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Light induced catalytic hydrodefluorination of perfluoroarenes by porphyrin rhodium

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1. General Considerations

D_2O and CD_3OD were purchased from Cambridge Isotope Laboratory Inc.; tetra (*p*-sulfonatophenyl) porphyrin from Tokyo Chemical Industry (TCI); $(Rh(CO)_2Cl)_2$ from Strem Chemical Inc.; and all other chemicals were purchased from Alfa Aesar or J&K Scientific Ltd. unless otherwise noted and used as received. ^{1}H NMR spectra were recorded on a Bruker AVII-400 spectrometer at ambient temperature. ^{1}F NMR spectra were recorded on a Bruker AVII-300 spectrometer and a Bruker AVII-400 spectrometer at ambient temperature. GC-MS results were obtained by the Agilent 7980A/5975C GC/MSD system equipped with the DB-17MS (30m, 0.25mm, 0.25 μ m) column. GC results were obtained by the Agilent 7980A system equipped with the DB-5MS UI (30 m, 0.25 mm, 0.50 μm) column. ESI-MS results were obtained by a Bruker Apex IV FTMS. Light irradiation experiments was performed using a 500W high-pressure mercury lamp (CHF-XM35-500W, Beijing Trusttech Co., Ltd.,) and the glass vessel was positioned about 15.0 cm away from the light source.

2. Preparation of $Na_4[(TSPP)Rh^{III}(H_2O)_2]$

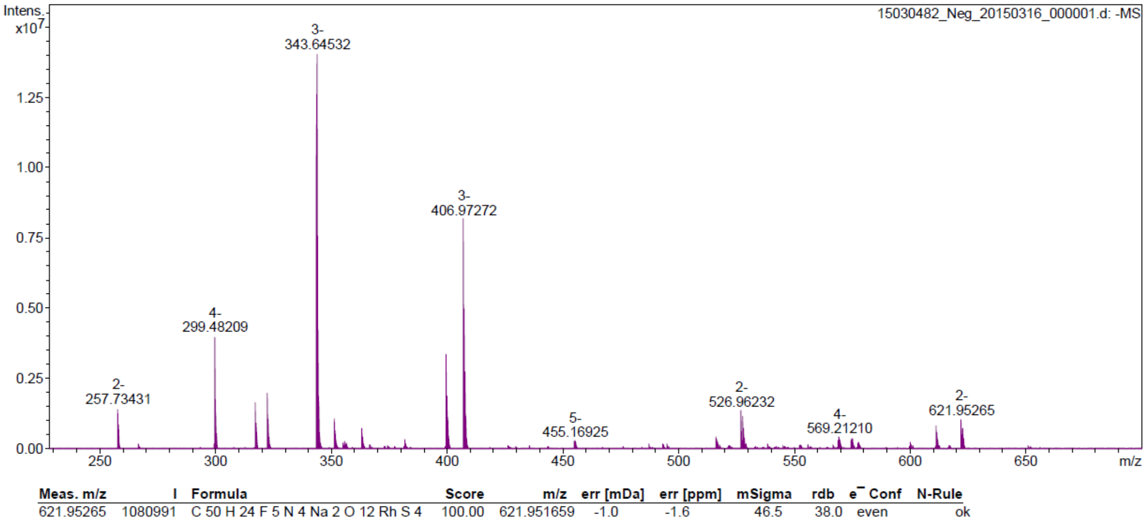
$Na_3[(TSPP)Rh^{III}(H_2O)_2]$ was synthesized by following literature methods of Ashley.[1] The equilibrium distribution of $[(TSPP)Rh^{III}(D_2O)_2]^{-3}$, $[(TSPP)Rh^{III}(D_2O)(OD)]^{-4}$ and $[(TSPP)Rh^{III}(OD)_2]^{-5}$

were reported in the previously published paper.[2] ^{1}HNMR (D_2O, 400 MHz) δ(ppm): 9.15 (s, 8H, pyrrole), 8.44 (d, 8H, *o*-phenyl, $J_{H\text{-}H}$ =8 Hz), 8.25 (d, *m*-phenyl, $J_{H\text{-}H}$=8 Hz). The stock solution of (TSPP)Rh^{III} was prepared in H_2O.

3. Spectra forMechanistic Studies

3.1 Synthesis of (TSPP)Rh^I

(TSPP)Rh^I was synthesized following our previous reported method[3]. 10μL of triethylamine was added to 2mL aqueous solution of (TSPP)Rh^{III} (1.0 mM) in 10 mL Schlenk flask. After being degassed by three freeze-pump-thaw cycles, the mixture was stirred at 50 °C for 2 hours, yielding (TSPP)Rh^I quantitatively. The water, excessive triethylamine and other volatile by-products were removed under vacuum line. Then the (TSPP)Rh^I was dissolved in 0.8 mL methanol solution of 12.0 mM sodium borate buffer which was used for stoichiometric and catalytic reactions with the concentration of (TSPP)Rh^I 2.5mM.



Meas. m/z	I	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
621.95265	1080991	C 50 H 24 F 5 N 4 Na 2 O 12 Rh S 4	100.00	621.951659	-1.0	-1.6	46.5	38.0	even	ok

(ESI-MS : 1243.91 and Exact Mass: 1243.91)

Figure 1S ESI-MS of anion $[(TSPP)Rh\text{-}C_6F_5]Na_2^{2-}$

(TSPP)Rh-C_6F_5: ^{1}HNMR (CD_3OD, 400 MHz) δ (ppm): 8.77 (s, 8H, pyrrole), 8.22 (d, 8H, *o*-phenyl, $J_{H\text{-}H}$ =8 Hz), 8.17 (d, *m*-phenyl, $J_{H\text{-}H}$=8 Hz).

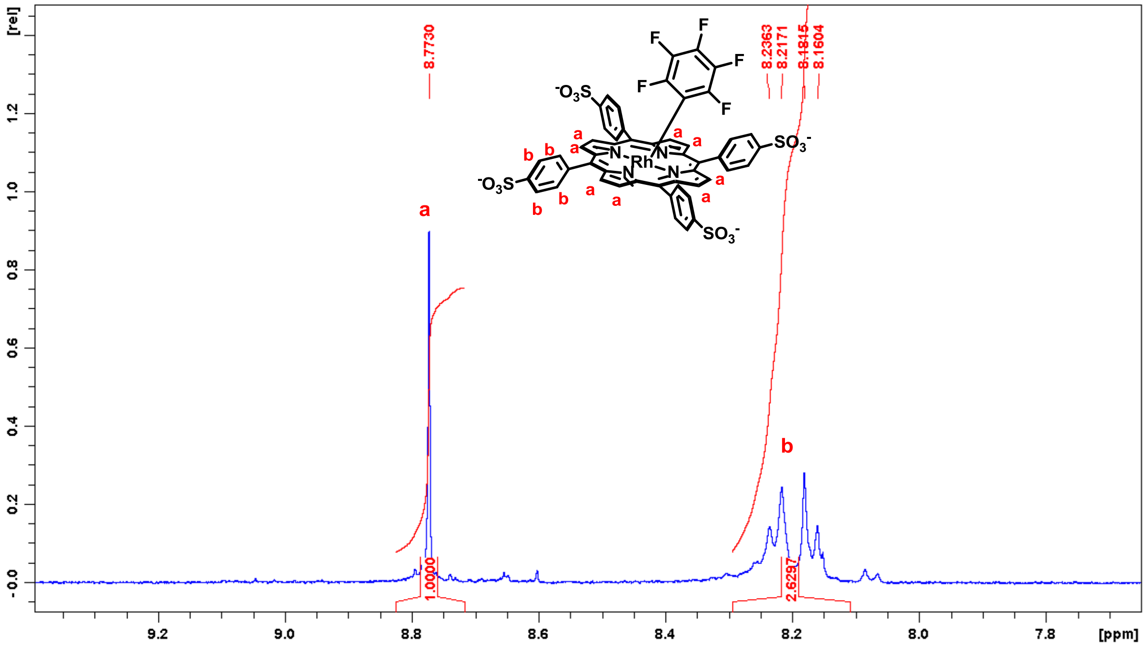


Figure 2S ^{1}H NMR of (TSPP)Rh-C_6F_5 in CD_3OD

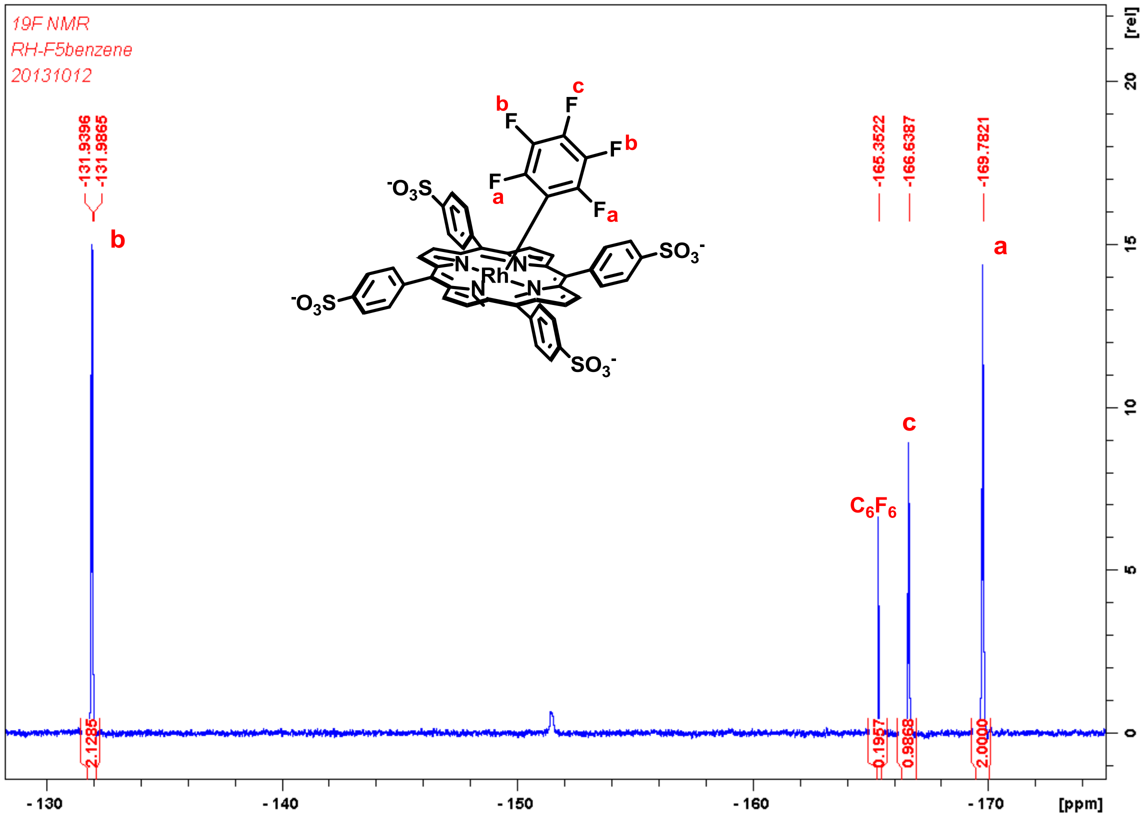
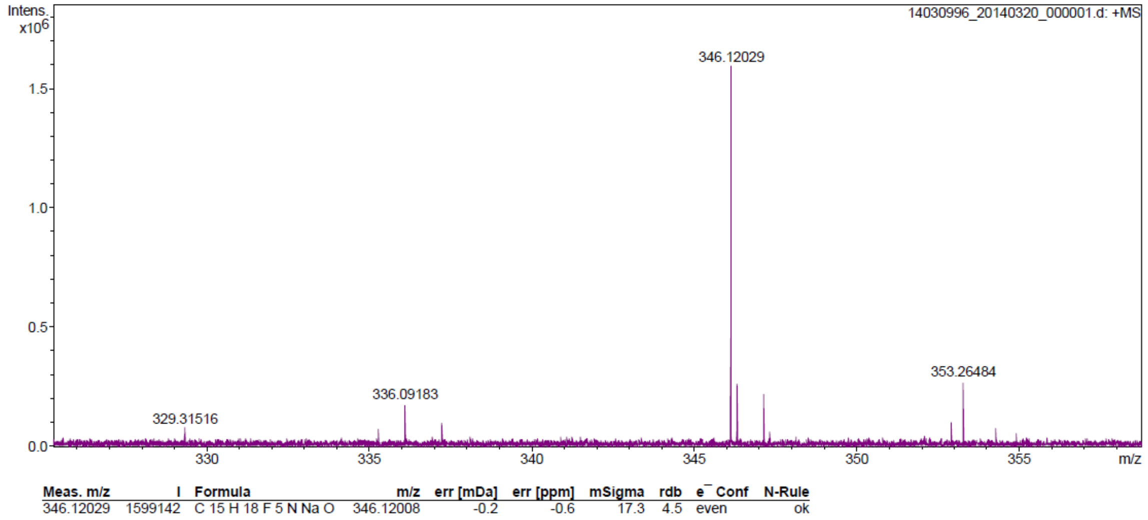


Figure 3S ^{19}F NMR of (TSPP)Rh-C_6F_5 in CD_3OD

The C_6F_5 radical, which is the photo-cleavage product of Rh-C bond, was trapped by TEMPO(TEMPO=2,2,6,6-Tetramethylpiperidine-1-oxyl)**(Figure 4S)**

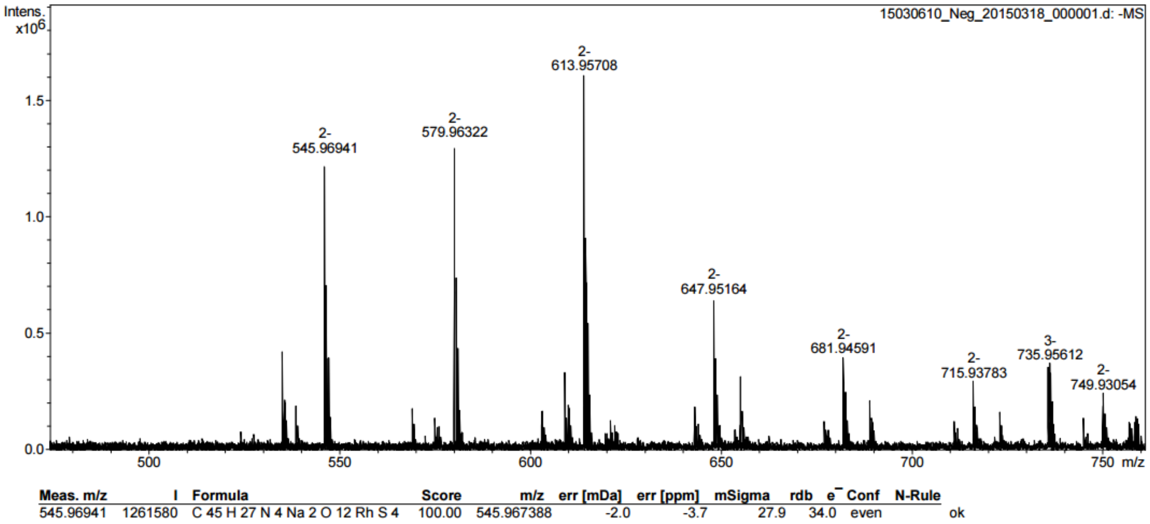


Meas. m/z	I	Formula	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
346.12029	1599142	C 15 H 18 F 5 N Na O	346.12008	-0.2	-0.6	17.3	4.5	even	ok

Figure 4S ESI-MS of TEMPO-C_6F_5

(ESI-MS: 346.120 and Exact Mass: 346.120)

The generation of (TSPP)Rh^I upon treatment of (TSPP)Rh^{III} with Me_2EtSiH was confirmed by trapping with CH_3I, yielding the known (TSPP)Rh^{III}-CH_3 complex.



Meas. m/z	I	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
545.96941	1261580	C 45 H 27 N 4 Na 2 O 12 Rh S 4	100.00	545.967388	-2.0	-3.7	27.9	34.0	even	ok

Figure 5S ESI-MS of (TSPP)Rh-CH_3

(ESI-MS: 1091.94 and Exact Mass: 1091.94)

4. Effects of Silanes

Table 1S Effects of silanes[a]

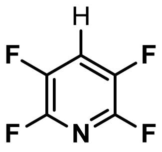
entry	NEt_3	R_3SiH	turnover[b]
1	no	0.2 mmol Me_2PhSiH	13.5
2	no	0.2 mmol Et_3SiH	21.3
3	no	0.2 mmol Ph_2MeSiH	15.5
4	no	0.2 mmol $(EtO)_2MeSiH$	15.5
5	no	0.2 mmol Et_2MeSiH	30.5
6[c]	no	ethylene glycol 30 uL 0.2 mmol $EtMe_2SiH$	65.9

[a] Reaction conditions: 12 μL (0.1 mmol) hexafluorobenzene and different kinds of silanes (2 mmol) were added to 0.4 mL methanol solution of (TSPP)Rh^{III} (2.5mM) and sodium borate (0.012M), stirring at 60 °C under light irradiation (500 W Hg lamp, 15 cm distance) for 36 hours. [b] GC results, [c] hexafluorobenzene 24μL (0.2 mmol) was used.

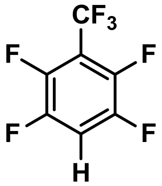
5. General Procedure for Catalytic Hydrodefluorination Catalyzed by Porphyrin Rhodium

In a 25 mL Schlenk flask sealed with a Teflon cap, 1.0 mmol perfluoroarenes and 270 μL (2.0 mmol) Me_2EtSiH were added to 0.50 mL methanol solution of (TSPP)Rh^{III} (2mM) and sodium borate (0.012M), then 0.5 mL ethylene glycol were added. After being degassed by three freeze-pump-thaw cycles, the mixture was stirred at 60 °C under light irradiation for 36 hours. (500 W Hg lamp, 15 cm distance). In addition, the catalytic hydrodefluorination of pentafluorotoluene and N,N-dimethylpentafluoroaniline didn't occur under our standard reaction condition, indicating that our system showed no hydrodefluorination activity for pentafluorotoluene and N,N-dimethylpentafluoroaniline.

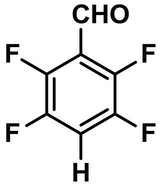
6. Spectral Data for Selected Compounds



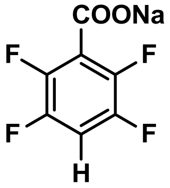
2,3,5,6-Tetrafluoropyridine ^{19}F NMR (282 MHz) δ (ppm) -30.18 (m, 2F), -78.06 (m, 2F).



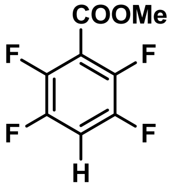
2,3,5,6-Tetrafluorobenzotrifluoride. ^{19}F NMR (282 MHz) δ (ppm) 5.90(m, 3F), -74.1 (m, 2F), -78.0 (m, 2F).



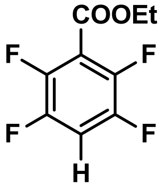
2,3,5,6-Tetrafluorobenzaldehyde. ^{19}F NMR (282 MHz) δ (ppm) -73.5 (m, 2F), -81.3 (m, 2F).



Sodium 2,3,5,6-tetrafluorobenzoate. ^{19}F NMR (282 MHz). δ (ppm) -77.4 (m,2F), -81.8 (m, 2F).



Methyl 2,3,5,6-Tetrafluorobenzoate. ^{19}F NMR (282 MHz). δ (ppm) -75.8 (m, 2F), -78.3 (m, 2F).



Ethyl 2,3,5,6-tetrafluorobenzoate. ^{19}F NMR (282 MHz). δ (ppm) -75.8(m,2F), -78.6 (m, 2F).

Reference

(1) K. R. Ashley, S. B. Shyu and J. G. Leipoldt, *Inorg. Chem.*, 1980, **19**, 1613.

(2) X. Fu and B. B. Wayland, *J. Am. Chem. Soc.*, 2004, **126**, 2623.

(3) Z. Ling, L. Yun, L. Liu, B. Wu and X. Fu, *Chem. Commun.*, 2013, **49**, 4214.