Electronic Supporting Information

Ruthenium-Catalyzed Nucleophilic Fluorination of Halobenzenes

Andrey I. Konovalov, Evgeniya O. Gorbacheva, Fedor M. Miloserdov and Vladimir V. Grushin

Contents

I. General Information

Ruthenium trichloride hydrate, $RuCl_3 \cdot xH_2O$ (~40% Ru) was purchased from Precious Metals Online, PMO Pty Ltd, Australia. Cesium fluoride (Apollo Scientific) was finely ground in an electric coffee grinder inside an argon-filled glove-box, dried under vacuum (~0.1 mm Hg) at 120 ^oC (oil bath) for 12 h, and brought back to the glove-box without exposure to air. The grinding-drying was repeated twice, after which the fine powder of dry CsF was stored in the glove-box. All other chemicals, solvents, and deuterated solvents were purchased from Aldrich, Alfa Aesar, Deutero, Strem, TCI, Apolo Scientific and Fluka chemical companies. All reactions were conducted under argon using either glove-box or standard Schlenk techniques, unless noted otherwise. [Cp*Ru(napht)]PF_6, [1] [CpRu(napht)]BF_4, [2] [Cp*Ru$(CH_3CN)_3$]BF_4, [3] [Cp*RuCl_2]$_2$, [4] [Cp*RuCl]$_4$, [5] [Cp*Ru$(PPh_3)_2Cl$], [6] [$(benzene)_2$Ru]$(BF_4)_2$, [7] [Cp*RhCl_2]$_2$, [8] and 1,3-bis(2,6-diisopropylphenyl)-2-dichloroimidazolium chloride (IPr-Cl)[9] were prepared according to the literature procedures. Anhydrous DMF from an MBraun SPS was kept over freshly activated 4 Å molecular sieves in the glove-box. All other solvents and liquid substrates were degassed and kept over freshly activated 4 Å molecular sieves in the glove-box. ^1H and ^{19}F NMR spectra were recorded on Bruker Avance Ultrashield 400 MHz and 500 MHz spectrometers. Quantitative ^{19}F NMR analysis was carried out with D1 = 5 s. An Agilent Technologies 7890A chromatograph equipped with a 5975C MSD unit was used for GC-MS analysis. Single-crystal X-ray diffraction studies were performed using a Bruker-Nonius diffractometer equipped with an APEX II 4K CCD area detector.

II. Preparation of Ru and Rh Complexes

[Cp*Ru(napht)]BF_4 (1). This complex was prepared by a modified procedure for [Cp*Ru(napht)]PF_6.[1] A solution of $RuCl_3 \cdot xH_2O$ (0.97 g, 4 mmol) in degassed ethanol (25 mL) was kept under reflux in a two-neck round bottom flask until the color of the solution turned green (ca. 2 h). Pentamethylcyclopentadiene (3 mL, 20 mmol) and naphthalene (2.56 g, 20 mmol) were added to the reaction mixture, and the resulting solution was heated at reflux for 6 h. The reaction mixture was worked up in air. After the solvent was evaporated, water (15 mL) was added to the residue, and the solids were filtered off. The filtrate was treated with aqueous HBF_4 (48%, 10 mL) and extracted with CH_2Cl_2 (3 x 40 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated to give crude **1**. A solution of the crude product in a minimal amount of acetone was filtered through neutral alumina (150 mesh), which was then washed with acetone. Evaporation of the combined filtrate and the washings gave purified **1** that was recrystallized by the addition of ether to its concentrated acetone solution and subsequently dried under vacuum. The yield of bright-yellow **1** was 1.45 g (81%). ^{1}H NMR (CD_2Cl_2), δ: 1.69 (s, 15H, Cp*), 5.98-6.02 (m, 2H, $C_{10}H_8$), 6.44-6.47 (m, 2H, $C_{10}H_8$), 7.51-7.56 (m, 2H, $C_{10}H_8$), 7.70-7.75 (m, 2H, $C_{10}H_8$).

[Cp*Ru(PhX)]PF_6 (X = F or Cl). A mixture of [Cp*Ru(napht)]PF_6 (51 mg, 0.1 mmol), PhCl or PhF (0.5 mL), and CH_3CN (0.2 mL) in 1,2-dichloroethane (7 mL) was kept under reflux until the bright-yellow solution turned almost colorless (ca. 15 h). The product was isolated in air. The volatiles were evaporated to yield a residue that was washed with ether (2 x 5 mL) and dissolved in a minimal amount of acetone. This solution was filtered through neutral alumina, which was then washed with acetone. The combined filtrate and the

washings were concentrated on a rotary evaporator and treated with ether. The white precipitate of the product was separated, washed with ether, and dried under vacuum. The yield of [Cp*Ru(PhF)]PF_6 was 41 mg (86%). ^{1}H NMR (CD_2Cl_2), δ: 2.0 (s, 15H, Cp*), 5.71-5.75 (m, 1H, PhF), 5.87-5.91 (m, 2H, PhF), 5.99-6.01 (m, 2H, PhF). ^{19}F NMR (CD_2Cl_2), δ: -72.6 (d, J_{P-F} = 711 Hz, 6F, PF_6^-), -144.8 (s, 1F, PhF). The yield of [Cp*Ru(PhCl)]PF_6 was 43 mg (88%). ^{1}H NMR (CD_2Cl_2), δ: 2.01 (s, 15H, Cp*), 5.83-5.92 (m, 3H, PhCl), 5.96-5.99 (m, 2H, PhCl).

[Cp*Ru(PhCl)]BF_4. This complex was prepared similarly to [Cp*Ru(PhCl)]PF_6 (see above). A mixture of [Cp*Ru(napht)]BF_4 (181 mg, 0.4 mmol), PhCl (5 mL), CH_3CN (0.8 mL), and 1,2-dichloroethane (10 mL) was kept under reflux until the bright-yellow solution turned almost colorless (ca. 15 h). The product was isolated in air. The volatiles were evaporated to give a residue that was washed with ether (2 x 5 mL) and dissolved in a minimal amount of acetone. This solution was filtered through neutral alumina, which was then washed with acetone. The combined filtrate and the washings were concentrated on a rotary evaporator and treated with ether. The white precipitate of the product was separated, washed with ether, and dried under vacuum. The yield of [Cp*Ru(PhCl)]BF_4 was 160 mg (92%). ^{1}H NMR ([D_6]acetone), δ: 2.08 (s, 15H, Cp*), 6.14-6.17 (m, 1H, PhCl), 6.21-6.24 (m, 2H, PhCl), 6.40-6.42 (m, 2H, PhCl).

[Cp*Ru(4,4'-difluorobiphenyl)]BF_4. A mixture of [Cp*Ru(napht)]BF_4 (45 mg, 0.1 mmol), 4,4'-difluorobiphenyl (95 mg, 0.5 mmol), CH_3CN (0.2 mL), and 1,2-dichloroethane (5 mL) was kept under reflux until the bright-yellow solution turned almost colorless (ca. 24 h). The product was isolated in air. The solvent was evaporated to give a residue that was washed

with ether (2 x 5 mL) and dissolved in a minimal amount of acetone. This solution was filtered through neutral alumina, which was then washed with acetone. The combined filtrate and the washings were concentrated on a rotary evaporator and treated with ether. The yellowish precipitate was separated, washed with ether, and dried under vacuum. The yield of [Cp*Ru(4,4'-difluorobiphenyl)]BF_4 was 35 mg (70%). ^{1}H NMR (CD_2Cl_2), δ: 1.87 (s, 15H, Cp*), 6.20-6.24 (m, 2H, $FC_6H_4C_6H_4F$), 6.39-6.42 (m, 2H, $FC_6H_4C_6H_4F$), 7.26-7.32 (m, 2H, $FC_6H_4C_6H_4F$), 7.63-7.68 (m, 2H, $FC_6H_4C_6H_4F$). ^{19}F NMR (CD_2Cl_2), δ: -110.0 (s, 1F, $FC_6H_4C_6H_4F$), -147.1 (s, 1F, $FC_6H_4C_6H_4F$), -151.8 (4F, BF_4). The product contained unreacted [Cp*Ru(napht)]BF_4 (~20%) that could not be completely removed without significant losses of [Cp*Ru(4,4'-difluorobiphenyl)]BF_4.

[Cp*Rh(CH_3CN)$_3$](BF_4)$_2$. A mixture of [Cp*$RhCl_2$]$_2$, (309 mg, 0.5 mmol), $AgBF_4$ (390 mg, 2.0 mmol), and CH_3CN (10 mL) was stirred at room temperature for 4 h. The solution was filtered through a pad of Celite and evaporated to dryness. The bright-yellow solid was recrystallized by the addition of ether to its solution in CH_3CN and dired under vacuum. The yield of [Cp*Rh(CH_3CN)$_3$](BF_4)$_2$ was 520 mg (97%). ^{1}H NMR (CD_3CN), δ: 1.74 (s, 15H, Cp*), 1.96 (s, 9H, CH_3CN).

III. Catalyst Scouting

All experiments described below were carried out in the presence of 4,4'-difluorobiphenyl as an internal standard to monitor the reactions by ^{19}F NMR. Although the internal standard is an aromatic compound and, therefore, could possibly bind to the metal center, no signal from

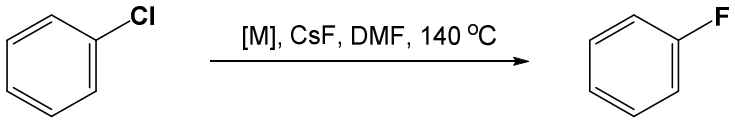
*[Cp*Ru(4,4'-difluorobiphenyl)]BF_4 (see above) was detected in the ^{19}F NMR spectra in any of the fluorination experiments, showing that 4,4'-difluorobiphenyl does not compete with PhCl and PhF for binding to the Ru atom.*

General Procedure. A thoroughly dried 50-mL Schlenk tube equipped with a J. Young high-vacuum valve and a magnetic stir-bar was charged in air with a catalyst (1 equiv, Table S1, entries 1-4 and 8-10)[10] and 4,4'-difluorobiphenyl (4 mg, 0.02 mmol, 0.5 equiv, internal standard) and brought to an argon-filled glove-box. In the glove-box, CsF (334 mg, 2.2 mmol, 50 equiv), PhCl (0.5 mL, 4.4 mmol, 100 equiv) and DMF (1.5 mL) were added. The tube was sealed, brought out, and its contents were agitated at 140 °C (oil bath). After 4 h, the Schlenk tube was allowed to cool to room temperature and its contents were frozen in a liquid nitrogen bath. The upper section of the tube above the frozen mixture was gently heated with a heat gun in order to condense vapors of the PhF product and all other volatiles. The tube was then allowed to warm up to room temperature and brought to the glove box. An aliquot of the reaction mixture (ca. 0.1 mL) was withdrawn, diluted with DMF (0.5 mL), and analyzed by ^{19}F NMR. The Schlenk tube was resealed, brought out, and placed in the oil bath to resume the reaction. Quantitative ^{19}F NMR analysis was performed again after an additional 20 h, following the same procedure. The results are summarized in Table S1. Efficient agitation of the reaction mixtures is important because of the poor solubility of CsF. As can be seen from Table S1, all Cp*Ru complexes examined, exhibited similar catalytic activity, except [Cp*Ru(PPh_3)$_2$Cl]. Complex **1** was selected for further studies for the following reasons:

1. **1** is more easily accessible than [Cp*Ru(CH_3CN)$_3$]BF_4 and [Cp*RuCl]$_4$;

2. unlike $[Cp^*Ru(CH_3CN)_3]BF_4$, $[Cp^*RuCl_2]_2$ and $[Cp^*RuCl]_4$, **1** is air- and moisture-stable; and
3. **1** may serve as a multi-target catalyst, whereas using $[Cp^*Ru(PhCl)]BF_4$ with substrates ArX where Ar ≠ Ph might result in contamination of the desired product with PhF.

Table S1. Catalyst screening for fluorination of chlorobenzene.



entry	catalyst [M]	[M], mg	yield of PhF, mol/mol [M] (TON)	
			after 4 h	after 24 h
1	$[Cp^*Ru(napht)]BF_4$ (**1**)	20	1.2	4.3
2	$[CpRu(napht)]BF_4$	17	1.1	1.1
3	$[Cp^*Ru(PhCl)]BF_4$	19	1.7	4.5
4	$[Cp^*Ru(PhCl)]PF_6$	22	1.0	3.4
5	$[Cp^*Ru(CH_3CN)_3]BF_4$	20	2.6	4.3
6	$[Cp^*RuCl_2]_2$	14	2.9	3.4
7	$[Cp^*RuCl]_4$	12	2.8	3.1
8	$[Cp^*Ru(PPh_3)_2Cl]$	35	0	0
9	$[(p\text{-cymene})RuCl_2]_2$	14	0	0
10	$[(benzene)_2Ru)](BF_4)_2$	19	0	0
11	$[Cp^*Rh(CH_3CN)_3](BF_4)_2$	24	0	0

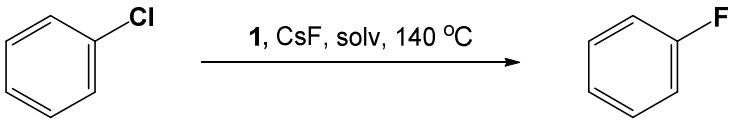
GC-MS analysis of the reaction mixtures confirmed the formation of PhF (entries 1-7) and indicated the presence of small quantities of benzene, <5 mol % of the amount of PhF produced. It is likely that the formation of PhH was prompted by a Ru-promoted high-temperature reaction in the hot GC-MS injector because the PhF to PhH ratio varied directly with the yield of PhF during the fluorination. From one of these experiments, $[Cp^*Ru(PhNMe_2)]BF_4$ has been isolated and structurally characterized (see below).

Isolation of [Cp*Ru(PhNMe$_2$)]BF$_4$. In one of the experiments with **1** after 48 h of agitation at 140 °C, the reaction mixture was filtered through a pad of Celite and the filtrate treated with ether to prompt precipitation. Slow diffusion of ether vapors into a solution of the crude precipitate in 1,2-dichloroethane produced X-ray quality crystals of [Cp*Ru(PhNMe$_2$)]BF$_4$.[11] ^{1}H NMR (CD_3CN), δ: 2.05 (s, 15H, Cp*), 3.09 (s, 6H, Me), 5.64-5.67 (m, 1H, Ph), 5.69-5.71 (m, 2H, Ph), 5.79-5.83 (m, 2H, Ph). The Cp analogue of this complex, [CpRu(PhNMe$_2$)]PF$_6$, has been reported.[12]

IV. Ru-Catalyzed Fluorination of PhCl with CsF in Various Solvents

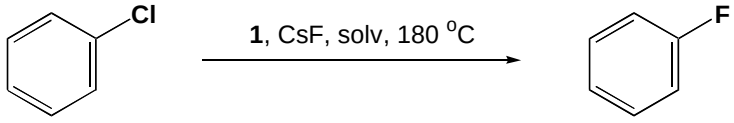
General Procedure. A thoroughly dried 50-mL Schlenk tube equipped with a J. Young high-vacuum valve and a magnetic stir-bar was charged in air with **1** (20 mg, 0.044 mmol, 1 equiv) and 4,4'-difluorobiphenyl (4 mg, 0.02 mmol, 0.5 equiv, internal standard) and brought to an argon-filled glove-box. In the glove-box, CsF (334 mg, 2.2 mmol, 50 equiv), PhCl (0.5 mL, 4.4 mmol, 100 equiv) and a solvent (1.5 mL; see Table S2) were added. The tube was sealed, brought out, and its contents were agitated at 140 °C (oil bath). The monitoring and quantitative analysis of the reaction mixtures by ^{19}F NMR were performed as described above. The results are summarized in Table S2. Experiments in selected solvents were repeated at 180 ^{o}C (see Table S3).

Table S2. Ru-catalyzed fluorination of chlorobenzene in various solvents at 140 ºC.



entry	solvent	yield of PhF, mol/mol **1** (TON)		
		after 4 h	after 24 h	after 48 h
1	DMF	1.2	4.3	5.2
2	DMA	0.3	1.6	1.6
3	NMP	0.8	2.6	3.5
4	DMI	0.4	2.6	3.3
5	PhCl (neat)	2.2	3.6	3.9
6	Diglyme	0.5	0.6	0.6
7	Decaline	0.2	0.6	0.6
8	DMSO	0.2	0.2	0.2
9	PhCN	0	0	0
10	DMPU	0	0	0
11	Propylene carbonate	0	0	0
12	Sulfolane	0	0	0
13	Triglyme	0	0	0
14	HMPA	0	0	0
15	$BMIM^+$ BF_4^-	0	0	0

Table S3. Ru-catalyzed fluorination of chlorobenzene in various solvents at 180 ºC.



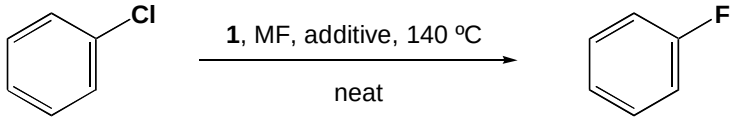
entry	solvent	yield of PhF, mol/mol **1** (TON)	
		after 4 h	after 24 h
1	DMA	4.0	7.5
2	NMP	5.0	8.3
3	DMI	3.8	5.4

A minor peak (broad singlet) was observed in the ^{19}F NMR spectra at -146 ppm and assigned to bifluoride HF_2^- that originates from residual trace water in the solvents or from their deprotonation with basic fluoride. In the reactions in neat PhCl, no bifluoride formation was observed.

V. Ru-Catalyzed Fluorination of PhCl with Various Fluorides

General Procedure. A thoroughly dried 50-mL Schlenk tube equipped with a J. Young high-vacuum valve and a magnetic stir-bar was charged in air with **1** (20 mg, 0.044 mmol, 1 equiv) and 4,4'-difluorobiphenyl (4 mg, 0.02 mmol, 0.5 equiv, internal standard) and brought to an argon-filled glove-box. In the glove-box, CsF or KF (2.2 mmol, 50 equiv; see Table S4 for specifics) and PhCl (2.0 mL) were added. The tube was sealed, brought out, and its contents were agitated at 140 °C (oil bath). The monitoring and quantitative analysis of the reaction mixtures by ^{19}F NMR were performed as described above. The experiment with CsF was repeated in the presence of (a) finely ground, dry KCl (13 mg, 0.22 mol, 5 equiv) and (b) IPr-Cl (61 mg, 0.13 mmol, 3 equiv). The experiment with KF was repeated in the presence of (a) diglyme (63 μL, 0.44 mmol, 10 equiv) and (b) 18-crown-6 (58 mg, 0.22 mmol, 5 equiv). The results are summarized in Table S4.

Table S4. Ru-catalyzed fluorination of PhCl (no solvent) with CsF or KF in the absence and in the presence of additives.

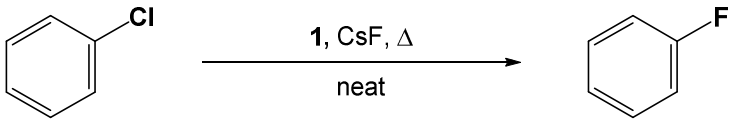


Entry	MF (mg)	additive (equiv)	yield of PhF, mol/mol **1** (TON)	
			after 4 h	after 24 h
1	CsF (334)		2.2	4.4
2	CsF (334)	KCl (5)	2.1	4.3
3	CsF (334)	IPr-Cl (3)	2.0	4.1
4	AgF (279)		0	0
5	KF (128)		0	0.2
6	KF (128)	diglyme (10)	0	0.1
7	KF (128)	18-crown-6 (5)	0.2	0.6

VI. Reaction of 1 with PhCl and CsF at 100-180 ^{o}C

General Procedure. A thoroughly dried 50-mL Schlenk tube equipped with a J. Young high-vacuum valve and a magnetic stir-bar was charged in air with **1** (20 mg, 0.044 mmol, 1 equiv) and 4,4'-difluorobiphenyl (4 mg, 0.02 mmol, 0.5 equiv, internal standard) and brought to an argon-filled glove-box. In the glove-box, CsF (334 mg, 2.2 mmol, 50 equiv) and PhCl (2.0 mL) were added. The tube was sealed, brought out, and its contents were agitated at a specified temperature (Table S5). The monitoring and quantitative analysis of the reaction mixtures by ^{19}F NMR were performed as described above. The results are summarized in Table S5 and Figure S1.

Table S5. Ru-catalyzed fluorination of PhCl (no solvent) with CsF at various temperatures.



entry	temperature, ºC	yield of PhF, mol/mol **1** (TON)					
		2 h	4 h	6 h	8 h	24 h	48 h
1	100	0	0	0	0.1	0.3	0.4
2	120	0.6	0.9	1.2	1.4	2.0	2.4
3	140	1.6	2.2	2.6	2.8	4.0	4.4
4	160	3.6	4.8	5.3	5.6	6.2	6.4
5	180	5.7	7.1	7.6	7.7	8.6	8.8

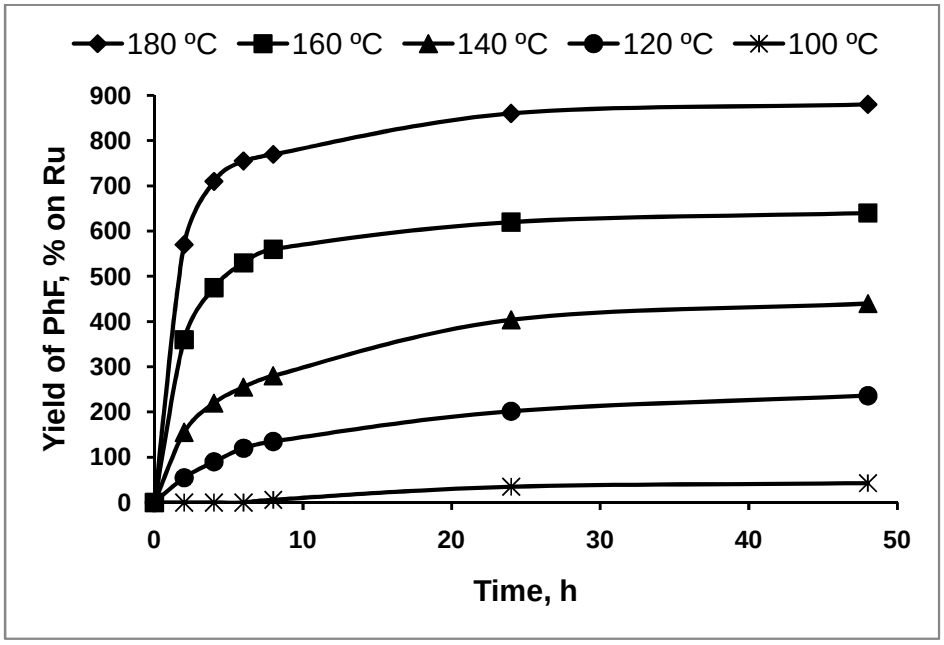
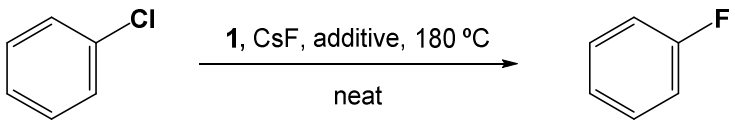


Figure S1. Ru-catalyzed fluorination of PhCl (no solvent) with CsF at various temperatures.

VII. Ru-Catalyzed Fluorination of PhCl at 180 °C under Solvent-Free Conditions

A thoroughly dried 50-mL Schlenk tube equipped with a J. Young high-vacuum valve and a magnetic stir-bar was charged in air with **1** (20 mg, 0.044 mmol, 1 equiv) and 4,4'-difluorobiphenyl (4 mg, 0.02 mmol, 0.5 equiv, internal standard) and brought to an argon-filled glove-box. In the glove-box, CsF (334 mg, 2.2 mmol, 50 equiv) and PhCl (2.0 mL) were added. The tube was sealed, brought out, and its contents were agitated at 180 °C. The monitoring and quantitative analysis of the reaction mixture by ^{19}F NMR was performed as described above. After 24 h, fresh CsF (334 mg, 2.2 mmol, 50 equiv) was added to the mixture and the reaction was continued at 180 ºC for an additional 12 h. This experiment was repeated with (a) a new portion of **1** (20 mg, 0.044 mmol, 1 equiv), (b) IPr-Cl (61 mg, 0.13 mmol, 3 equiv) and (c) Zn dust (9 mg, 0.13 mmol, 3 equiv) in place of the second portion of CsF. See Table S6 for the results.

Table S6. Ru-Catalyzed Fluorination of PhCl at 180 °C.



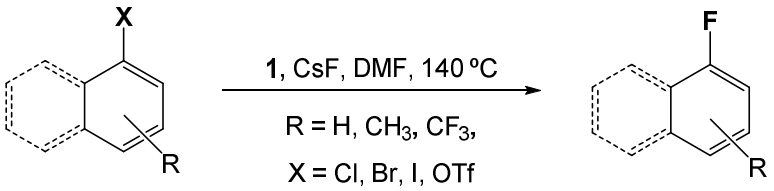
entry	yield of PhF (TON)		additive (equiv)	yield of PhF (TON) after an additional 12 h
	after 4 h	after 24 h		
1	4.7	6.1	CsF (50)	6.1
2	5.2	8.5	**1** (1)	17.5
3	6.9	8.9	IPr-Cl (3)	13.8
4	5.4	7.1	Zn dust (3)	7.2

VIII. Fluorination of Other Aryl Halides

These reactions have not been optimized

General Procedure A. A thoroughly dried 50-mL Schlenk tube equipped with a J. Young high-vacuum valve and a magnetic stir-bar was charged in air with **1** (20 mg, 0.044 mmol, 1 equiv) and 4,4'-difluorobiphenyl (4 mg, 0.02 mmol, 0.5 equiv, internal standard) and brought to an argon-filled glove-box. In the glove-box, CsF (334 mg, 2.2 mmol, 50 equiv), an aryl halide (Table S7), and DMF (1.5 mL) were added. The tube was sealed, brought out, and its contents were agitated at 140 ^{o}C. The monitoring and quantitative analysis of the reaction mixture by ^{19}F NMR was performed as described above. The results are summarized in Table S7.

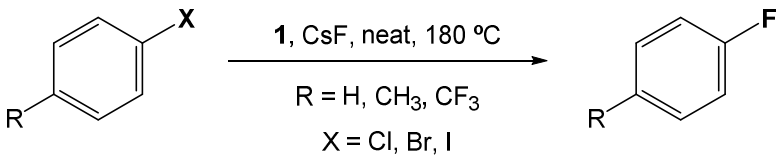
Table S7. Ru-catalyzed fluorination at 140 ^{o}C.



entry	substrate (mL)	^{19}F NMR, δ	yield of ArF, mol/mol **1** (TON)	
			after 4 h	after 24 h
1	PhBr (0.5)	-113.6	0.1	0.1
2	PhI (0.5)	-113.6	traces	traces
3	PhOTf (0.7)	-113.6	traces	0.2
4	*para*-$ClC_6H_4CH_3$ (0.5)	-119.0	0	traces
5	*para*-$ClC_6H_4CF_3$ (0.6)	-107.8, -61.2 (CF_3)	traces	0.2
6	*meta*-$ClC_6H_4CF_3$ (0.6)	-111.2, -60.4 (CF_3)	0.2	0.2
7	α-Cl-naphthalene (0.6)	-124.3	0.3	0.4

General Procedure B. A thoroughly dried 50-mL Schlenk tube equipped with a J. Young high-vacuum valve and a magnetic stir-bar was charged in air with **1** (20 mg, 0.044 mmol, 1 equiv) and 4,4'-difluorobiphenyl (4 mg, 0.02 mmol, 0.5 equiv, internal standard) and brought to an argon-filled glove-box. In the glove-box, CsF (334 mg, 2.2 mmol, 50 equiv) and an aryl halide (2 mL, see Table S8) were added. The tube was sealed, brought out, and its contents were agitated at 180 ^{o}C. The monitoring and quantitative analysis of the reaction mixture by ^{19}F NMR was performed as described above. The results are summarized in Table S8.

Table S8. Ru-catalyzed fluorination at 180 ºC.



entry	substrate	^{19}F NMR, δ	yield of ArF, mol/mol [M] (TON)	
			after 4 h	after 24 h
1	PhBr	-113.6	2.5	5.2
2	PhI	-113.6	2.2	3.0
3	*para*-$ClC_6H_4CH_3$	-119.0	0.1	0.4
4	*para*-$ClC_6H_4CF_3$[13]	-107.8, -61.2 (CF_3)	0.8	0.8

IX. References

[1] B. T. Loughrey, B. V. Cunning, P. C. Healy, C. L. Brown, P. G. Parsons and M. L. Williams, *Chem. Asian J.*, 2012, **7**, 112.

[2] D. S. Perekalin, E. E. Karslyan, P. V. Petrovskii, A. O. Borissova, K. A. Lyssenko and A. R. Kudinov, *Eur. J. Inorg. Chem.*, 2012, 1485.

[3] B. Steinmetz and W. A. Schenk, *Organometallics*, 1999, **18**, 943.

[4] N. Oshima, H. Suzuki and Y. Moro-Oka, *Chem. Lett.*, 1984, 1161.

[5] P. J. Fagan, M. D. Ward and J. C. Calabrese, *J. Am. Chem. Soc.*, 1989, **111**, 1698.

[6] M. S. Chinn and D. M. Heinekey, *J. Am. Chem. Soc.*, 1990, **112**, 5166.

[7] M. I. Rybinskaya, A. R. Kudinov and V. S. Kaganovich, *J. Organomet. Chem.*, 1983, **246**, 279.

[8] C. White, A. Yates, P. M. Maitlis and D. M. Heinekey, *Inorg. Synth.*, 1992, **29**, 228.

[9] a) D. Mendoza-Espinosa, B. Donnadieu and G. Bertrand, *J. Am. Chem. Soc.*, 2010, **132**, 7264; b) P. Tang, W. Wang and T. Ritter, *J. Am. Chem. Soc.*, 2011, **133**, 11482.

[10] Other catalysts (Table S1, entries 5-7 and 11) were kept and handled in the glove-box due to their air- and moisture sensitivity.

[11] CCDC 1063666 contains the supplementary crystallographic data for $[Cp^*Ru(PhNMe_2)]BF_4$. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif

[12] C. M. Standfest-Hauser, K. Mereiter, R. Schmid and K. Kirchner, *Dalton Trans.*, 2003, 2329.

[13] Small quantities of *meta*-$FC_6H_4CF_3$ were produced (^{19}F NMR and GC-MS), apparently from *meta*-$ClC_6H_4CF_3$ impurity in the *para*-$ClC_6H_4CF_3$ substrate.