Formation of ArF from LPdAr(F): Catalytic Conversion of Aryl Triflates to Aryl Fluorides

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Formation of ArF from LPdAr(F): Catalytic Conversion of Aryl Triflates to Aryl Fluorides

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Despite increasing pharmaceutical importance, fluorinated aromatic organic molecules remain difficult to synthesize. Present methods require either harsh reaction conditions or highly specialized reagents, making the preparation of complex fluoroarenes challenging. Thus, the development of general methods for their preparation that overcome the limitations of those techniques currently in use is of great interest. We have prepared [LPd(II)Ar(F)] complexes, where L is a biaryl monophosphine ligand and Ar is an aryl group, and identified conditions under which reductive elimination occurs to form an Ar-F bond. On the basis of these results, we have developed a catalytic process that converts aryl bromides and aryl triflates into the corresponding fluorinated arenes by using simple fluoride salts. We expect this method to allow the introduction of fluorine atoms into advanced, highly functionalized intermediates.

A large number of pharmaceuticals and agrochemicals contain fluorinated aromatic (Ar–F) groups, which enhance solubility, bioavailability, and metabolic stability compared with nonfluorinated analogs (*1*–*4*). Furthermore, radioactive ^{18}F-labeled organic compounds are also widely used as contrast agents for positron emission tomography (PET) (*5*, *6*).

However, traditional methods for the introduction of a fluorine atom into an aromatic framework usually require harsh conditions that are incompatible with many functional groups. Such methods include direct fluorination (*7*), the conversion of amines via the aryldiazonium salt with HBF_4 (Balz-Schiemann reaction) (*8*), and the nucleophilic substitution of electron-poor bromo- or chloroarenes with KF (Halex reaction) (*9*), as well as the more recent transformation of aryl iodides with CuF_2 (*10*). A modified Balz-Schiemann process, of particular use for PET (*11*), uses aryliodonium salts that are produced under highly acidic or oxidizing conditions (*12*). In a recent important advance, the Halex reaction was performed at room temperature by using anhydrous tetrabutylammonium fluoride, but the substrate scope was limited and the fluoride source is not readily amenable to the preparation of ^{18}F-labeled compounds (*13*). Because of these limitations, fluorine atoms are often introduced to aromatic compounds early in synthetic sequences and before the introduction of substantial molecular complexity, which greatly increases the difficulty of accessing target molecules.

Recently, transition-metal promoted Ar-F bond formation has been achieved with use of electrophilic "F$^+$" reagents such as Selectfluor (Air Products and Chemicals, Incorporated, Allentown, PA) or *N*-fluoropyridinium salts (*14*–*20*). These interesting reactions are believed to proceed via high-valent Pd or Ag intermediates and have been used to access highly functionalized aryl fluorides. However, these reactions have some limitations with respect to preparative chemistry. In many cases, stoichiometric amounts of the transition metal must be used. In the reported examples that proceed with a catalytic quantity of metal, specific directing groups on the substrate are required to facilitate a C-H activation process, thus diminishing the general applicability of the methods (*14*, *15*, *21*). An additional drawback of this approach is that electrophilic ^{18}F reagents are not available with high specific activity, lessening the utility of these methods for PET applications (*12*, *22*).

In light of the importance of fluorinated arenes and the practical limitations of current methods for their preparation, the metal-catalyzed conversion of an aryl halide or sulfonate (e.g., triflate, abbreviated as OTf) with a nucleophilic fluorine source (such as an alkali metal fluoride) to yield the corresponding aryl fluoride is a highly desirable transformation (Fig. 1). For a process operating at reasonable temperatures and in the absence of electrophilic reagents, high functional group compatibility and a wide substrate scope might be expected. This is of particular importance in the preparation of biologically active compounds, where often late-stage modifications are key in identifying medicinal targets. In addition, such a strategy would be ideal for the preparation of PET imaging agents because mildly nucleophilic ^{18}F$^-$ reagents, especially Cs^{18}F, can be readily prepared.

Grushin's elegant mechanistic studies of isolated [L_nMAr(F)] complexes (L is a ligand and M is Pd or Rh) have demonstrated that reductive elimination to form an Ar-F bond is extremely challenging (*22*–*27*). These experiments have shown that undesired reaction pathways involving supporting ligands and fluoride dominate the chemistry of these complexes. This is due to both the high barrier to Ar-F bond formation as well as favorable pathways involving ligand-based P-F or C-F bond formation. In addition, the accessibility of stable [L_nPdAr(F)]$_2$ dimers has been suggested to contribute to the difficulty in achieving the desired reductive elimination (*28*). These results have cast doubt on whether a catalytic cycle as depicted in Fig. 1 is viable. We note, however, that for the heavier halides the reductive elimination of ArX (X is Cl, Br, or I) from a Pd(II) intermediate is precedented (*29*). In addition, it was recently shown that the dimeric Pd complex [(*o*-tol)$_3$PPd(*p*-$NO_2C_6H_4$)(F)]$_2$ yielded 10% of *para*-fluoronitrobenzene upon heating in benzene in the presence of an excess of ligand **1** (*28*), a ligand initially developed in our laboratories for use in C-N bond-forming reactions (Fig. 2). Although it has been questioned whether this latter reaction proceeds via a conventional reductive elimination (*30*), we were intrigued by the possibility that biaryl monophosphine ligands could promote this type of difficult reductive elimination to form Ar-F bonds.

Herein, we report the preparation of a well-characterized Pd(II) complex that undergoes reductive elimination producing an aryl fluoride. On the basis of this result, we have developed a palladium-catalyzed method for the preparation of aryl fluorides from aryl triflates using CsF that proceeds with high functional group tolerance under mild reaction conditions.

Ar–F reductive elimination from a Pd(II) complex. Recently, we reported a monophosphine ligand, BrettPhos (**2**), for use in aryl amination reactions (*31*) (Fig. 2). Nuclear magnetic resonance (NMR) and crystallographic studies of [**2**·PdAr(X)] (X is Cl or Br) complexes revealed that they were monomeric both in solution and in the solid state. We decided to prepare analogous [**2**·PdAr(F)] complexes in order to determine whether they were also monomeric and to see whether **2** could be useful as a ligand in promoting reductive elimination to form Ar-F bonds (*32*). We found that these targets were best accessed by transmetalation of the [**2**·PdAr(Br)] complexes with AgF at room temperature

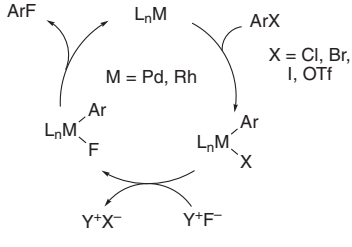

Fig. 1. Metal-catalyzed aryl fluorination.

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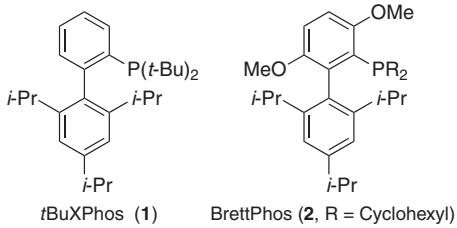
in dichloromethane (Fig. 3). The isolated [**2**·PdAr(F)] complexes exhibit a characteristic doublet in ^{31}P and ^{19}F NMR spectra with a coupling constant $^{2}J_{PF}$ of ~175 Hz, depending on the aryl group. The x-ray structure of **4** (Ar is 2-methyl-4-trifluoromethylphenyl) confirmed the monomeric nature of the complex (Fig. 4).

We next examined the thermolysis of **4** and **5** at 100°C in toluene and found that reductive elimination to form **6** and **7** occurs in yields of 15% and 25%, respectively (Fig. 3), which demonstrates that Ar-F bond formation is possible with use of these complexes. The yields in these reactions could be increased to 45% of **6** and 55% of **7** if the reductive eliminations were conducted in the presence of an excess of the corresponding aryl bromide (*33*, *34*). In these cases, the ^{31}P NMR spectra of the reaction mixtures showed that the oxidative-addition complexes [**2**·PdAr(Br)] were formed as the only phosphorous-containing products, suggesting LPd(0) is formed along with the ArF product.

Having demonstrated that oxidative addition, halide exchange (transmetalation), and reductive elimination were all possible, we next examined the catalytic conversion of ArBr **8** to ArF **7**. Upon treatment of **8** with AgF (1.5 equivalents) and 10 mole percent (mol%) each of **2** and [(COD)Pd($CH_2TMS)_2$] (COD is 1,5-cyclooctadiene) (*35*) at 110°C for 18 hours, a 52% yield of **7** was observed, which was increased to 74% after optimization of the reaction conditions (Fig. 5). No product was detected in control experiments that omitted **2** and/or the Pd precatalyst. This result demonstrates that Pd complexes supported by BrettPhos can catalyze the conversion of an aryl bromide to an aryl fluoride. However, the scope of aryl bromides that could be effectively transformed is to date limited to electron-poor substrates bearing an ortho substituent, in line with the observation that no reductive elimination took place from [**2**·PdAr(F)] complexes with Ar being 3,5-dimethylphenyl or 4-*n*-butylphenyl.

Efficient catalysis with aryl triflates. Concurrently, we also examined the use of aryl triflates as substrates. Although initial reactions of the triflate of 1-naphthol (**9**) provided only a trace of product **10**, the use of CsF in place of AgF as the fluoride source gave **10** in 30% yield (Fig. 6). In addition, 5% of naphthalene (**11**) was also observed. We also found that the readily prepared and more stable [(cinnamyl)PdCl]$_2$ could be used as the Pd precatalyst with a similar outcome. Overall, this result is important because it demonstrates that the fluorination can be carried out without needing a stoichiometic quantity of a noble metal component while still using a nucleophilic fluoride source.

In order to optimize the Ag-free reaction, a broad range of ligands were examined; under these conditions (Fig. 6), only ligands closely related to **2** provided more than a trace amount of **10** (*36*, *37*). Best results were obtained with use of *t*BuBrettPhos (**3**) (Fig. 2) as ligand; a 71% yield of **10** was realized, with only 1% of reduction product **11** observed. Further optimization of the reaction conditions increased the yield of **10** to 79%. Because the reaction proved to be sensitive to water (*38*), commercially obtained CsF was dried at 200°C under vacuum overnight and handled in a nitrogen-filled glovebox. Replacing CsF with spray-dried KF afforded **10** in 52% yield. No reaction was observed in the

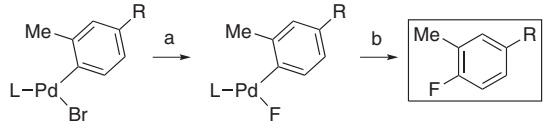


*t*BuXPhos (**1**)

BrettPhos (**2**, R = Cyclohexyl)
*t*BuBrettPhos (**3**, R = *t*-Bu)

Fig. 2. Ligands for the successful reductive elimination of Ar-F.

Fig. 3. Preparation of and reductive elimination from [**2** · PdAr(F)] complexes.



4 R = CF_3 74%
5 R = CN 70%
6 15%
7 25%

L = **2**. [a] 5 equiv. AgF, CH_2Cl_2, 25 °C, exclusion of light, 12 to 24 h. [b] toluene, 100 °C, 2 h, yields determined by ^{19}F NMR spectroscopy.

Fig. 4. X-ray structure of complex **4** [ORTEP (www.ornl.gov/sci/ortep/ortep.html) drawing at 50% probability, hydrogen atoms omitted for clarity].

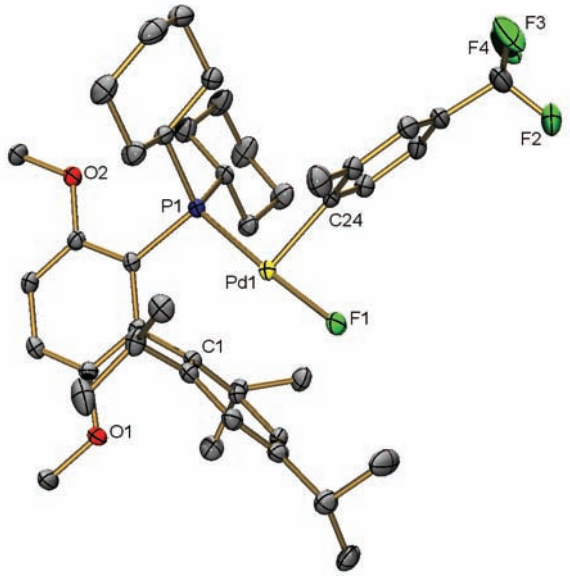
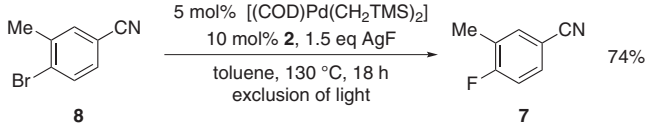


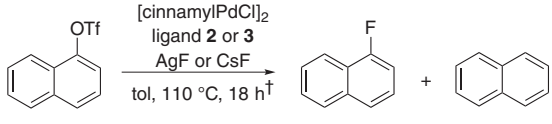
Fig. 5. Catalytic conversion of aryl bromide **8** to aryl fluoride **7**.



8 **7**

Yield was determined by NMR spectroscopy due to volatility of product. (1% of reduced substrate, *m*-tolunitrile, was also observed.)

Fig. 6. Optimization of aryl triflate fluorination. Conversion and yield were determined by GC.



9 **10** **11**

Pd (mol%)*	Ligand (mol%)	F^- source (eq)	Conversion	**10**	**11**
10	**2** (10)	AgF (1.5)	‡	trace	‡
10	**2** (10)	CsF (1.5)	90%	30%	5%
10	**3** (10)	CsF (1.5)	100%	71%	1%
2	**3** (3)	CsF (2.0)	100%	79%	1%

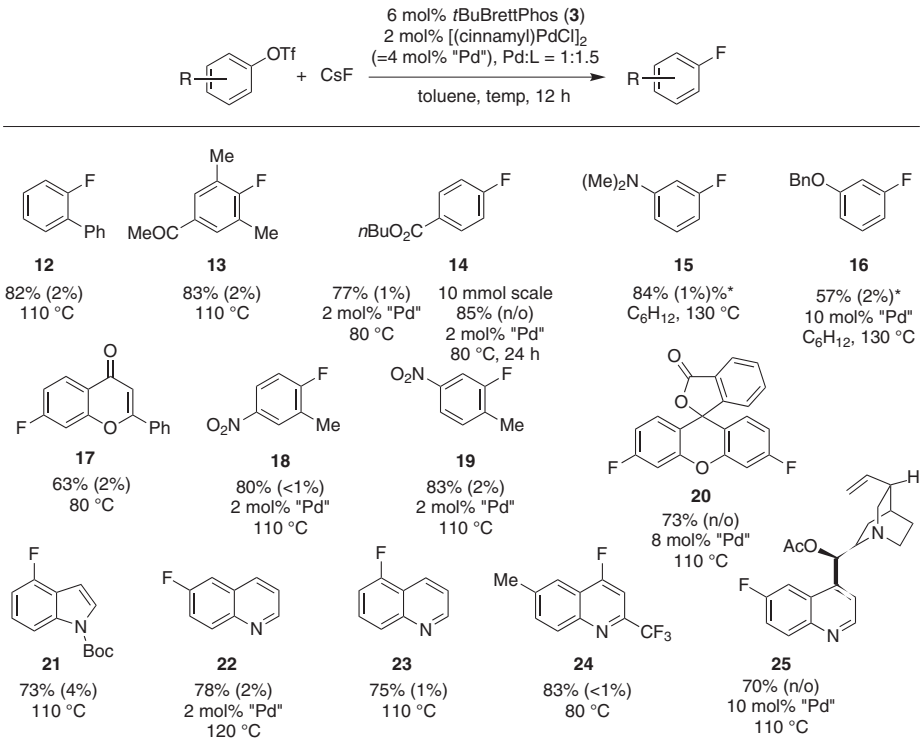
* mol% of palladium equivalents ("Pd"), † time not optimized, ‡ not determined

absence of the catalyst, ruling out both classic nucleophilic aromatic substitution (S_NAr) and aryne mechanisms (*39*).

We realized that for some applications, including PET, it was necessary to have a faster process. We found that the conversion of **9** to **10**, using 5 mol% [(COD)Pd(CH_2TMS)$_2$] as precatalyst, 10 mol% of **3** as supporting ligand, and 3 equivalents of CsF, was complete in 2.5 hours in toluene at 110°C, yielding 80% of **10**. Increasing the amount of CsF to 6 equivalents and adding 30 mol% of the solubilizing agent poly(ethylene glycol) dimethyl ether (Me_2PEG) led to full conversion in less than 30 min, albeit in yield of 71%. Similar rates of reaction could be achieved by using [(cinnamyl)PdCl]$_2$; with 5 mol% of this palladium source and 15% ligand, the reaction proceeds to completion in ≤2 hours in 79% yield (NMR). We are in the process of identifying conditions to achieve faster conversion of the substrate without diminishing the yield, as required for PET applications.

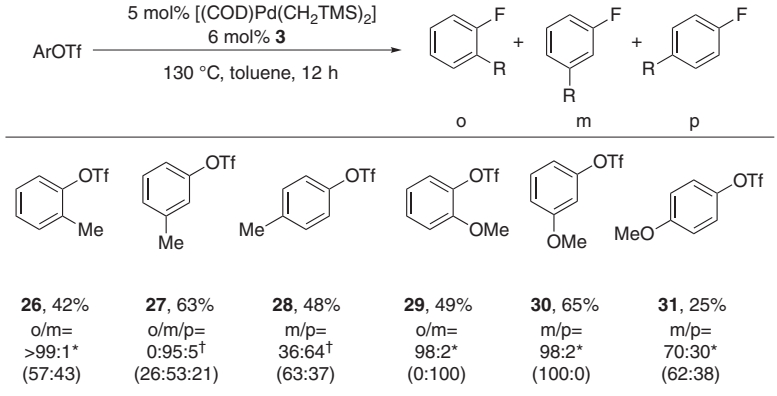
As can be seen in Fig. 7, the fluorination of aryl triflates has substantial scope. Simple aromatic substrates, such as *ortho*-biphenyl triflate, react rapidly to provide aryl fluorides in high yield. Hindered substrates such as 4-acetyl-2,6-dimethylphenyl triflate are also efficiently converted to product (**13**). Electron-deficient arenes can be efficiently transformed by using only 2 mol% of catalyst (**14**, **18**, and **19**). Important from a practical standpoint, a variety of heterocyclic substrates can also be successfully fluorinated by using these conditions. Flavones (**17**), indoles (**21**), and quinolines (**22** to **24**) were all converted in good yield. More complex aryl triflates derived from fluorescein (**20**) and quinine (**25**) could also be effectively converted to their fluorinated analogs, demonstrating that this method can be used in the preparation of pharmaceutically relevant compounds. In some cases, product formed in high yield at 80°C (**14**, **17**, and **24**). On a 10 mmol scale, butyl 4-fluorobenzoate **14** was prepared at 80°C with no observable formation of reduced by-product (in general, 2% or less reduction product was observed across the range of substrates screened).

Many functional groups are tolerated, an exception being Lewis basic groups such as amines or carbonyls in the ortho position of the aryl triflate. No reaction takes place in these instances, presumably because the basic group coordinates the Pd center, possibly preventing transmetalation. As in the Pd-catalyzed formation of Ar-O bonds, the transformation of electron-rich substrates was more challenging. We found that good yields were obtained at higher temperatures (130°C).



* Cyclohexane (C_6H_{12}) was used as a solvent to decrease the amount of reduced product.

Fig. 7. Fluorination of aryl triflates. Isolated yields are an average of at least two independent reactions. Values in parentheses denote the amount of reduced starting material based on the isolated product yield (n/o indicates not observed). In cases with different palladium loading, the ligand amount was adjusted accordingly ("Pd":L = 1:1.5). Quotation marks around Pd symbols indicate the amount of Pd, not of the Pd dimer.



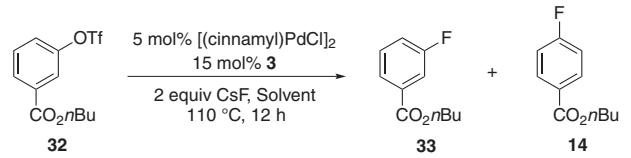
*Product ratios and yield determined by GC. † Product ratios and yield determined by ^{19}F NMR Spectroscopy.

Fig. 8. Regioisomers in tolyl and anisole fluorination. Chemical yields are given as the sum of ArF products. Traces of reduction products were also observed. Ratios are compared with those of a reported fluorination of bromoaryls that proceeds via a benzyne intermediate (in parentheses) (*39*).

Formation of regioisomers. Unexpectedly, regioisomeric products were formed in a few cases (Figs. 8 and 9). Because control experiments did not yield any product in the absence of catalyst, we believe that isomer formation is also a palladium-catalyzed process. Investigating a series of tolyl (**26** to **28**) and anisole (**29** to **31**) triflates, we found that for substrates **26**, **27**, and **29** the observed selectivities are quite distinct from those reported for a benzyne process (*39*) (Fig. 8). Experiments with 2,6-dideuterated anisole triflate **31** showed a reduced rate of formation of the undesired regioisomer, whereas the rate of formation of the desired product remained largely unchanged, leading to a 2.5-fold increase in selectivity in comparison to the reaction with unlabeled **31**. Thus, at least for this substrate, we conclude that two competing pathways are involved; it is evident that hydrogen abstraction is the rate-limiting or the first irreversible step in regioisomer formation and that little or none of the desired isomer is formed from the path that finally leads to the regioisomer.

Although we do not have a complete mechanistic understanding of the pathway leading to the regioisomers, we have found that the product ratio

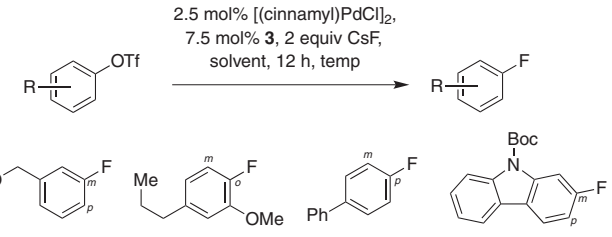
Fig. 9. Solvent screen and fluorination of triflates that gave regioisomers. Unless otherwise noted, yields and ratios determined by GC and ^{19}F NMR.



Solvent	conversion	combined yield	ratio **33**/**14**	ArH
Toluene	100	71%	78:22	2%
Benzene	100	69%	90:10	*
THF	95	18%	78:22	*
Cyclohexane	100	60%	>98:2	1%
n-Heptane	100	39%	85:15	*
Cyclohexane†	100	80%	99:1	1%

* Yield not determined. † Optimized condition 100 °C, isolated yield.

Fig. 10. Use of cyclohexane as solvent to suppress formation of regioisomers. Desired isomer is shown. Product ratios are for regioisomeric aryl fluorides as indicated. Isolated yields are for the major isomer, with values in parentheses denoting the amount of reduced starting material based on the isolated product yield.



tol*	*m*/*p* = 87:13	*o*/*m* = 77:23	*p*/*m* = 93:7	*m*/*p* = 93:7
cy†	*m*/*p* = 96:4 90% (<1%) 110 °C	*o*/*m* = 98:2 61% (~8%) 130 °C	*p*/*m* = >98:2 80% (3%) 100 °C	*m*/*p* = >98:2 77% (2%) 110 °C

* 2.5–5 mol% [(cinnamyl)PdCl]$_2$, 7.5-15 mol% **3**, solvent = toluene.
†solvent = cyclohexane.

can be strongly affected by solvent polarity; the desired pathway is favored in highly apolar media. Examination of a number of solvents for the conversion of **32** to **33** revealed that the formation of the undesired isomer **14** is almost completely suppressed with use of cyclohexane (Fig. 9). This trend appears to be general; in most instances in which the undesired regioisomer was observed with use of toluene, switching to cyclohexane afforded almost exclusively the desired product. For example, fluorinated aryls **33** to **37** could be prepared with greater than 95:5 selectivity favoring the desired isomer (Fig. 10). This modification provides a highly practical means to minimize formation of regioisomeric by-products.

Outlook. Starting from the observation of the reductive elimination of ArF from a [**2**·PdAr(F)] complex, we have developed a metal-catalyzed direct conversion of aryl bromides and aryl triflates into the corresponding aryl fluorides using simple fluoride sources such as AgF and CsF. In particular, the transformation of aryl triflates exhibits a wide substrate scope and tolerates a number of functional groups, allowing for the introduction of fluorine atoms into highly functionalized organic molecules. Key to these findings was the use of the sterically demanding, electron-rich biaryl monophosphine *t*BuBrettPhos **3** as the supporting ligand. We believe that this ligand not only promotes reductive elimination of the Ar-F bond because of its large size but also prevents the formation of dimeric [LPdAr(F)]$_2$ complexes. At present, both of these factors appear to be critical in the successful catalytic reaction. Although some limitations remain with regard to substrate scope and reaction conditions, we expect this method to be applicable to the preparation of biologically active and radiolabeled aryl fluorides.

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33. The lower yield in the absence of added aryl bromide suggests that the **2**·Pd(0) complex that results from reductive elimination further reacts with remaining [**2**·PdAr(F)] complex. Increased product yields have previously been observed in the reductive elimination of C-S bonds from Pd(II) centers when Pd^0 scavengers (exogenous ligand) have been added to the reaction. See (*34*).
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36. After this paper was submitted, we found that the closely related hetero-biaryl ligand 5-(di-*tert*-butylphosphino)-1-(1,3,5-triphenyl-1H-pyrazol-4-yl)-1H-pyrazole (Bippyphos) reported by Singer and co-workers [see (*37*) and citations therein] can also provide catalysts with moderate levels of activity for fluorination. For example, with use of 10 mol% of this ligand and 5 mol% [(cinnamyl)ClPd]$_2$, a 52% yield of **10** along with 11% reduction product was observed after heating for 12 hours at 150°C in toluene.
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38. We followed the reaction of **9** to **10** by gas chromatography (GC) and found that, after a brief initial period in which about 20% of **9** was consumed, **10** began to form. By adding 20 mol% water, we observed that the initial loss of material increased to 60%. This result indicates that one molecule of water consumes two molecules of **9** under the reaction conditions. Nevertheless, the reaction proceeded to give 40% **10**. We believe that the initial loss of mass balance is due to formation of biaryl ether: Presumably, adventitious water results in the formation of phenol, which further reacts with a second molecule of ArOTf in a Pd-catalyzed process.
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Supporting Online Material

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Materials and Methods
Figs. S1 to S60
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References

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Research Articles: "Formation of ArF from LPdAr(F): Catalytic conversion of aryl triflates to aryl fluorides" by D. A. Watson *et al*. (25 September 2009, p. 1661). The permanent address for M. Su should have been listed as Singapore-MIT Alliance, E4-04-10, 4 Engineering Drive 3, 117576 Singapore.