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Catalytic C−F Bond Hydrogenolysis of Fluoroaromatics by $[(\eta^5\text{-}C_5Me_5)Rh^I(2,2'\text{-bipyridine})]$

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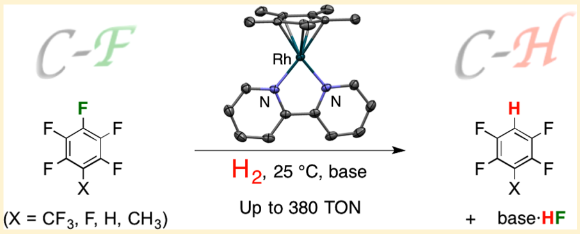
Supporting Information

ABSTRACT: A new class of efficient catalyst, the Rh(I) complex $[(\eta^5\text{-}C_5Me_5)Rh^I(bpy)]$ (**1**; bpy = 2,2′-bipyridine), for the C−F bond hydrogenolysis of fluoroaromatics ($C_6F_5CF_3$, C_6F_6, C_6F_5H, and $C_6F_5CH_3$) is presented. The best turnover number of 380 for C_6F_6 is afforded by using 0.1 mol % of **1**, 0.8 MPa of H_2, and 2 equiv of Et_2NH in CH_3CN at 25 °C. The successful isolation of the C−F bond cleavage product $[(\eta^5\text{-}C_5Me_5)Rh^{III}(bpy)(C_6F_5)](F)$ as a plausible intermediate of the catalytic hydrogenolysis of C_6F_6 by **1** is also described.



Catalytic activation and transformation of the C−F bonds under mild conditions are a challenge in synthetic chemistry.[1−6] Hydrodefluorination is the reaction that converts the C−F bonds into C−H bonds and can provide partially fluorinated molecules as synthetic building blocks for biologically active compounds and functional materials.[1a,2−6] In 1994, Aizenberg and Milstein reported the first example of "catalytic" hydrodefluorination by using Rh complexes and R_3SiH (R = Ph, EtO) as catalysts and hydrogen sources, respectively.[2] Since then, various transition-metal catalysts for hydrodefluorination have been developed in combination with hydrogen sources such as silanes,[3] aluminum hydrides,[4] pinacolborane,[5] and H_2.[6] Among them, systems using H_2 as the hydrogen source, which can be referred to as "catalytic C−F bond hydrogenolysis", are attractive from fundamental, economical, and environmental points of view. However, a limited number of transition-metal catalysts have been reported so far and, especially for the hydrogenolysis of unreactive substrates such as hexafluorobenzene (C_6F_6), the systems require the conditions of high H_2 pressure (>0.1 MPa) and/or high temperature (>25 °C).[6] To overcome these situations, a new class of efficient catalysts that can provide a new concept for the C−F bond hydrogenolysis is required.

Transition-metal complexes of the general composition $[(\pi\text{-arene})M(\alpha\text{-diimine})]^n$ (M = Fe(0), Ru(0), Co(I), Rh(I), etc.; *n* = charge of the complex), which have an electron-rich metal center, have received much attention because of their unique electronic structures and reactivities.[7−9] In our efforts to develop novel reactivities of this class of metal complexes,[7a] we have now found that the Rh(I) complex $[(\eta^5\text{-}C_5Me_5)Rh^I(bpy)]$ (**1**; bpy = 2,2′-bipyridine) catalyzes the C−F bond hydrogenolysis of C_6F_6 *under mild conditions* (0.1 MPa of H_2, 25 °C). Herein we report the catalytic reactivity of **1** toward fluoroaromatics ($C_6F_5CF_3$, C_6F_6, C_6F_5H, and $C_6F_5CH_3$), together with a hitherto unknown crystal structure of **1**. We also report the successful isolation of the C−F bond cleavage product $[(\eta^5\text{-}C_5Me_5)Rh^{III}(bpy)(C_6F_5)](F)$ (**2**(F)) as a plausible intermediate of the catalytic hydrogenolysis of C_6F_6 by **1**.

The Rh(I) complex **1** was prepared by a modified literature method via reduction of the Rh^{III}−chloro complex $[(\eta^5\text{-}C_5Me_5)Rh^{III}(bpy)Cl](Cl)$ (**3**(Cl))[10] with sodium metal in THF at room temperature.[8] Whereas the synthesis and characterization of **1** have been reported,[8,9] the X-ray structure has not yet been reported. Fortunately, purple crystals of **1** suitable for X-ray diffraction analysis were grown from a saturated THF solution at room temperature. The molecular structure of **1** is depicted in Figure 1, along with selected interatomic data (Table S1 in the Supporting Information). The Rh atom of **1** is coordinated by the one C_5 ring of C_5Me_5 and two nitrogen atoms of bpy. Notably, the inter-ring distance (C15−C16) of the coordinated bpy ligand in **1** (1.423(5) Å) is consistent with the previously reported theoretical value (1.435

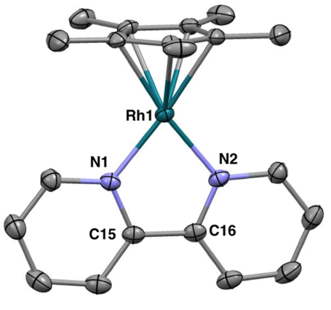


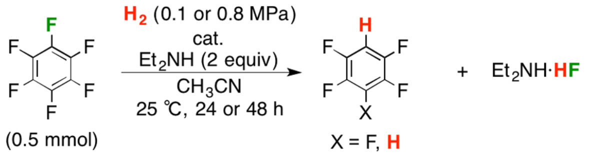
Figure 1. ORTEP drawing of **1** with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angle (deg): average $Rh1-C(\eta^5\text{-}C_5Me_5)_{ring}$ = 2.204(4), Rh1−N1 = 1.997(3), Rh1−N2 = 2.003(3), C15−C16 = 1.423(5), N1−Rh1−N2 = 78.21(11).

Received: June 18, 2014
Published: August 19, 2014

Å)[9a] and is much shorter than that of the uncoordinated bpy (1.490(3) Å).[11] This is the structural evidence for the ligand (bpy) reduction discussed in the structurally related [(π-arene)M(α-diimine)]^n complexes.[7a,b,d,h,9a,b] So far, this class of metal complexes has not been applied to the C−F bond activation.

The catalytic ability of **1** (5 mol %) toward the C−F bond hydrogenolysis of C_6F_6 with 0.1 MPa of H_2 at 25 °C for 24 h was investigated under various conditions (Tables S2 and S3 in the Supporting Information). The effect of solvent was examined using toluene, THF, 1,2-dimethoxyethane (DME), CH_3OH, CH_3CN, and DMSO (Table S2). The effect of the base that works as a trap for the released HF was also examined using Cs_2CO_3, pyridine, Et_3N, and Et_2NH (Table S3).[6] The over 99% conversion of C_6F_6 with a turnover number (TON, in units of (mol of product)/(mol of catalyst)) of 19.8 for C_6F_5H was obtained by using CH_3CN and Et_2NH as a solvent and base, respectively (Table S3, entry 4, and Table 1, entry 1). The result of Hg(0) drop experiments indicates that there is no heterogeneous metal particle under the present reaction conditions (Table 1, entries 1 and 2). Further optimization showed that the best TON of 380 for C_6F_5H was afforded by using 0.1 mol % of **1**, 0.8 MPa of H_2, and 1.0 mmol of Et_2NH (2 equiv) (Table 1, entry 6). The blank experiments without the catalyst or H_2 did not yield any products (Table 1, entries 7 and 8). The necessity of H_2 as a hydrogen and an electron source was further supported by the labeling experiment using D_2 (Table 1, entry 9). Notably, the double-hydrogenolysis product "p-HC_6F_4H" is obtained by the chemo- and regioselective hydrogenolysis of C_6F_5H (Tables S2 and S3, Table 1, and Figures S1 and S2 in the Supporting Information).[12]

Table 1. Catalytic C−F Bond Hydrogenolysis of C_6F_6 in CH_3CN[a]

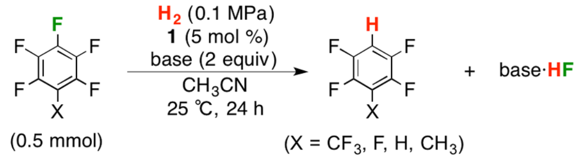


entry	amt of cat. (mol %)	H_2 (MPa), time (h)	TON[b] C_6F_5H[c]	TON[b] p-HC_6F_4H[d]	conversn (%)[b]
1[e]	**1** (5)	0.1, 24	19.8	3.9	99
2[f]	**1** (5)	0.1, 24	19.0	2.5	95
3	**1** (2.5)	0.1, 24	24.8	0.9	62
4	**1** (2.5)	0.8, 24	38.0	5.3	95
5	**1** (1)	0.8, 48	93.0	10.7	93
6	**1** (0.1)	0.8, 48	380	5.7	38
7	–	0.8, 24		n.r.[g]	
8	**1** (2.5)	–, 24		n.r.[g]	
9[h]	**1** (2.5)	0.1, 24	29.2[i]	1.3	73
10	**2**(F) (2.5)	0.1, 24	26.8	1.2	67
11	**3**(Cl) (2.5)	0.8, 24	37.2	4.7	93

[a] The catalytic reactions were investigated in CH_3CN under various conditions (0.1 or 0.8 MPa of H_2, 25 °C, 24 or 48 h) using 0.5 mmol (200 mM) of C_6F_6. [b] Turnover numbers (TON, in units of (mol of product)/(mol of catalyst)) and conversions (conversn (%)) were determined by integration of the peaks in the ^{19}F NMR spectra using 0.25 mmol of 1-fluoropentane as an internal standard (precision limits are ±3% of the given value). [c] TON for C_6F_5H: ((mol of C_6F_5H) + (mol of p-HC_6F_4H))/(mol of catalyst). [d] TON for p-HC_6F_4H: (mol of p-HC_6F_4H)/(mol of catalyst). [e] The same data of Table S3, entry 4 (Supporting Information). [f] The reaction was carried out in the presence of an Hg drop (ca. 60 mg). [g] No reaction. [h] D_2 (99.5%) was used instead of H_2. [i] Molar ratio of the products: C_6F_5D/C_6F_5H = 90/10 (Figure S2 in the Supporting Information); C_6F_5H may be produced by D/H exchange at a certain stage in step II in Scheme 1.

The catalytic C−F bond hydrogenolysis of other fluoroaromatics was also investigated under mild conditions (Table 2 and Figures S3−S5 in the Supporting Information). In general, the hydrodefluorination of the electron-rich fluoroaromatics is difficult and the examples are very rare.[3b,d] The reaction of $C_6F_5CF_3$,[13] C_6F_5H, and $C_6F_5CH_3$ with 0.1 MPa of H_2 in the presence of **1** (5 mol %) and base provided the selective C−F bond hydrogenolysis products (p-$HC_6F_4CF_3$, p-HC_6F_4H, and p-$HC_6F_4CH_3$) with conversions of 26, 51, and 19%, respectively.[12] Thus, **1** can catalyze the C−F bond hydrogenolysis of fluoroaromatics both more electron deficient ($C_6F_5CF_3$) and rich (C_6F_5H and $C_6F_5CH_3$) than C_6F_6; **1** cannot catalyze the reaction of fluoroaromatics (p-HC_6F_4H) more electron rich than $C_6F_5CH_3$ (5 mol % of **1**, 0.1 MPa of H_2, 25 °C, 24 h).

Table 2. Catalytic C−F Bond Hydrogenolysis of Fluoroaromatics in CH_3CN under Mild Conditions (0.1 MPa of H_2, 25 °C, 24 h)[a]



entry	X	base (amt (equiv))	TON[b]	conversn (%)[b]
1	CF_3	Et_3N (2)	5.2	26
2[c]	F	Et_2NH (2)	19.8	99
3	H	Et_2NH (2)	10.2	51
4	CH_3	Et_2NH (2)	3.8	19

[a] The catalytic reactions were investigated using 0.5 mmol (200 mM) of C_6F_5X (X = CF_3, F, H, CH_3). [b] Turnover numbers (TON, in units of (mol of single hydrogenolysis product)/(mol of catalyst)) and conversions (conversn (%)) were determined by integration of the peaks in the ^{19}F NMR spectra using 0.25 mmol of 1-fluoropentane as an internal standard (precision limits are ±3% of the given value). [c] The same data of Table 1, entry 1.

A clue to elucidate the catalytic cycle has been obtained by the isolation of the C−F bond cleavage product **2**(F). The reaction of **1** with C_6F_6 "without H_2" at room temperature afforded **2**(F). The monocationic Rh(III) complex **2** was characterized by NMR (^1H and ^{19}F) and UV−vis−NIR spectroscopy, electrospray ionization mass spectrometry (ESI-MS), X-ray diffraction, and elemental analysis (Figures S6−S8 in the Supporting Information). The positive-ion ESI mass spectrum of **2**(F) dissolved in CH_3CN shows a signal at m/z 561.2 (relative intensity (I) = 100% in the range m/z 200−1200), which has a characteristic isotopic distribution that matches well with the calculated isotopic distribution for the monocation **2**.

The molecular structure of **2** was confirmed by X-ray crystallography (Table S1). Yellow crystals of **2**(BPh_4)·Et_2O were obtained by diffusion of Et_2O into an AcOEt/CH_3CN (5/1) solution of **2**(BPh_4) which was prepared by anion exchange of **2**(F) with $NaBPh_4$ in THF. Figure 2 shows an ORTEP drawing of the monocationic Rh(III) complex **2**. The Rh atom

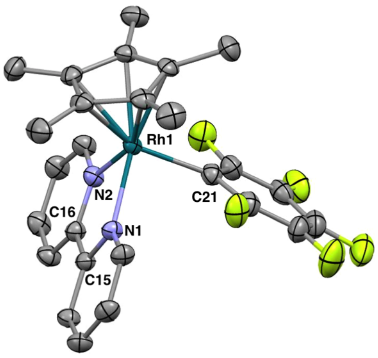


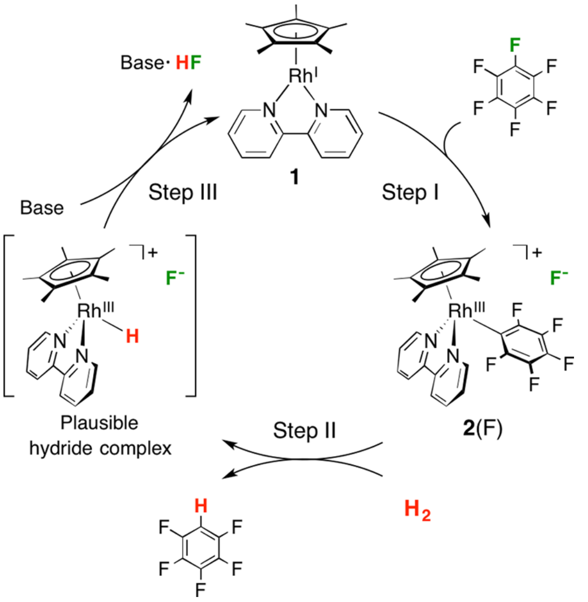
Figure 2. ORTEP drawing of monocation **2** with 50% probability ellipsoids. Hydrogen atoms, solvent, and BPh_4 anion are omitted for clarity. Selected bond lengths (Å) and angle (deg): average Rh1−C(η^5-C_5Me_5)$_{ring}$ = 2.182(4), Rh1−C21 = 2.099(4), Rh1−N1 = 2.111(3), Rh1−N2 = 2.104(3), C15−C16 = 1.471(4), N1−Rh1−N2 = 77.11(10).

of **2** is coordinated by the one C_5 ring of C_5Me_5, two nitrogen atoms of bpy, and one carbon atom of C_6F_5. The inter-ring distance (C15−C16) of the coordinated bpy ligand in **2** (1.471(4) Å) is longer than that of the Rh(I) complex **1** (1.423(5) Å) and is consistent with that of the Rh^{III}−chloro complex **3** (1.480(11) Å).[10] The metal−perfluoroarene distance (Rh1−C21) in **2** (2.099(4) Å) is slightly longer than that found in [(η^5-C_5Me_5)Rh^{III}(PMe_3)(C_6F_5)Cl] (2.070(5) Å).[14]

The reaction of **2**(F) with 0.1 MPa of H_2 in the presence of Et_2NH in CH_3CN at 25 °C yielded the Rh(I) complex **1**, C_6F_5H, and *p*-HC_6F_4H (Figure S9 in the Supporting Information). Furthermore, **2**(F) catalyzed the hydrogenolysis of C_6F_6 with much the same efficiency and selectivity as **1** (Table 1, entries 3 and 10). Thus, **2**(F) must be one of the intermediates in the catalytic cycle. The base (Et_2NH) likely assists heterolytic cleavage of H_2, as discussed in the H_2 activation chemistry.[15]

Scheme 1 shows a plausible catalytic cycle for the C−F bond hydrogenolysis of C_6F_6 by the Rh(I) complex **1** on the basis of the findings described above. In step I, **1** reacts with the substrate "C_6F_6" to form the C_6F_5-coordinated Rh(III) complex **2**. The reaction likely proceeds via a nucleophilic aromatic substitution (S_NAr) pathway that is proposed in the reaction of the neutral Ir(I) complex [(η^5-C_5Me_5)$Ir^I(CO)_2$] with C_6F_5CN,[16] whereas an electron-transfer[2,6d,17] and oxidative-addition[18] pathway cannot be excluded at the present stage. In step II, **2** reacts with H_2 to liberate the product "C_6F_5H" and may transfer to a Rh^{III}−H species. The reaction includes Rh−C and H−H bond cleavage and Rh−H and C−H bond formation processes and may proceed with ring slippage of the C_5Me_5 ligand.[19] The rate-determining step is involved in this step, as supported by the following observations: (i) the solution during the catalytic reaction is pale yellow due to **2** (Figures S1 and S9) and (ii) the TON increases with increasing H_2 pressure (Table 1, entries 3 and 4). In step III, the Rh^{III}−H species reacts with the base to regenerate **1** (deprotonation of hydride species).[20] The following points should be noted. (i) **1** does not react with 0.8 MPa of H_2 in the presence of Et_2NH: the possibility for the oxidative addition of H_2 to the Rh(I) center can be excluded under the catalytic conditions (Figure S10 in the Supporting Information) (ii) The practically useful Rh^{III}−chloro complex **3** can catalyze the hydrogenolysis of C_6F_6 (Table 1, entry 11): this supports the formation of the Rh^{III}−H species in the catalytic cycle, because some Rh(III) complexes are known to react with H_2 to form Rh^{III}−H species.[21] Further studies to elucidate the reaction mechanism are now in progress.

Scheme 1. Plausible Catalytic Cycle for the C−F Bond Hydrogenolysis of C_6F_6 by 1



In conclusion, we have demonstrated that the Rh(I) complex **1** is a new class of efficient catalyst for C−F activation. To date, the development of transition-metal catalysts for C−F bond activation has been mainly focused on metal hydride and fluoride species as catalysts or intermediates.[1−6] We believe that our findings offer attractive new insight into the construction of novel efficient catalysts, not only for the hydrogenolysis of fluoroaromatics but also for the further functionalization of fluoroorganic compounds.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, tables, figures, and CIF files giving experimental details and characterization data for **1**, **2**(F), and **2**(BPh_4) and X-ray crystallographic data for **1** and **2**(BPh_4)·Et_2O. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by grants-in-aid 26000008 (Specially Promoted Research), 26410074, 26810038, and 24109016 (Scientific Research on Innovative Areas "Stimuli-responsive Chemical Species") and the World Premier International Research Center Initiative (WPI Program) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT, Japan).

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