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Ar−F Reductive Elimination from Palladium(II) Revisited[†]

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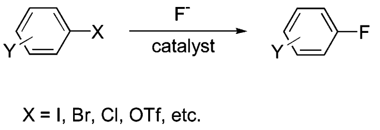
In contrast with [(o-Tol$_3$P)$_2$Pd$_2$(p-C$_6$H$_4$X)$_2$(μ-F)$_2$] (**1**; X = NO$_2$; *J. Am. Chem. Soc*. **2007**, *129*, 1342), its nonactivated congeners (X = H, Me, and MeO) do not produce ^{19}F NMR-detectable quantities of p-FC$_6$H$_4$X upon thermal decomposition in the presence of Buchwald's ligand t-Bu$_2$P-2-C$_6$H$_4$C$_6$H$_2$(i-Pr)$_3$-2′,4′,6′ (**BL**). These results do not support the previously asserted "net Ar−F reductive elimination", given that for X = NO$_2$ some quantities of p-FC$_6$H$_4$X might conceivably be formed from **1** via a variety of other, S$_N$Ar-type paths.

Introduction

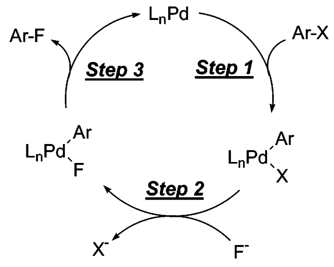
Over the past 15 years, remarkable progress has been made in the area of Pd-catalyzed C−N and C−O bond forming reactions of nonactivated haloarenes.[1] An efficient similar process leading to aryl fluorides (eq 1) is highly sought but has not been reported, thus far.[2] Thus, the Balz−Schiemann reaction of costly and hazardous dizaonium compounds, first published in 1927,[3] remains the only practical method to selectively introduce fluorine into the aromatic ring.[4]



(1)

In 2002, a concept article[5] was published on potential use of palladium catalysis for nucleophilic fluorination of haloarenes (eq 1 and Scheme 1). This paper[5] summarized our early work in the area,[6−12] including the synthesis of the first aryl palladium fluorides, their full characterization in the solid state and in solution, and demonstration that the problematic step of the desired catalytic loop (Scheme 1) is Ar−F reductive elimination from the Pd(II) center (step 3). Thermal enforcement of reductive elimination from aryl palladium fluorides led to no ArF formation, and only P−C and P−F bond forming reactions occurred instead.[11]

Scheme 1



Since then, we have made a number of attempts to suppress the P−F bond formation and promote the desired Ar−F reductive elimination. Mono- and dinuclear phenyl palladium fluorides stabilized by trialkylphosphines, including Me$_3$P and bulky Cy$_3$P and i-Pr$_3$P have been prepared[13] and found to produce no PhF upon thermal decomposition. A novel phenyl palladium fluoride has been designed, [(BINAP(O))Pd(Ph)F], in which the F ligand is cis to the Ph and trans to the only P-donor atom on the molecule.[14] Nonetheless, the thermal decomposition of this complex did not result in Ph−F bond formation and only P−F and P−C bonds were formed.[14] Having recently solved the problem of very difficult[15,16] Ar−CF$_3$ reductive elimination from Pd(II) by using Xantphos,[17] we attempted the thermal decomposition of [(Xantphos)Pd(F)Ph]. Again, however, no C−F reductive elimination took place and only P−F bond formation was observed.[17]

Unlike reductive elimination from Pd(II), which commonly occurs from a tricoordinate species and thus may be somewhat controlled by adding or scavenging extra phosphine, the P−F bond forming reactions at Pd[11,13,14,17] and Rh[18,19] do not require

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[†] DuPont CR&D contribution No. 8783.

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(1) For selected reviews, see: Muci, A. R.; Buchwald, S. L. *Top. Curr. Chem*. **2002**, *219*, 131. Hartwig, J. F. *Synlett* **2006**, 1283. Schlummer, B.; Scholz, U. *Adv. Synth. Catal*. **2004**, *346*, 1599.

(2) The high demand for new reactions leading cleanly to Ar−F bond formation is largely driven by biological activity of selectively fluorinated organic molecules. "As many as 30−40% of agrochemicals and 20% of pharmaceuticals on the market are estimated to contain fluorine, including half of the top 10 drugs sold in 2005." Thayer, A. M. *Chem. Eng. News* **2006**, *84*, No. 23 (June 5), 15.

(3) Balz, G.; Schiemann, G. *Chem. Ber.* **1927**, *60*, 1186.

(4) Aromatic substrates containing strong electron-withdrawing groups (e.g., NO$_2$ and CN) on the ring are well-known to undergo S$_N$Ar fluorination via a Meisenheimer complex.[4a] Similarly, polyfluorinated benzenes can be made from the corresponding polychlorinated compounds and alkali fluorides in the so-called "Halex" process.[4b] With highly reactive fluoride sources employed, aromatic nucleophilic fluorination of activated, electron-deficient substrates can easily occur at as low as room temperature.[4c] (a) Adams, D. J.; Clark, J. H. *Chem. Soc. Rev.* **1999**, *28*, 225. (b) Langlois, B.; Gilbert, L.; Forat, G. *Ind. Chem. Libr*. **1996**, *8*, 244. (c) Sun, H.; Dimagno, S. G. *Angew. Chem., Int. Ed.* **2006**, *45*, 2720.

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(14) Marshall, W. J.; Grushin, V. V. *Organometallics* **2003**, *22*, 555.

(15) Culkin, D. A.; Hartwig, J. F. *Organometallics* **2004**, *23*, 3398.

(16) Grushin, V. V.; Marshall, W. J. *J. Am. Chem. Soc.* **2006**, *128*, 4632.

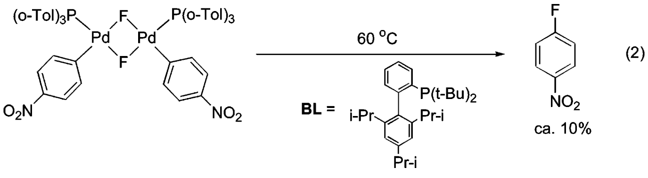
(17) Grushin, V. V.; Marshall, W. J. *J. Am. Chem. Soc.* **2006**, *128*, 12644.

10.1021/om700469k CCC: \$37.00

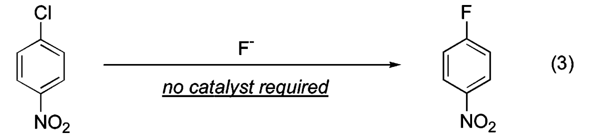
coordinative unsaturation (see below). These reactions are governed by a different mechanism that involves intramolecular nucleophilic attack of the coordinated fluoride on the phosphine ligand to produce a metallophosphorane intermediate.[20,21]

Avoiding P-ligands altogether was obvious to consider, even though tertiary phosphines seem to play an important role in stabilization of the late transition metal−fluorine bond.[22] Our brief exposure to N-heterocyclic carbenes (NHCs)[23] made it clear that NHC−Ar reductive elimination from Pd(II) can be remarkably facile and hence kinetically favored over the desired Ar−F bond formation. That prompted us to discontinue our work with NHCs as suitable ligands for reaction 1. The first examples of Ar−F bond formation from ArX (Ar = phenyl, 2-naphthyl; X = I, Br) in the presence of CuF_2 and N,N-ligands were disclosed by us in 2005 and since then have received patent protection.[24] We are not aware of any other reported metal-induced transformations leading to fluoroarenes from the corresponding *nonactivated* aryl iodides, bromides, chlorides, triflates, etc.[25]

Most recently, Yandulov and Tran[26] reported their computational study of Ar−F reductive elimination from Pd(II) to reconfirm our conclusions above. They also described some experimental work, including a new example of Ar−F bond formation leading to p-$FC_6H_4NO_2$ in ca. 10% yield upon thermal decomposition of $[L_2Pd_2(p\text{-}C_6H_4NO_2)_2(\mu\text{-}F)_2]$, where L = o-Tol_3P (**1**) or t-Bu_3P (**2**), in the presence of Buchwald's ligand (**BL**), t-Bu_2P-2-$C_6H_4C_6H_2(i\text{-}Pr)_3$-2′,4′,6′ (eq 2).[26,27] The formation of Ar−F was reported[26] only for Ar = p-$C_6H_4NO_2$, a Meisenheimer-type aryl whose para- (and ortho-) halide derivatives readily undergo S_NAr reactions,[28,29] nucleophilic fluorination included (eq 3),[4,30] *in the absence of any catalyst*. For this reason (compare eqs 2 and 3), in our studies we deal only with nonactivated aryls (Y ≠ a strong electron acceptor, such as NO_2 or CN in eq 1). Strangely, the Yandulov−Tran account, while being vast and apparently complete, did not mention Ar−F bond formation from similar fluoro palladium aryls devoid of an electron-withdrawing activator on the benzene ring. Because knowing if the Ar−F bond can be formed without this activator is critical for further developments in the area, we have now carried out such experiments and describe them herein.



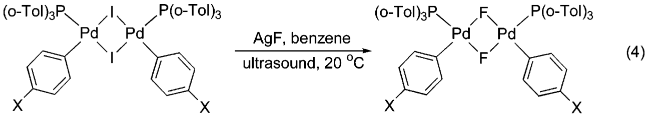
(2)



(3)

Results

Analogues of **1** with H (**3**), Me (**4**), and MeO (**5**) in place of the nitro group were synthesized by our original method[6,7,13] from the corresponding iodides[31] and AgF under sonication (eq 4). All three complexes were isolated as slightly yellowish crystalline solids and characterized by elemental analysis, NMR, and single-crystal X-ray diffraction data.



3 (X = H), 79%
4 (X = Me), 88%
5 (X = MeO), 62%

(4)

As seen from the ORTEP drawings in Figures 1−4, all fluoride dimers **3**, **4**, **5**, and also **1** are syn in the crystalline state. This is in contrast with our earlier X-ray structures of *anti*-$[(R_3P)_2Pd_2(Ph)_2(\mu\text{-}F)_2]$ (R = i-Pr, Cy)[13] and similar to the syn geometry found for crystalline **2**.[26] Selected geometry parameters for the structures are collected in Table 1.

The values in Table 1 point to an increase in both Pd−F and Pd−C bond lengths when going from the more electron-deficient p-nitrophenyl complex (**1**) to the electroneutral phenyl (**3**) and further to electron-enriched p-tolyl (**4**) and p-anisyl (**5**) dimers. As expected,[8] the trend is more pronounced for the Pd−F bond distances trans to the aryls, in accord with the structural data previously reported for *trans*-$[(Ph_3P)_2Pd(F)(Ph)]$[6] and *trans*-$[(Ph_3P)_2Pd(F)(p\text{-}C_6H_4NO_2)]$.[8] The effect may be rationalized in terms of alleviation of $p_\pi(F)$−$d_\pi(Pd)$ filled/filled repulsion via push−pull interaction of the lone electron pair on F with π^* of the σ-aryl through filled d orbitals on the metal.[8,9] Unlike $[(Cy_3P)_2Pd_2(Ph)_2(\mu\text{-}F)_2]$, which forms a stable adduct with three

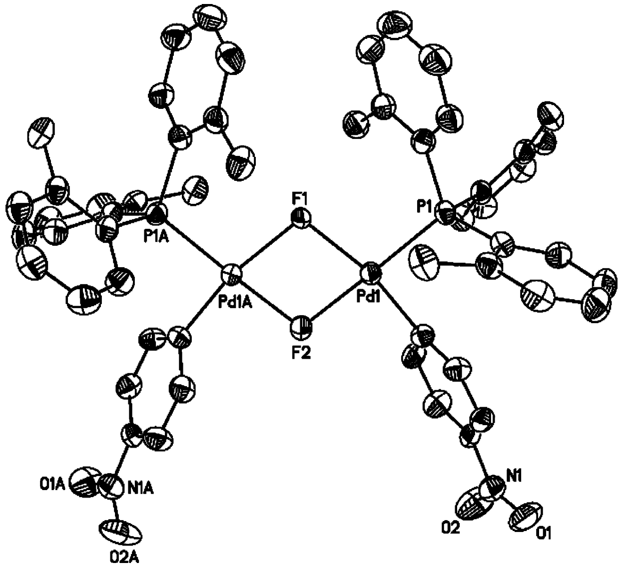


Figure 1. ORTEP drawing of **1** with thermal ellipsoids drawn at the 50% probability level and all H atoms omitted for clarity.

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(23) Marshall, W. J.; Grushin, V. V. *Organometallics* **2003**, *22*, 1591.

(24) Grushin, V. U.S. Patent 7,202,388, 2007.

(25) Hull, Anani, and Sanford have recently reported an interesting exotic example of fluorination of Ar−H bonds via cyclopalladation, followed by electrophilic cleavage of the Pd−C bond with *N*-fluoropyridinium reagents. This approach cannot allow the highly sought nucleophilic displacement of Cl, Br, and I of nonactivated haloarenes with fluoride by definition. Hull, K. L.; Anani, W. Q.; Sanford, M. S. *J. Am. Chem. Soc.* **2006**, *128*, 7134.

(26) Yandulov, D. V.; Tran, N. T. *J. Am. Chem. Soc.* **2007**, *129*, 1342.

(27) The use[26] of **BL** was apparently inspired by the recent remarkable development of the synthesis of ArOH from ArX (X = Br, Cl) and alkali, catalyzed by Pd_2dba_3/**BL**: Anderson, K. W.; Ikawa, T.; Tundel, R. E.; Buchwald, S. L. *J. Am. Chem. Soc.* **2006**, *128*, 10694.

(28) Terrier, F. *Nucleophilic Aromatic Displacement: The Influence of the Nitro Group*; VCH: New York, 1991.

(29) Miller, J. *Aromatic Nucleophilic Substitution*; Elsevier: London 1968.

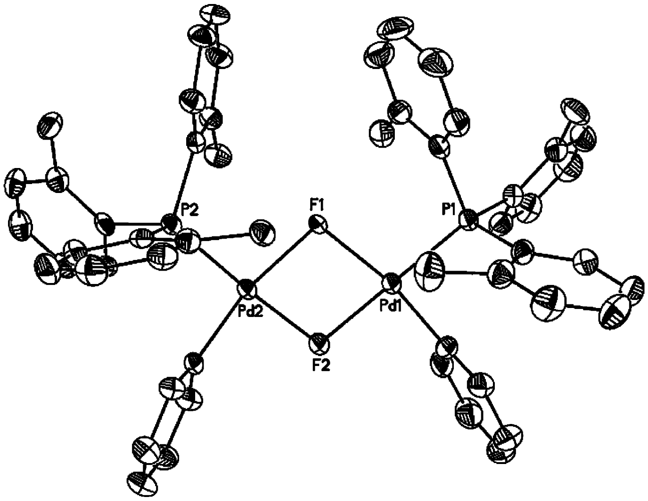


Figure 2. ORTEP drawing of **3** with thermal ellipsoids drawn at the 50% probability level and all H atoms omitted for clarity.

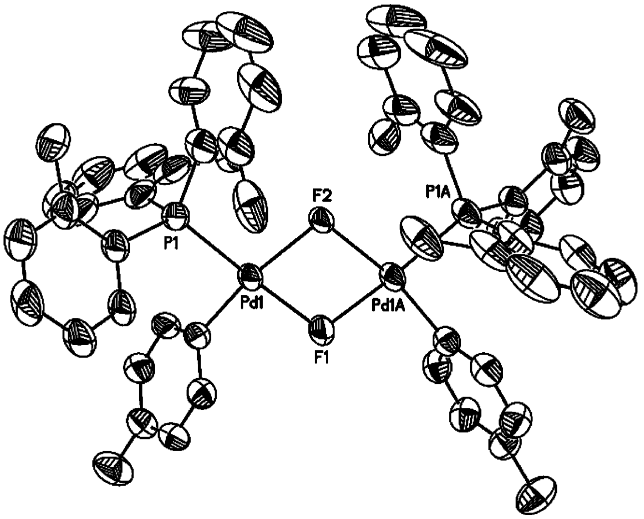


Figure 3. ORTEP drawing of **4** with thermal ellipsoids drawn at the 50% probability level and all H atoms omitted for clarity.

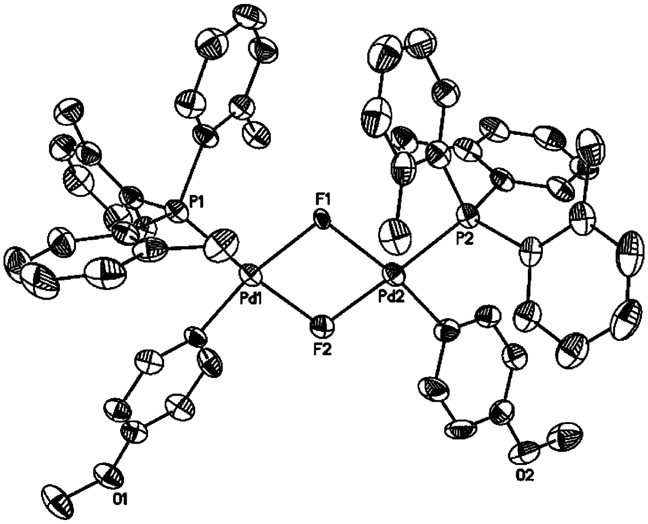
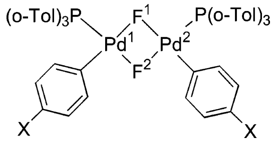


Figure 4. ORTEP drawing of **5** with thermal ellipsoids drawn at the 50% probability level and all H atoms omitted for clarity.

Table 1. Selected Geometry Parameters for 1, 3, 4, and 5

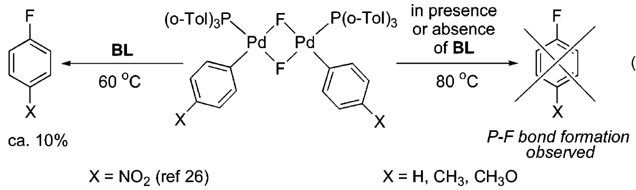


geometry param, Å or deg	$\mathbf{1}\cdot 5C_6H_6$ ($X = NO_2$)	$\mathbf{3}\cdot 3CH_2Cl_2$ ($X = H$)	$\mathbf{4}\cdot 2CH_2Cl_2\cdot 2C_6H_{14}$ ($X = Me$)	$\mathbf{5}\cdot 5CH_2Cl_2$ ($X = MeO$)
Pd(1)−F(1)	2.102(2)	2.105(2)	2.123(2)	2.125(3)
Pd(2)−F(1)	2.103(2)	2.124(2)	2.123(2)	2.134(3)
Pd(1)−F(2)	2.087(2)	2.094(2)	2.086(2)	2.103(4)
Pd(2)−F(2)	2.087(2)	2.092(2)	2.086(2)	2.101(4)
Pd(1)−C	1.972(3)	1.980(3)	1.984(4)	1.988(6)
Pd(2)−C	1.972(3)	1.976(4)	1.984(4)	1.980(7)
Pd(1)−P	2.234(1)	2.216(1)	2.229(1)	2.220(2)
Pd(2)−P	2.234(1)	2.216(1)	2.229(1)	2.225(2)
Pd(1)−F(1)−Pd(2)	100.6(1)	99.6(1)	99.1(1)	99.1(1)
Pd(1)−F(2)−Pd(2)	101.6(1)	101.0(1)	101.5(2)	100.9(2)
F(1)−Pd(1)−F(2)	78.9(1)	79.4(1)	79.8(1)	80.1(1)
F(1)−Pd(2)−F(2)	78.9(1)	79.1(1)	79.8(1)	79.9(1)
F(1)−Pd(1)−P	99.4(1)	97.4(1)	97.2(1)	96.9(1)
F(1)−Pd(2)−P	99.4(1)	98.4(1)	97.2(1)	96.1(1)
F(2)−Pd(1)−C	89.4(1)	90.2(1)	90.2(1)	90.8(2)
F(2)−Pd(2)−C	89.4(1)	90.6(1)	90.2(1)	90.3(2)

CH_2Cl_2 molecules H-bonded to the basic F centers,[13] **3**−**5** do not display H-bonding interactions between the fluorine atoms and cocrystallized molecules of dichloromethane. This is likely due to the larger cone angle and lower basicity of *o*-Tol_3P as compared to Cy_3P.[32]

In solution, complexes **3**−**5** exist as mixtures of syn- and anti-isomers, much like $[(R_3P)_2Pd_2(Ph)_2(\mu\text{-}F)_2]$ (R = *i*-Pr, Cy),[13] as well as **1** and **2**.[26] Like **1**, **3**−**5** exhibited broadened NMR signals, possibly due to syn−anti isomerization[13] and hindered rotation of the bulky phosphine ligands.[26] Nonetheless, the syn and anti structures were reliably established and isomer ratios calculated at ca. 1.3−2:1 (see the Experimental Section).

The thermal decomposition of **3**, **4**, and **5** in dry benzene under N_2, in glass or Teflon, in the presence or in the absence of **BL**, did not result in ^{19}F NMR-observable quantities of fluoroaromatics (eq 5). In all cases, only mixtures of P−F bond containing products were detected, mainly $R_2R'PF_2$ (see the Experimental Section). This indicated that Pd−Ar/P−Ar′ exchange was occurring in parallel with the P−F bond forming



(5)

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(30) See, for example: (a) Finger, G. C.; Kruse, C. W. *J. Am. Chem. Soc*. **1956**, *78*, 6034. (b) Aksenov, V. V.; Vlasov, V. M.; Moryakina, I. M.; Rodionov, P. P.; Fadeeva, V. P.; Chertok, V. S.; Yakobson, G. G. *J. Fluorine Chem.* **1985**, *28*, 73.

(31) The starting iodo dimers were prepared by the literature methods: Paul, F.; Patt, J.; Hartwig, J. F. *Organometallics* **1995**, *14*, 3030. Widenhoefer, R. A.; Zhong, H. A.; Buchwald, S. L. *Organometallics* **1996**, *15*, 2745. Widenhoefer, R. A.; Buchwald, S. L. *Organometallics* **1996**, *15*, 2755. The *p*-tolyl and *p*-methoxy complexes are known compounds, whereas the phenyl analogue has not been reported. Anal. Calcd for $C_{54}H_{52}I_2P_2Pd_2$: C, 52.7; H, 4.3. Found: C, 52.7; H, 4.3.

(32) (a) However, characteristic[32b] C−H···F contacts to the ligands that are shorter than the sum of the van der Waals radii of F (1.47 Å) and H (1.20 Å) are found in all four structures. The fluorine trans to C forms two C−H···F contacts of 2.13 Å (in **1**) and 2.36 Å (in **4**) to a methyl group of each of the *o*-Tol_3P ligands. In **3**, the F trans to C interacts with one methyl group of one of the phosphines (2.21 Å) and two methyls of the other (2.53 and 2.54 Å). The same pattern is observed for **5** (2.49, 2.56, and 2.58 Å). In addition, **3** exhibits an intermolecular contact between the fluorine trans to P and an aromatic CH of another molecule of **3**. In **5**, this F atom interacts intramolecularly with one ortho H of each anisyl ligand (2.56 and 2.67 Å). (b) Brammer, L.; Bruton, E. A.; Sherwood, P. *Cryst. Growth Des.* **2001**, *1*, 277.

processes, as expected.[11] We did not carry out a detailed analysis of the reaction mixtures. As stated above, our goal was only to determine whether or not congeners of **1** bearing non-Meisenheimer σ-aryls would undergo Ar−F reductive elimination.[33]

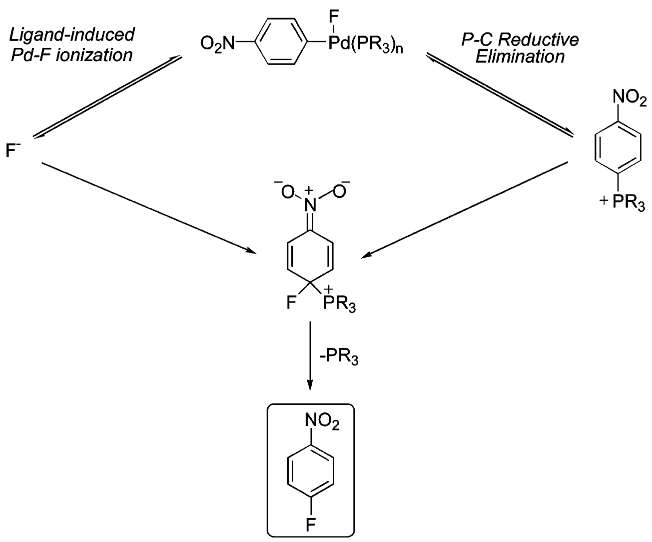
Discussion

Metal-promoted halogen exchange reactions of nonactivated (non-Meisenheimer; see above) haloarenes are rare,[34,35] and well-defined examples of aryl−halogen reductive elimination from a transition metal center, particularly Pd(II), are even scarcer.[36,37] Therefore, the formation of *p*-nitrofluorobenzene from **1** (eq 2)[26] is an interesting observation.

Our results indicate that the nitro group in the "right" para position of the σ-aryl ligand of **1** is critical for the Ar−F bond formation. It is understood[26,38] that much like, or even more so than, Ar−OR reductive elimination from Pd(II),[39] analogous Ar−F reductive elimination is probably of considerable S_NAr character. Therefore conditions under which p-XC_6H_4−F bond formation from **1**/**BL** was observed ($X = NO_2$)[26] may not be suitable to give rise to p-XC_6H_4F (X = H, Me, and MeO) from **3**−**5**/**BL** (eq 5). However, no firm evidence has been presented for Ar−F reductive elimination as the very path leading to p-$FC_6H_4NO_2$ (eq 2).[26] While apparently facilitating Ar−F reductive elimination, electron-withdrawing groups, especially NO_2, in the para position also open up the possibility of the Meisenheimer chemistry to occur, a totally different, "hidden" path that may lead to the same ArF product.

A nitro group on the benzene ring is well-known to make the latter susceptible to classical S_NAr as well as ipso- and kine-substitution reactions.[28,29] Considering the ability of palladium fluorides to release highly reactive fluoride,[10] one can propose a variety of transformations yielding some quantities of *p*-nitrofluorobenzene from **1**/**BL** (eq 2). For instance (Scheme 2), a *p*-nitrophenyl phosphorus electrophile (e.g., a phosphonium cation)[11] formed from **1** might undergo S_NAr with fluoride to give p-$NO_2C_6H_4F$. Although phosphonium salts were not detected[26] among the *final* products of the thermolysis reactions of **1** and **2**, their intermediacy in the reactions is manifested[11] by the fact that Pd−Ar/P−Ar′ exchange did occur under the conditions employed for the thermal decomposition of **1**, **2**,[26] and **3**−**5** (this work). Nitrite would result from ipso substitution,[28,29] which then might produce *p*-dinitrobenezene upon Ar−NO_2 reductive elimination or S_NAr with an active *p*-nitrophenyl phosphorus electrophile. Poorly solvated fluoride has been shown[4c] to react with *p*-dinitrobenzene to afford p-$NO_2C_6H_4F$ in >95% yield in less than 5 min at room temperature. These are just a few plausible reaction paths other than Ar−F reductive elimination that might give rise to p-$NO_2C_6H_4F$ under the conditions employed for reaction 2.[26] Therefore the line of reasoning apparently used[26] to declare "net Ar−F reductive elimination"[40] being the mechanism for the C−F bond formation in reaction 2 would be a mere logical fallacy.[41] The entire set of the experimental data reported[26] can neither prove nor disprove that Ar−F reductive elimination is the mechanism of the C−F bond formation from **1**.

Scheme 2



A comment is due on the mechanism of P−F bond formation from various previously studied palladium fluoride complexes,[5,11,13,14,17] as well as **1**,[26] **2**,[26] and **3**−**5** (this work). To account for the observed products of the thermal decomposition of $[(Ph_3P)_2Pd(Ph)F]$ (eq 6), we have earlier proposed[5,11] a

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[33] The formation of a small quantity of fluorobenzene (ca. 1%) was observed after a mixture of PhBr, $[Me_4N]^+ F^-$, Pd_2dba_3 (3%), and **BL** (6%) in toluene was stirred in a Teflon reactor at 110 °C (oil bath) for 2 days. Considering the low yield of PhF, the high basicity of the fluoride source, reaction conditions, and the fact that much finely dispersed Pd black was quickly formed in this reaction, we hesitate to assert Ph−F reductive elimination from a soluble PhPdF intermediate, although this path should not be ruled out.

[34] (a) For a recent review, see: Berkenbusch, T. *Sci. Synth.* **2006**, *25*, 689. (b) Takagi, K.; Hayama, N.; Okamoto, T. *Chem. Lett.* **1978**, 191. (c) Takagi, K.; Hayama, N.; Inokawa, S. *Bull. Chem. Soc. Jpn* **1980**, *53*, 3691. (d) Tsou, T. T.; Kochi, J. K. *J. Org. Chem.* **1980**, *45*, 1930. (e) Suzuki, H.; Kondo, A.; Ogawa, T. *Chem. Lett.* **1985**, 411. (f) Meyer, G.; Rollin, Y.; Perichon, J. *Tetrahedron Lett.* **1986**, *27*, 3497. (g) Yang, S. H.; Li, C. S.; Cheng, C. H. *J. Org. Chem.* **1987**, *52*, 691. (h) Bozell, J. J.; Vogt, C. E. *J. Am. Chem. Soc.* **1988**, *110*, 2655. (i) Klapars, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 14844. (j) Zanon, J.; Klapars, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 2890. (k) Arvela, R. K.; Leadbeater, N. E. *Synlett* **2003**, 1145. (l) Toto, P.; Gesquiere, J.-C.; Cousaert, N.; Deprez, B.; Willand, N. *Tetrahedron Lett.* **2006**, *47*, 4973.

[35] For Pd-promoted halide exchange in otherwise unreactive, pseudo-aromatic 9-iodo-*m*-carborane, see: Marshall, W. J.; Young, R. J., Jr.; Grushin, V. V. *Organometallics* **2001**, *20*, 523.

[36] Roy, A. H.; Hartwig, J. F. *J. Am. Chem. Soc.* **2001**, *123*, 1232. Stambuli, J. P.; Bühl, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 9346. Roy, A. H.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 13944. Roy, A. H.; Hartwig, J. F. *Organometallics* **2004**, *23*, 1533. Stambuli, J. P.; Incarvito, C. D.; Bühl, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2004**, *126*, 1184.

[37] (a) Recently, Vigalok et al.[37b] claimed reductive elimination of Ar−Br in the reaction of some complexes of the type $[(P{-}P)Pt(Ar)_2]$ with bromine. It is conceivable, however, that the *instantaneous* formation of ArBr upon treatment of $[(P{-}P)Pt(Ar)_2]$ with Br_2[37b] might be due to classical electrophilic cleavage of the Pt−Ar bond with bromine (S_EAr), rather than Br−Br oxidative addition, followed by Ar−Br reductive elimination. In Vigalok's report,[37b] we could not find any proof ruling out S_EAr, nor any unambiguous evidence for the alleged Ar−Br reductive elimination path for the *immediate* reaction of $[(P{-}P)Pt(Ar)_2]$ with Br_2. (b) Yahav-Levi, A.; Goldberg, I.; Vigalok, A. *J. Am. Chem. Soc.* **2006**, *128*, 8710.

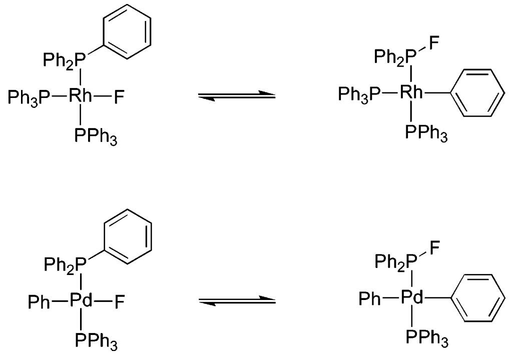
[38] Macgregor, S. A. Unpublished results.

[39] Widenhoefer, R. A.; Zhong, H. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 6787. Widenhoefer, R. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1998**, *120*, 6504. Mann, G.; Shelby, Q.; Roy, A. H.; Hartwig, J. F. *Organometallics* **2003**, *22*, 2775.

[40] From ref 26: "This is the first indication, to our knowledge, of net Ar-F reductive elimination operating to a quantifiable extent from a transition metal aryl fluoride." "The limited yet measurable success of $P(C_6H_4$-2-Trip)(t-Bu)$_2$ in enabling net Ar-F reductive elimination is therefore doubtless due to its ability to destabilize sterically the fluoride-bridged Pd dimer beyond the extent possible with $P(t\text{-}Bu)_3$." "However, use of Buchwald's L = $P(C_6H_4$-2-Trip)(t-Bu)$_2$ provided the additional steric pressure on the $[PdArL(\mu\text{-}F)]_2$ core needed to enable formation of aryl-fluoride net reductive elimination product in quantifiable yields (10%) in reactions with both **17** and **18** at 60° over 22 h."

[41] The logical fallacy, in which it is claimed that a premise is true only because it has not been proven false or that a premise is false only because it has not been proven true. See, for example: Copi, I. M.; Cohen, C. *Introduction to Logic*, 12th ed.; Prentice Hall: Upper Saddle River, NJ, 2004.

Scheme 3



mechanism that involved the formation of [$(Ph_3P)Pd(Ph_2PF)$] and/or isomeric [$(Ph_3P)Pd(Ph_2P)(F)$] upon Ph−Ph reductive elimination from the corresponding $Pd(Ph)_2$ species. The latter

$$[(Ph_3P)_2Pd(Ph)F] \xrightarrow[110\text{-}120\ ^{\circ}C]{toluene,\ N_2} [(Ph_3P)_3Pd] + Pd + Ph_2 + Ph_3PF_2 + Ph_2PPPh_2 \quad (6)^{5,11}$$

was believed to emerge from α-elimination of a phenyl on P or a P−F reductive elimination/C−P oxidative addition sequence. The recent studies[18−21] of closely related [$(Ph_3P)_3RhF$] and its facile rearrangement to *cis*-[$(Ph_3P)_2Rh(Ph_2PF)(Ph)$] suggest that palladium fluorides might undergo a similar transformation. In particular, [$(Ph_3P)_2Pd(Ph)F$] would be converted to [$(Ph_3P)(Ph_2PF)Pd(Ph)(Ph)$], much like the Rh fluoride rearranges to the Rh−Ph isomer (Scheme 3).

The two reactions shown in Scheme 3 share an important feature: both are not decelerated by extra phosphine.[11,18,19] This is characteristic of a metallophosphorane[19−21] mechanism, rather than reversible P−C reductive elimination that governs the slightly more facile, simultaneously occurring Pd−Ar/P−Ar exchange reaction of [$(Ph_3P)_2Pd(Ph)F$].[5,11]

An updated version of the earlier proposed mechanism[5,11] for reaction 6 is presented in Scheme 4. The first step involves the aforementioned Pd−F/P−Ph to Pd−Ph/P−F rearrangement (Scheme 3), followed by Ph−Ph reductive elimination. The disproportionation reaction of the resulting [$(Ph_3P)Pd(Ph_2P)(F)$], possibly via its dimer, accounts for the formation of all products observed, except for biphenyl, which is formed in a preceding step (Scheme 4).

Conclusions

Unlike **1**,[26] its congeners bearing H, Me, or MeO substituents in place of the nitro group do not produce observable (^{19}F NMR) quantities of any fluoroarenes upon thermolysis, in the presence or in the absence of Buchwald's ligand (**BL**). Strong support would have been provided for the alleged[26] "net Ar−F reductive elimination"[40] from **1** if fluoroarenes had been produced from **3**, **4**, or **5**, but they were not (eq 5). While being an important observation, the formation of *p*-nitrofluorobenzene from **1**/**BL** (eq 2) may or may not have resulted from Ar−F reductive elimination, and further experimental work is needed to unambiguously elucidate the mechanism of this C−F bond formation. This task is left to the authors of the report.[26]

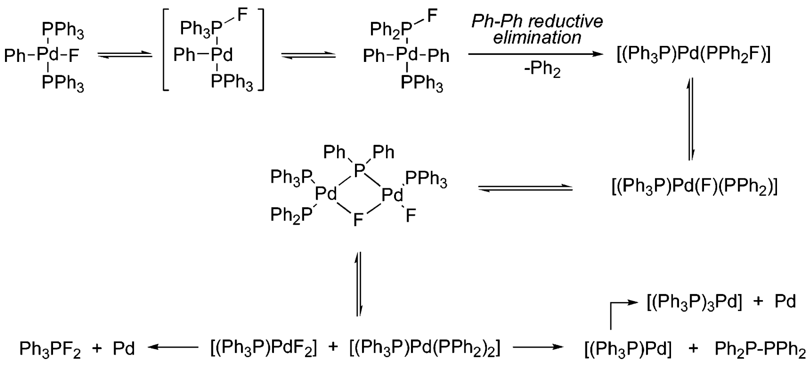
Experimental Section

All chemicals were purchased from Aldrich and Strem chemical companies and used as received. The solvents were thoroughly dried using standard techniques and stored over freshly calcined molecular sieves (4 Å) in a glovebox. All manipulations were carried out under nitrogen in a glovebox, unless otherwise noted. NMR spectra were obtained with a Bruker Avance DRX400 spectrometer. A Bruker-CCD instrument was used for single-crystal X-ray diffraction studies. Microanalyses were performed by Micro-Analysis, Inc., Wilmington, DE.

[$(o\text{-}Tol_3P)_2Pd_2(Ph)_2(\mu\text{-}F)_2$] (3). Inside a glovebox, a 20 mL vial was charged with [$(o\text{-}Tol_3P)_2Pd_2(Ph)_2(\mu\text{-}I)_2$][31] (0.30 g; 0.24 mmol), AgF (0.12 g; 0.94 mmol), *o*-Tol_3P (5 mg),[42] and benzene (6 mL). The vial was sealed under N_2, brought out, and sonicated at 20 °C for 6 h. After that, the vial was brought back in the glovebox and unsealed. The mixture was diluted with CH_2Cl_2 (6 mL) and filtered through Celite. The Celite was then washed with 4 mL of CH_2Cl_2. After the combined filtrate and the washings were evaporated to ca. 1.5 mL, ether (6 mL) was added and the solution was kept at −25 °C for 3 h. The pale yellow needles of **3** were washed with a small amount of cold ether, then hexanes, and dried under vacuum. The yield of **3** was 0.195 g (79%). Anal. Calcd for $C_{54}H_{52}F_2P_2Pd_2$: C, 64.0; H, 5.2. Found: C, 64.0; H, 5.4. A solution of **3** for characterization by NMR was obtained by dissolving the complex in C_6D_6 at gentle heating to ca. 50 °C and allowing the solution to cool to ambient temperature. ^{19}F NMR (20 °C): δ −286 (br dt; trans-J_{P-F} = ca. 160 Hz; J_{F-F} = ca. 50 Hz; 1F; syn-F trans to P), −289 (br; 1.5 F; anti-F), −313 (br; 1F; syn-F cis to P). ^{31}P NMR (20 °C): δ 31.2 (br m). Under such conditions, the syn−anti ratio was ca. 1.3:1 (^{19}F NMR). Single crystals were grown by slow diffusion of hexanes into a CH_2Cl_2 solution of **3**.

[$(o\text{-}Tol_3P)_2Pd_2(p\text{-}Tol)_2(\mu\text{-}F)_2$] (4). Inside a glovebox, a 20 mL vial was charged with [$(o\text{-}Tol_3P)_2Pd_2(p\text{-}Tol)_2(\mu\text{-}I)_2$][31] (0.304 g; 0.24 mmol), AgF (0.12 g; 0.94 mmol), *o*-Tol_3P (5 mg),[42] and benzene (6 mL). The vial was sealed under N_2, brought out, and sonicated at 20 °C for 6 h. After that, the vial was brought back in the glovebox and unsealed. The mixture was diluted with CH_2Cl_2 (6 mL) and filtered through Celite. The Celite was then washed with 5 mL of CH_2Cl_2. After the combined filtrate and the washings were evaporated to ca. 1 mL, ether (5 mL) was added and the solution was kept at −25 °C overnight. The pale yellow crystals

Scheme 4



were washed with ether, then hexanes, and dried under vacuum. The yield of **4**·$0.5C_6H_6$ was 0.23 g (88%). Anal. Calcd for $C_{59}H_{59}F_2P_2Pd_2$: C, 65.6; H, 5.5. Found: C, 65.3; H, 5.7. A solution of **4** for characterization by NMR was obtained by dissolving the complex in C_6D_6 at gentle heating to ca. 50 °C and allowing the solution to cool to ambient temperature. ^{1}H NMR (20 °C): δ 2.1 (br s; CH_3), 2.5 (br s; CH_3), 2.65 (br s; CH_3), 6.6−8.1 (m; aromatic H). ^{19}F NMR (20 °C): δ −283 (br dt; trans-J_{P-F} = ca. 165 Hz; J_{F-F} = ca. 55 Hz; 1F; syn-F trans to P), −286 (br; 1 F; anti-F), −309 (br; 1F; syn-F cis to P). ^{31}P NMR (20 °C): δ 34.1 (br m). Under such conditions, the syn−anti ratio was 2:1 (^{19}F NMR). Single crystals were grown by slow diffusion of hexanes into a CH_2Cl_2 solution of **3**.

[(*o*-Tol$_3$P)$_2$Pd$_2$(*p*-MeOC$_6$H$_4$)$_2$(μ-F)$_2$] (5). Inside a glovebox, a 20 mL vial was charged with [(*o*-Tol$_3$P)$_2$Pd$_2$(*p*-MeOC$_6$H$_4$)$_2$(μ-I)$_2$][31] (0.308 g; 0.24 mmol), AgF (0.12 g; 0.94 mmol), *o*-Tol$_3$P (5 mg),[42] and benzene (6 mL). The vial was sealed under N_2, brought out, and sonicated at 20 °C for 5 h. After that, the vial was brought back in the glovebox and unsealed. The mixture was diluted with CH_2Cl_2 (6 mL) and filtered through Celite. The Celite was then washed with 2 mL of CH_2Cl_2. After the combined filtrate and the washings were evaporated, ether (2 mL) was added and the precipitated yellow oil quickly solidified upon swirling. More ether (10 mL) was added, and the mixture was kept at −25 °C overnight. The yellow crystalline solid was separated, washed with hexanes, and dried under vacuum. The yield of **5**·C_6H_6 was 0.17 g (62%). Anal. Calcd for $C_{62}H_{62}F_2O_2P_2Pd_2$: C, 64.6; H, 5.4. Found: C, 64.2; H, 5.7. Because the complex was found insufficiently soluble even in warm benzene, its characterization by NMR was performed in CD_2Cl_2. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 2.3 (br s; CH_3), 2.5 (br s; CH_3), 3.6 (s; OCH_3), 6.1−7.8 (m; aromatic H). ^{19}F NMR (CD_2Cl_2, 20 °C): δ −284 (br; 1F; syn-F trans to P), −288 (br; 1.5 F; anti-F), −312 (br; 1F; syn-F cis to P). ^{31}P NMR (CD_2Cl_2, 20 °C): δ 32.5 (br m). Under such conditions, the syn−anti ratio was ca. 1.3:1 (^{19}F NMR). Single crystals were grown by slow diffusion of hexanes into a CH_2Cl_2 solution of **3**.

Thermal Decomposition of 3, 4, and 5 (a representative procedure). Inside a glovebox, a Teflon tube was charged with **3**, **4**, or **5** (0.03 mmol), **BL** (0.12 mmol), benzene (1 mL), and a Teflon-coated magnetic stirring bar. The tube was sealed and brought out. After the reaction mixture was agitated at 80−85 °C (oil bath) for 19 h, a black precipitate (likely Pd metal) was clearly seen at the bottom of the tube. The liquid phase was analyzed by ^{19}F and ^{31}P NMR (unlocked) to indicate high conversion. Resonances observed were as follows. For decomposed **3**, ^{19}F NMR: δ −25 (d, J_{P-F} = 633 Hz, minor), −30 (d, J_{P-F} = 642 Hz, major), −36 (d, J_{P-F} = 655 Hz, minor), −47 (d, J_{P-F} = 723 Hz, minor), −85 (d, J_{P-F} = 1056 Hz, trace). ^{31}P NMR: δ −39.8 (t, J_{P-F} = 642 Hz) from the major species observed in the ^{19}F NMR spectrum and other resonances. For decomposed **4**, ^{19}F NMR: δ −25 (d, J_{P-F} = 633 Hz, minor), −30 (d, J_{P-F} = 643 Hz, trace), −31 (d, J_{P-F} = 641 Hz, major), −37 (d, J_{P-F} = 653 Hz, minor), −47 (d, J_{P-F} = 718 Hz, minor), −85 (d, J_{P-F} = 1056 Hz, trace). ^{31}P NMR: δ −40.3 (t, J_{P-F} = 641 Hz) from the major species observed in the ^{19}F NMR spectrum and other resonances. For decomposed **5**, ^{19}F NMR: δ −25 (d, J_{P-F} = 633 Hz, minor), −29 (d, J_{P-F} = 645 Hz, trace), −32 (d, J_{P-F} = 641 Hz, major), −39 (d, J_{P-F} = 650 Hz, minor), −43 (d, J_{P-F} = 660 Hz, trace), −47 (dm, J_{P-F} = 714 Hz, trace), and many low-intensity doublets at −70 to −90 ppm with J_{P-F} = ca. 450−960 Hz. ^{31}P NMR: δ −41.4 (t, J_{P-F} = 641 Hz) from the major species observed in the ^{19}F NMR spectrum and other resonances. As seen from the NMR data, the major ^{19}F NMR-observable species was a mixed triaryldifluorophosphorane $R_2R'PF_2$ in all three cases.

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Supporting Information Available: Full details of the crystallographic data (CIF) for **1** and new complexes **3**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[42] As recommended[26] for the synthesis of **1**.