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Ruthenium-catalyzed nucleophilic fluorination of halobenzenes†

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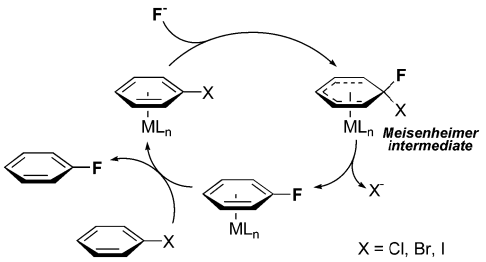
The first π-coordination-catalyzed nucleophilic fluorination of unactivated aryl halides has been demonstrated. Chlorobenzene reacts with alkali metal fluorides (CsF, KF) in the presence of a Cp*Ru catalyst at 120–180 °C to give fluorobenzene.

Fluorinated aromatic compounds are in demand as building blocks and intermediates for the synthesis of pharmaceuticals, agrochemicals, and materials.[1] The only industrially feasible general method for the selective introduction of fluorine into the benzene ring is the Balz–Schiemann diazofluorination.[2–4] A useful alternative to this reaction would be transition metal-catalyzed nucleophilic fluorination of unactivated aryl halides.[5] However, in sharp contrast to the long-known[6,7] electrophilic fluorination of aromatic nucleophiles with "positive" fluorine reagents, nucleophilic fluorination of ArX (X = Cl, Br, I) with fluoride is extremely challenging.[5] In 2006, one of us disclosed the first example of such a transformation mediated by a transition metal (Cu).[8] Since then, a substantially improved protocol for aryl iodides has been developed.[9,10] However, the reaction still employs stoichiometric copper and gives rise to considerable quantities of arenes (ArH) as side products[9] that cannot be efficiently separated from the desired products, ArF.

Numerous original attempts to form the Ar–F bond at a Pd^{II} centre have been unsuccessful because of the preference of the F ligand to bind to the P atom of a stabilizing phosphine rather than to the σ-aryl.[5] Buchwald *et al.* have recently reported the Pd-catalyzed fluorination of aryl triflates[11a,b] with CsF and of aryl bromides[11c] with AgF/KF. The key to the success was the design of the sophisticated bulky biarylphosphine ligands that coordinate tightly enough to Pd while being sufficiently sterically protected from the attack of fluoride on the phosphorus. The Pd-catalyzed fluorination of electron-rich ArX is poorly regioselective, although some improvements have been made lately.[11b,c]

Since our original report of the first aryl Pd fluorides in 1997[12] and detailed studies of this class of compounds,[5] it has been clear to us that simple, reasonably accessible ligands are not suitable for Ar–F reductive elimination from Pd^{II}. Therefore, we considered a methodologically distinct approach to metal-catalyzed nucleophilic aromatic fluorination.

Aryl halides ArX are conventionally activated by oxidative addition of the C–X bond to certain transition metals in low oxidation states, such as Pd^0, Ni^0 and Cu^I. Alternatively, however, unreactive haloarenes can be made susceptible to nucleophilic attack by η^6-coordination with a transition metal Lewis acid centre. The impact of such coordination on the reactivity can be dramatic: the effect of $Cr(CO)_3$, $Mn(CO)_3^+$ and $Rh(\eta^5\text{-}C_5Me_4Et)^{2+}$, η^6-coordinated to the benzene ring, is similar to that of one, two, and three nitro groups in the *ortho* and *para* positions, respectively.[13] As a result, such π-ArX complexes can undergo displacement of X^- with nucleophiles (Nu^-) *via* the S_NAr mechanism.[14] We therefore proposed a catalytic cycle for nucleophilic fluorination of unactivated haloarenes, catalyzed by transition metals *via* η^6-coordination (Scheme 1). The vast majority of S_NAr reactions of aryl halides π-coordinated to a metal centre, however, can be performed only stoichiometrically. To render them catalytic, the arene ligand ArNu produced in the S_NAr step must undergo ligand exchange with the substrate ArX.



Scheme 1 Proposed transition metal η^6-coordination-catalyzed nucleophilic fluorination of halobenzenes.

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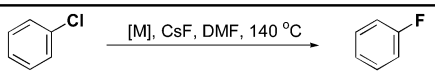
This has proved to be impossible for numerous η^6-arene complexes because of the high stability of arene ligands on the metal. Only a very limited number of η^6-coordination-*catalyzed* S_NAr reactions have been reported with Ru and Rh derivatives.[15]

In addition to the widely recognized inherent problem of the η^6-arene ligand exchange, there is another serious impediment to the targeted fluorination process outlined in Scheme 1. The order of reactivity of ArX in S_NAr reactions is usually X = F > Cl > Br > I for the same Ar,[14] with ArBr and ArI being particularly poor substrates. Although aryl chlorides can sometimes be used, it is the most reactive fluoroaromatic derivatives that are routinely the substrates of choice for both conventional and π-coordination-induced S_NAr reactions. For instance, the $[(\eta^5\text{-}C_5Me_4Et)Rh]^{2+}$-catalyzed methoxylation of ArX to give ArOMe readily occurs for X = F but not for X = Cl.[15c] All in all, the proposed η^6-coordination-catalyzed nucleophilic fluorination of unactivated haloarenes (Scheme 1) is exceedingly challenging. Herein we report that such fluorination is nonetheless possible.

For our studies, we selected a number of Cp*, Cp and π-arene complexes of Ru^{II}, Ru^{III}, and Rh^{III}. Table 1 summarizes the results of our screening tests, in which PhCl, CsF, and DMF were used as the substrate, fluoride source, and solvent, respectively. We were delighted to observe the formation of PhF from PhCl in the presence of some Cp*Ru and CpRu complexes (entries 1–7). Moreover, the reaction was catalytic, although the turnover numbers (TONs) were modest, not exceeding 4.5 after 24 h. The mono- and bis-arene Ru complexes lacking the Cp* or Cp ligand, $[(p\text{-cymene})RuCl_2]_2$ and $[(benzene)_2Ru](BF_4)_2$ (entries 9 and 10), and a Rh^{III} dicationic complex, $[Cp^*Rh(CH_3CN)_3](BF_4)_2$ (entry 11), were inactive. With $[Cp^*Ru(PPh_3)_2Cl]$, no fluorination took place (entry 8), obviously because the tightly bound PPh_3 blocks the η^6-coordination of PhCl to Ru. The Cp* complex $[Cp^*Ru(napht)]BF_4$ (**1**; napht = naphthalene) performed better than its Cp congener (entries 1 and 2). All other Cp*Ru complexes exhibited comparable activity. Although **1**, $[Cp^*Ru(PhCl)]BF_4$, and $[Cp^*Ru(CH_3CN)_3]BF_4$ were equally efficient (entries 1, 3, and 5), **1** was selected for further studies due to its air-stability and superior accessibility.[16]

Table 1 Catalyst screening for nucleophilic fluorination of PhCl. Reagent quantities: catalyst [M] (1 equiv.), PhCl (0.5 ml; 100 equiv.) and CsF (334 mg; 50 equiv.) in DMF (1.5 ml)



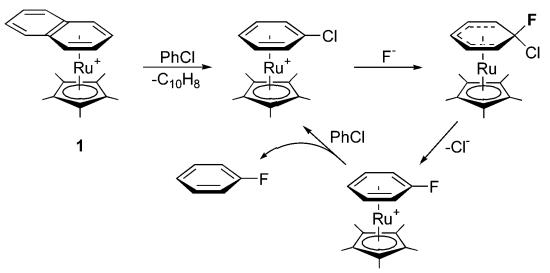
		Yield of PhF, mol mol^{-1} [M] (TON)	
Entry	Catalyst [M]	After 4 h	After 24 h
1	$[Cp^*Ru(napht)]BF_4$ (**1**)	1.2	4.3
2	$[CpRu(napht)]BF_4$	1.1	1.1
3	$[Cp^*Ru(PhCl)]BF_4$	1.7	4.5
4	$[Cp^*Ru(PhCl)]PF_6$	1.0	3.4
5	$[Cp^*Ru(CH_3CN)_3]BF_4$	2.6	4.3
6	$[Cp^*RuCl_2]_2$	2.9	3.4
7	$[Cp^*RuCl]_4$	2.8	3.1
8	$[Cp^*Ru(PPh_3)_2Cl]$	0	0
9	$[(p\text{-cymene})RuCl_2]_2$	0	0
10	$[(benzene)_2Ru](BF_4)_2$	0	0
11	$[Cp^*Rh(CH_3CN)_3](BF_4)_2$	0	0

See the ESI for details. Yields were determined by ^{19}F NMR with 4,4′-difluorobiphenyl as an internal standard.

The reaction of **1** with 4-chlorotoluene at 140 °C produced exclusively 4-fluorotoluene and no 3-isomer,[16] which rules out the aryne fluorination mechanism.[5b,17] Furthermore, **1** bearing a rather weakly bound naphthalene was found to react with PhCl and CsF at 100–120 °C to give, within a few hours, $[Cp^*Ru(PhF)]BF_4$[18] that was identified by its characteristic ^{19}F NMR chemical shift (δ = −144.8 ppm).[16] After 24 h, *ca.* 30% of the η^6-PhF complex produced was converted to free PhF (δ = −113.6 ppm). These data point to η^6-coordination-promoted S_NAr fluorination, as shown in Scheme 2.

As the choice of the medium can be critical for S_NAr reactions,[14] over a dozen different solvents were tested for the Ru-catalyzed reaction of PhCl with CsF at 140 °C.[16] DMF, NMP, DMI and DMA gave the best results. After 24 h at 180 °C in higher boiling point solvents DMA, NMP and DMI, the yields of PhF, based on the amount of **1** used, were 750%, 830% and 540%, respectively. No fluorination occurred in BMIM-BF_4, an ionic liquid; the reaction mixture quickly turned deep blue, evidently due to deprotonation of the BMIM cation with basic fluoride and coordination of the resultant N-heterocyclic carbene (NHC) to the Ru centre to give blue[19] [Cp*Ru(NHC)X]. From one of the reactions in DMF, $[Cp^*Ru(PhNMe_2)]BF_4$ was isolated and structurally characterized (Fig. 1).[20] Clearly, this complex was produced by the S_NAr reaction of $[Cp^*Ru(PhX)]^+$ with $HNMe_2$[15h] that emerged from the well-known[21] thermal decomposition of DMF. This reaction terminates the catalysis because electron-rich $PhNMe_2$ η^6-binds to Ru tightly, thereby shutting down the arene ligand exchange (Scheme 1).

To avoid the amide solvent decomposition problem, we tested the reaction in neat PhCl and were pleased to find that the fluorination occurred as efficiently. Further experiments



Scheme 2 Nucleophilic fluorination of PhCl, catalyzed by **1**.

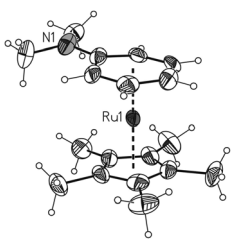


Fig. 1 ORTEP drawing of $[Cp^*Ru(PhNMe_2)]BF_4$ with the BF_4^- anion omitted for clarity and thermal ellipsoids drawn to the 50% probability level.

under such solvent-free conditions were then performed. No formation of PhF took place upon replacement of CsF with AgF. With KF, the fluorination at 140 °C was sluggish, resulting in TON = 0.2 and 0.6 after 24 h in the absence and in the presence of 18-crown-6 (5 equiv. per equiv. of **1**), respectively. As both CsF and KF are poorly soluble in non-aqueous media, the S_NAr step might take place predominantly or even entirely on their surface.

The reaction was not only faster at 180 °C than at 140–160 °C, but also produced PhF in higher yields.[16] At 180 °C, after reaching TONs of 5–7 and 6–9 within 4 and 24 h, respectively, the reaction stopped (Table 2). The addition of extra CsF to the reaction mixture did not revitalize the fluorination (entry 1), suggesting catalyst deactivation. This was confirmed in a separate experiment. After the reaction had produced 8.5 equiv. of PhF per Ru and stopped, an extra equiv. of **1** was added. Continuing the reaction for another 12 h doubled the yield (entry 2). The total TON value of 17.5 attained with 2 equiv. of **1** translates to *ca.* 90% yield of PhF at 10% catalyst loading.

The most reliable way to improve catalyst lifetime and performance is to gain insight into the processes leading to the loss of catalytic activity.[22] Our own experience[23] shows that detailed studies of catalyst deactivation can be vastly rewarding, yet are difficult and extremely time- and labor-consuming. Therefore, in the current preliminary work we probed only the most probable side reactions that might deactivate **1** in neat PhCl:

(1) Deliberately added water shut down the fluorination, probably not only due to a vast decrease in the nucleophilicity of fluoride upon hydration, but also because S_NAr hydrolysis of PhCl on the Ru centre can produce highly inert and hence inactive $[Cp^*Ru(\eta^5\text{-}C_6H_5O)]$[24] (Scheme 3). Although the glass reactors, CsF and PhCl used for the reactions were thoroughly dried,[16] minute quantities of residual water might still have been present in the reaction media. We therefore proposed that bis(2,6-diisopropylphenyl)-2-chloroimidazolium chloride[25] (IPr-Cl) in combination with CsF[26] could reactivate the catalyst by converting $[Cp^*Ru(\eta^5\text{-}C_6H_5O)]$ to $[Cp^*Ru(\eta^6\text{-PhF})]^+$. The addition of IPr-Cl (3 equiv. per equiv. of **1**) to the reaction mixture containing the stale catalyst after TON = 8.9 had been achieved and then continuing the process for an additional 12 h raised the yield of PhF to TON = 13.8 (Table 2, entry 3). Although this result was consistent with the proposal shown in Scheme 3, the addition of IPr-Cl to the reaction mixture at the beginning of the fluorination did not have a beneficial effect on the catalyst lifetime. Notably, 1,3-bis(2,6-diisopropylphenyl)-2,2-difluoro-4-imidazoline, the species that is produced *in situ* from IPr-Cl and CsF and that effects the OH/F exchange on the ring,[26] could be clearly observed by ^{19}F NMR in the liquid phase during the reaction. Given the extreme susceptibility of this difluoroimidazoline to hydrolysis, this observation suggests that the reaction medium was sufficiently anhydrous to avoid catalyst deactivation *via* hydrolysis (Scheme 3).

(2) While **1** is air-stable in the solid state and in solution, the catalytic system is oxygen-sensitive: in the presence of O_2, a black precipitate is quickly formed and no fluorination occurs. Although the reactions were performed under argon, the observed loss of catalytic activity might be due to residual O_2 in the system. The oxidation, however, is either irreversible or not the main cause of the deactivation as a reducing agent (Zn dust) did not revitalize the catalysis (Table 2, entry 4). It is worth noting that FEP reactors are not suitable for conducting the fluorination even in an inert atmosphere because FEP, a $CF_2{=}CF_2/CF_2{=}CFCF_3$ copolymer, is oxygen-permeable.[27,28]

(3) The Cl^- released in the reaction (Scheme 2) might compete with the F^- for the substrate, thereby triggering a degenerate Cl/Cl exchange. However, deliberately added KCl (5 equiv. per equiv. of **1**) at the beginning of the reaction did not have an observable negative impact on the fluorination.

As follows from the above, the loss of catalytic activity of **1** unlikely deals with adventitious H_2O and/or O_2 in our system. The catalyst might be ruined by slow deprotonation of a methyl group on the Cp* ring with basic fluoride to give fulvene species[29] that would be hard to detect due to their instability under the reaction conditions. The effect of the difluoroimidazoline generated *in situ* from IPr-Cl (see above) might deal with its reaction with ultimate rather than original products of the catalyst deactivation.

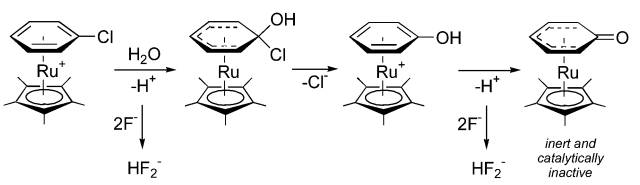
Fluorination of a broad variety of substrates was beyond the scope of this discovery project. A series of preliminary experiments without optimization for yield were nevertheless performed to demonstrate (i) fluorination of other PhX as well as electron-enriched and electron-deficient chloroarenes and (ii) the positional selectivity of the reaction (Table 3).[16] Unsurprisingly,[14] PhX (X = Br, I, OTf) were less reactive than PhCl. Chloroarenes bearing strong electron-withdrawing groups, such as NO_2, can undergo uncatalyzed S_NAr reaction with fluoride[30] and therefore were not included in the study.

In conclusion, we have demonstrated, for the first time, the concept of transition metal-catalyzed nucleophilic fluorination of unactivated haloarenes *via* η^6-coordination. A number of Ru and Rh complexes have been screened to identify **1** as the best catalyst for the reaction in terms of synthetic accessibility,

Table 2 Solvent-free Ru-catalyzed fluorination of PhCl with CsF at 180 °C. Reagent quantities: **1** (20 mg; 1 equiv.), CsF (334 mg; 50 equiv.), PhCl (2 ml)

Entry	Yield of PhF (TON) After 4 h	Yield of PhF (TON) After 24 h	Additive (equiv.)	Yield of PhF (TON) after additional 12 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

See the ESI for details. Yields were determined by ^{19}F NMR with 4,4′-difluorobiphenyl as an internal standard.



Scheme 3 Proposed catalyst deactivation *via* hydrolysis.

Table 3 Fluorination of various substrates with CsF in the presence of **1** after 24 h of reaction in DMF (140 °C) and under solvent-free conditions (180 °C)

Substrate	T, °C	Product	Yield, % on **1**
C_6H_5Cl	140	C_6H_5F	620
	180		890
C_6H_5Br	140	C_6H_5F	10
	180		520
C_6H_5I	140	C_6H_5F	<10
	180		300
C_6H_5OTf	140	C_6H_5F	20
4-$CH_3C_6H_4Cl$	180	4-$CH_3C_6H_4F$	40
4-$CF_3C_6H_4Cl$	140	4-$CF_3C_6H_4F$	20
	180		80
3-$CF_3C_6H_4Cl$	140	3-$CF_3C_6H_4F$	20
1-$C_{10}H_7Cl$	140	1-$C_{10}H_7F$	40

See the ESI for details. Yields were determined by ^{19}F NMR with 4,4′-difluorobiphenyl as an internal standard.

stability, and activity. The reaction exhibits excellent regio- and chemoselectivity. Given the extreme scarcity of methods for nucleophilic fluorination of unactivated aryl halides, the finding reported herein may become a new point of growth in the area of synthesis of fluoroaromatic compounds.

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