathrm{H_2} + \mathrm{C_6F_6} \rightarrow [(\mathrm{TSPP})\mathrm{Rh}\text{-}\mathrm{C_6F_5}]^{4-} + \mathrm{HF} + \mathrm{H^+} \quad (8)$$

The relatively low TON was ascribed to the shift of the equilibrium to the reactants in the reducing step (eqn (6)) with accumulation of HF acid. Considering both the reducing ability of the reductant and the affinity to F^-, silane would be a good candidate for driving the catalytic hydrodefluorination reaction. By a careful screening of different silanes (Table 1S†), Me_2EtSiH was found to show the best performance with 69 TONs under the same conditions (eqn (9)–(11)). The intermediate [(TSPP)Rh-C_6F_5]$^{4-}$ (eqn (11)) was characterized by ESI-MS, and ^{1}H NMR *in situ*. The regeneration of [(TSPP)Rh^{I}]$^{5-}$ (eqn (10)) was confirmed by the formation of [(TSPP)Rh-CH_3]$^{4-}$ upon trapping with CH_3I (eqn (12)), which is the signature reaction of nucleophilic [(TSPP)Rh^{I}]$^{5-}$, with characteristic ^{1}H NMR methyl resonance (δ(Rh–CH_3) = −6.59 ppm, ^2J(Rh–CH) = 2.4 Hz in CD_3OD)[23b] as well as ESI-MS results (m/z = 545.96830 corresponding to [(TSPP)Rh-CH_3] Na_2^{2-}) (Fig. 5S†). Furthermore, the resulting Me_2EtSiF was detected by GC-MS.

$$[(\mathrm{TSPP})\mathrm{Rh}^{\mathrm{III}}]^{3-} + \mathrm{Me_2EtSiH} \rightarrow [(\mathrm{TSPP})\mathrm{Rh}\text{-}\mathrm{H}]^{4-} + \mathrm{Me_2EtSi^+} \quad (9)$$

$$[(\mathrm{TSPP})\mathrm{Rh}\text{-}\mathrm{H}]^{4-} \rightleftharpoons [(\mathrm{TSPP})\mathrm{Rh}^{\mathrm{I}}]^{5-} + \mathrm{H^+} \quad (10)$$

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$$[(TSPP)Rh^{III}]^{3-} + Me_2EtSiH + C_6F_6 \rightarrow [(TSPP)Rh\text{-}C_6F_5]^{4-} + Me_2EtSiF + H^+ \quad (11)$$

$$[(TSPP)Rh^{I}]^{5-} + CH_3I \rightarrow [(TSPP)Rh\text{-}CH_3]^{4-} + I^- \quad (12)$$

In order to increase the solubility of Me_2EtSiH in methanol solution to further improve the catalytic efficiency, mixed solvents were examined, and the results of the experiments for solvent screening are illustrated in Table 1. Using a volume ratio of methanol/THF 1 : 1, 30 TONs were obtained, and for methanol/1,4-dioxane 1 : 1, the TON was 45 (Table 1, entries 1 and 2). Generally, dimethylsulfoxide (DMSO) and *N*,*N*-dimethylformamide (DMF) are considered as two commonly used aprotic polar solvents for S_N2 reactions. However, the TONs were not improved significantly for methanol/DMSO (1 : 1) as the solvent (Table 1, entry 3) while methanol/DMF (1 : 1) gave TONs of 350, and methanol/ethylene glycol (1 : 1) gave the highest TON (Table 1, entry 5). Apparently, the protic solvents facilitated nucleophilic C–F bond activation (Table 1, entry 5 *vs.* entries 1–4) due to their ability to stabilize the forming fluoride anion by hydrogen bonding, which agrees with Paquin's observation.[24] Employing pure glycol as the solvent, however, did not lead to further improvement (Table 1, entry 6).

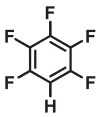
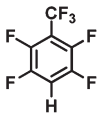
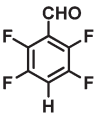
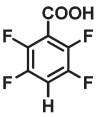
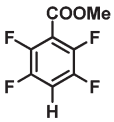
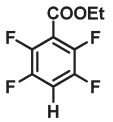
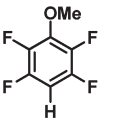
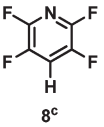
The catalytic hydrodefluorination of various perfluoroarenes under 1 : 1 of MeOH/ethylene glycol is listed in Table 2. Hexafluorobenzene underwent hydrodefluorination to give pentafluorobenzene (**1**) with a TON of 418, and the selectivity was 99.5%. Moreover, when one fluorine atom of the hexafluorobenzene was substituted by an electron withdrawing group such as trifluoromethyl (**2**), aldehyde (**3**), carboxyl (**4**) and esters (**5** and **6**), the hydrodefluorination products were obtained with good TON and high selectivity. However, when an electron-donating group (*i.e.* MeO, **7**) was present, no C–F bond activation occurred. This method could also be applied to pentafluoropyridine, which was smoothly converted to the tetrafluoro-derivative (**8**) with a TON of 420. The remarkable selectivity of this approach (>90% in all cases) was manifested in the lack of over-reduction, suggesting the high tolerance of different functional groups. Additionally, control experiments under the standard conditions revealed that both the catalyst and light irradiation were necessary.

Table 1 Solvent[a] screening for the light induced catalytic hydrodefluorination of C_6F_6 catalyzed by $[(TSPP)Rh^{I}]^{5-}$

Entry	Solvent	Selectivity[b]	TON
1	MeOH/THF = 1 : 1	25%	30
2	MeOH/1,4-dioxane = 1 : 1	45.9%	45
3	MeOH/DMSO = 1 : 1	32.4%	27.5
4	MeOH/DMF = 1 : 1	97.2%	350
5	MeOH/glycol = 1 : 1	99.5%	418
6	1 ml glycol	87%	252.5

[a] Reaction conditions: 60 °C under light irradiation (500 W Hg lamp, 15 cm distance) for 36 hours. [b] Determined by ^{19}F NMR resonances, selectivity = yield/conversion.

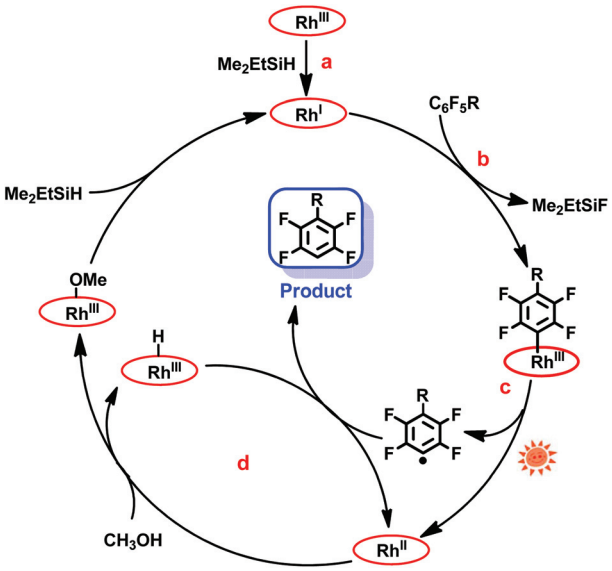
Table 2 Scope of the perfluoroarene substrates[a]

	 1[c]	 2[c]	 3	 4[d]
Selectivity[b]:	99.5%	98%	96%	93%
TON:	418	880	565	355
	 5	 6	 7	 8[c]
Selectivity[b]:	92%	91%	—	95%
TON:	838	757	0	420

[a] Reaction conditions: 60 °C under light irradiation (500 W Hg lamp, 15 cm distance) for 36 hours. [b] Determined by ^{19}F NMR, selectivity = yield/conversion. [c] GC results. [d] 1 mmol NaOH was added.

Proposed mechanism

The mechanism of the hydrodefluorination of perfluoroarenes catalyzed by $[(TSPP)Rh^{I}]^{5-}$ was envisioned to proceed through a four-step cycle depicted in Scheme 3: (a) the reaction of $[(TSPP)Rh^{III}]^{3-}$ with Me_2EtSiH to produce $[(TSPP)Rh^{I}]^{5-}$ under basic conditions; (b) the nucleophilic aromatic substitution of $[(TSPP)Rh^{I}]^{5-}$ at the *para*-carbon of the perfluoroarene giving the key intermediate; (c) photolysis of the $[(TSPP)Rh\text{-}C_6F_4R]^{4-}$ complex yielding the C_6F_4R radical and $[(TSPP)Rh^{II}]^{4-}$; (d) subsequently, $[(TSPP)Rh^{II}]^{4-}$ reacted with methanol rapidly producing $[(TSPP)Rh\text{-}H]^{4-}$ and $[(TSPP)Rh\text{-}OMe]^{4-}$,[21,25] followed by the hydrogen atom abstraction from $[(TSPP)Rh\text{-}H]^{4-}$ by the C_6F_4R radical yielding the final product HC_6F_4R. The high efficiency of C–F bond activation was attributed to the for-



Scheme 3 Proposed mechanism of photo-induced hydrodefluorination of perfluoroarenes catalyzed by rhodium porphyrins.

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mation of Si–F and Rh–C bonds which provided sufficient thermodynamic driving force for the reaction.

Considering that the reduction potential of C_6F_6 was as negative as −2.22 eV in 75% dioxane/water,[26] and the oxidation potential of $(TPP)Rh^{I}$ to $(TPP)Rh^{II}$ in DMSO was −1.1691 eV (TPP = tetraphenylporphyrin),[27] a single electron transfer mechanism is probably too endothermic to be operative, although the redox potentials cannot be compared quantitatively due to the differences in ligands (TSPP *vs.* TPP) and solvents (dioxane/water *vs.* DMSO) used. The nucleophilic aromatic substitution pathway for the C–F bond activation was preferred in this system, however, the single electron transfer pathway could not be firmly ruled out.

In addition, the mechanism is quite different from Weaver's work.[9c] In our system, the Rh–C bond cleavage of the intermediate ($[(TSPP)Rh\text{-}C_6F_4R]^{4-}$) only occurs with the assistance of light irradiation to complete the catalytic cycle, while in Weaver's system, light was used to promote the catalyst ($Ir(ppy)_3$) to the excited state, releasing an electron to the LUMO of perfluoroarenes to trigger the photocatalytic hydrodefluorination.

Conclusions

In summary, we have developed a new strategy for catalytic hydrodefluorination of perfluoroarenes utilizing $[(TSPP)Rh^{I}]^{5-}$ through a nucleophilic aromatic substitution pathway. The key intermediate $[(TSPP)Rh\text{-}C_6F_4R]^{4-}$ was observed, which underwent light-induced Rh–C bond cleavage to produce hydrodefluorination products. By integrating the light harvesting ability of the porphyrin ligand with unique organometallic reactions of the rhodium metal center, we illustrated a novel photocatalytic approach which provides an alternate route to the design of efficient photocatalysts.

Acknowledgements

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