

Ar–F Reductive Elimination from Palladium(II) Revisited†

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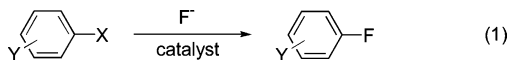
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Received May 11, 2007

In contrast with [(*o*-Tol₃P)₂Pd₂(*p*-C₆H₄X)₂(*μ*-F)₂] (**1**; X = NO₂; *J. Am. Chem. Soc.* **2007**, 129, 1342), its nonactivated congeners (X = H, Me, and MeO) do not produce ¹⁹F NMR-detectable quantities of *p*-FC₆H₄X upon thermal decomposition in the presence of Buchwald's ligand *t*-Bu₂P-2-C₆H₄C₆H₂(*i*-Pr)₃-2',4',6' (**BL**). These results do not support the previously asserted “net Ar–F reductive elimination”, given that for X = NO₂ some quantities of *p*-FC₆H₄X might conceivably be formed from **1** via a variety of other, S_NAr-type paths.

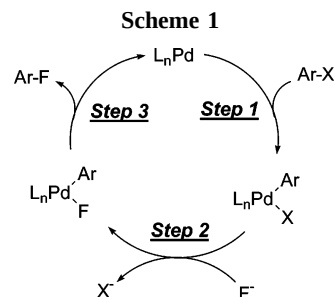
Introduction

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 diazonium compounds, first published in 1927,³ remains the only practical method to selectively introduce fluorine into the aromatic ring.⁴



X = I, Br, Cl, OTf, etc.

In 2002, a concept article⁵ was published on potential use of palladium catalysis for nucleophilic fluorination of haloarenes (eq 1 and Scheme 1). This paper⁵ 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

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 Me₃P and bulky Cy₃P and *i*-Pr₃P have been prepared¹³ 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–CF₃ 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

† DuPont CR&D contribution No. 8783.

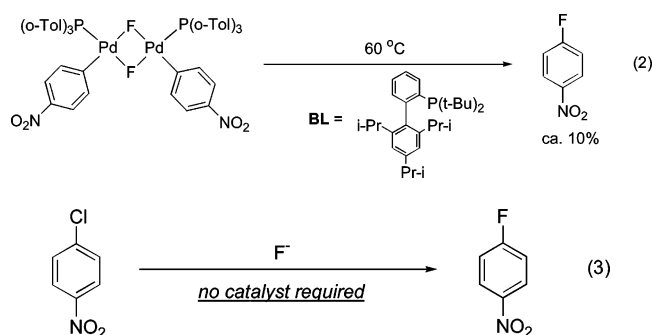
* Corresponding author. E-mail: vlad.grushin-1@usa.dupont.com.

(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., NO₂ and CN) on the ring are well-known to undergo S_NAr fluorination via a Meisenheimer complex.^{4a} Similarly, polyfluorinated benzenes can be made from the corresponding polychlorinated compounds and alkali fluorides in the so-called “Halax” 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.(5) Grushin, V. V. *Chem.–Eur. J.* **2002**, 8, 1006.(6) Fraser, S. L.; Antipin, M. Yu.; Khroustalyov, V. N.; Grushin, V. V. *J. Am. Chem. Soc.* **1997**, 119, 4769.(7) Pilon, M. C.; Grushin, V. V. *Organometallics* **1998**, 17, 1774.(8) Marshall, W. J.; Thorn, D. L.; Grushin, V. V. *Organometallics* **1998**, 17, 5427.(9) Flemming, J. P.; Pilon, M. C.; Borbulevitch, O. Ya.; Antipin, M. Yu.; Grushin, V. V. *Inorg. Chim. Acta* **1998**, 280, 87.(10) Grushin, V. V. *Angew. Chem., Int. Ed.* **1998**, 37, 994.(11) Grushin, V. V. *Organometallics* **2000**, 19, 1888.(12) Roe, D. C.; Marshall, W. J.; Davidson, F.; Soper, P. D.; Grushin, V. V. *Organometallics* **2000**, 19, 4575.(13) Grushin, V. V.; Marshall, W. J. *Angew. Chem., Int. Ed.* **2002**, 41, 4476.(14) Marshall, W. J.; Grushin, V. V. *Organometallics* **2003**, 22, 555.(15) Culkun, 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.

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 CuF₂ 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 Tran²⁶ 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*-FC₆H₄NO₂ in ca. 10% yield upon thermal decomposition of [L₂Pd₂(*p*-C₆H₄NO₂)₂(μ-F)₂], where L = *o*-Tol₃P (**1**) or *t*-Bu₃P (**2**), in the presence of Buchwald's ligand (**BL**), *t*-Bu₂P-2-C₆H₄C₆H₂(*i*-Pr)_{3-2',4',6'} (eq 2).^{26,27} The formation of Ar–F was reported²⁶ only for Ar = *p*-C₆H₄NO₂, 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

- (18) Grushin, V. V.; Marshall, W. J. *J. Am. Chem. Soc.* **2004**, *126*, 3068.
 (19) Macgregor, S. A.; Roe, D. C.; Marshall, W. J.; Bloch, K. M.; Bakhmutov, V. I.; Grushin, V. V. *J. Am. Chem. Soc.* **2005**, *127*, 15304.
 (20) Macgregor, S. A. *Chem. Soc. Rev.* **2007**, *36*, 67.
 (21) Macgregor, S. A.; Wondimagegn, T. *Organometallics* **2007**, *26*, 1143.
 (22) Marshall, W. J.; Grushin, V. V. *Organometallics* **2004**, *23*, 3343.
 (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 use²⁶ of **BL** was apparently inspired by the recent remarkable development of the synthesis of ArOH from ArX (X = Br, Cl) and alkali, catalyzed by Pd₂dba₃/BL: Anderson, K. W.; Ikawa, T.; Tundel, R. E.; Buchwald, S. L. *J. Am. Chem. Soc.* **2006**, *128*, 10694.

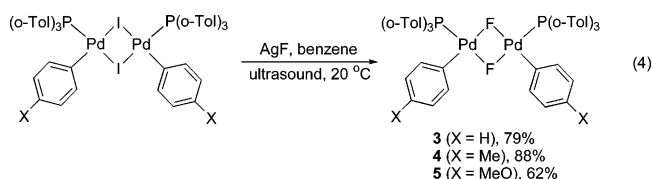
(28) Terrier, F. *Nucleophilic Aromatic Displacement: The Influence of the Nitro Group*; VCH: New York, 1991.

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

nonactivated aryls (Y ≠ a strong electron acceptor, such as NO₂ 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.

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 iodides³¹ 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.



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*-[(R₃P)₂Pd₂(Ph)₂(μ-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*-[(Ph₃P)₂Pd(F)(Ph)]⁶ and *trans*-[(Ph₃P)₂Pd(F)(*p*-C₆H₄NO₂)]⁸. The effect may be rationalized in terms of alleviation of p_π(F)–d_π(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 [(Cy₃P)₂Pd₂(Ph)₂(μ-F)₂], which forms a stable adduct with three

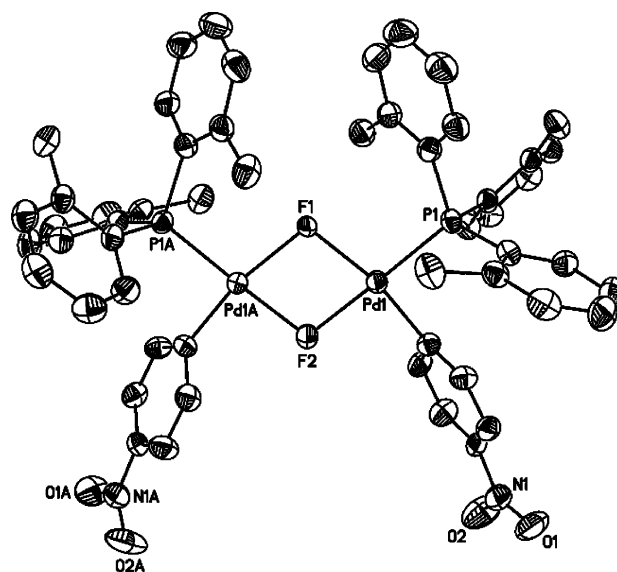


Figure 1. ORTEP drawing of **1** with thermal ellipsoids drawn at the 50% probability level and all H atoms omitted for clarity.

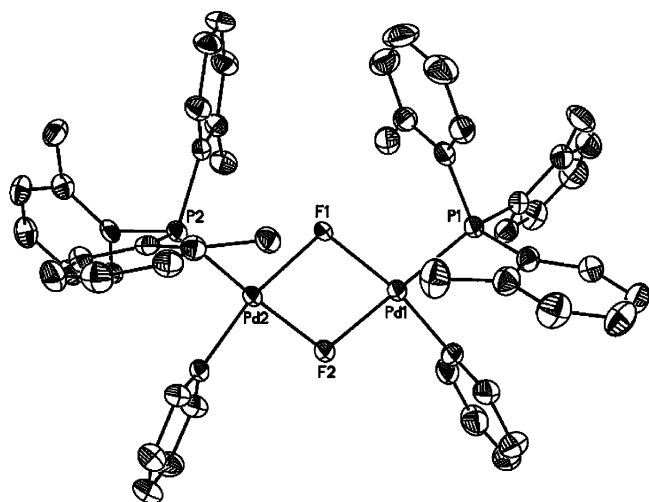


Figure 2. ORTEP drawing of **3** with thermal ellipsoids drawn at the 50% probability level and all H atoms omitted for clarity.

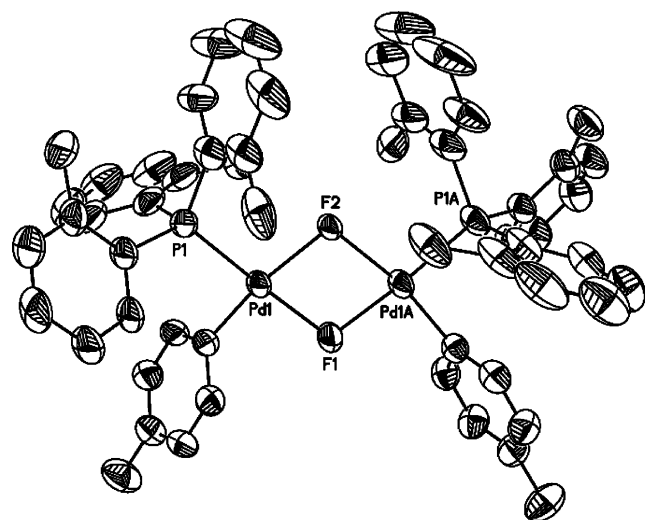


Figure 3. ORTEP drawing of **4** with thermal ellipsoids drawn at the 50% probability level and all H atoms omitted for clarity.

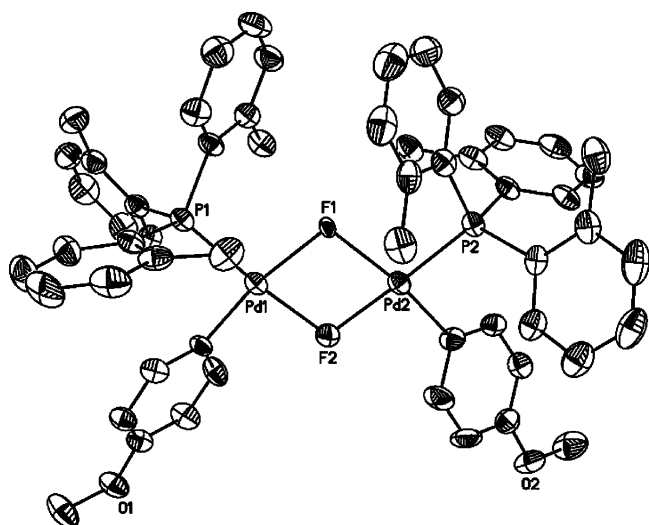


Figure 4. ORTEP drawing of **5** with thermal ellipsoids drawn at the 50% probability level and all H atoms omitted for clarity.

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

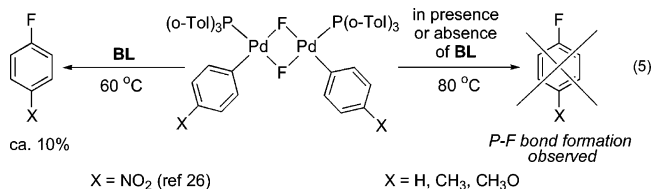
Table 1. Selected Geometry Parameters for **1**, **3**, **4**, and **5**

geometry param, Å or deg	1 ·5C ₆ H ₆ (X = NO ₂)	3 ·3CH ₂ Cl ₂ (X = H)	4 ·2CH ₂ Cl ₂ ·2C ₆ H ₁₄ (X = Me)	5 ·5CH ₂ Cl 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)

due to the larger cone angle and lower basicity of *o*-Tol₃P as compared to Cy₃P.³²

In solution, complexes **3**–**5** exist as mixtures of syn- and anti-isomers, much like [(R₃P)₂Pd₂(Ph)₂(μ-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 isomerization¹³ 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 N₂, in glass or Teflon, in the presence or in the absence of **BL**, did not result in ¹⁹F NMR-observable quantities of fluoroaromatics (eq 5). In all cases, only mixtures of P–F bond



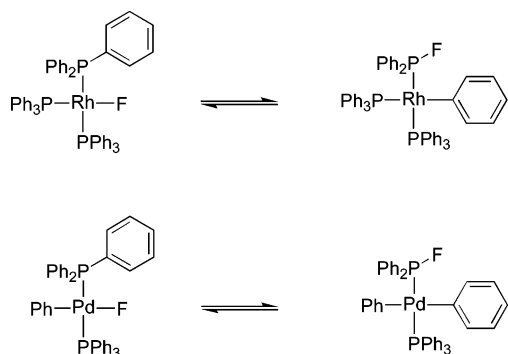
containing products were detected, mainly R₂R'PF₂ (see the Experimental Section). This indicated that Pd–Ar/P–Ar' exchange was occurring in parallel with the P–F bond forming

(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.

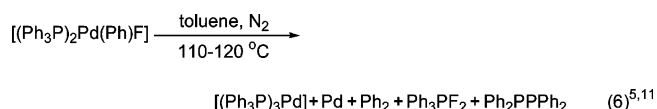
(31) The starting iodo dimers were prepared by the literature methods: Paul, F.; Patt, J.; Hartwig, J. F. *Organometallics* **1995**, *14*, 3030. Widenhoefer, R. A.; Zhong, H. A.; Buchwald, S. L. *Organometallics* **1996**, *15*, 2745. Widenhoefer, R. A.; Buchwald, S. L. *Organometallics* **1996**, *15*, 2755. The *p*-tolyl and *p*-methoxy complexes are known compounds, whereas the phenyl analogue has not been reported. Anal. Calcd for C₅₄H₅₂I₂P₂D₂: 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*-Tol₃P 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.

Scheme 3



mechanism that involved the formation of $[(\text{Ph}_3\text{P})\text{Pd}(\text{Ph}_2\text{PF})]$ and/or isomeric $[(\text{Ph}_3\text{P})\text{Pd}(\text{Ph}_2\text{P})(\text{F})]$ upon Ph–Ph reductive elimination from the corresponding $\text{Pd}(\text{Ph})_2$ species. The latter



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 $[(\text{Ph}_3\text{P})_3\text{RhF}]$ and its facile rearrangement to *cis*- $[(\text{Ph}_3\text{P})_2\text{Rh}(\text{Ph}_2\text{PF})(\text{Ph})]$ suggest that palladium fluorides might undergo a similar transformation. In particular, $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{Ph})\text{F}]$ would be converted to $[(\text{Ph}_3\text{P})(\text{Ph}_2\text{PF})\text{Pd}(\text{Ph})(\text{Ph})]$, 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 $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{Ph})\text{F}]$.^{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 $[(\text{Ph}_3\text{P})\text{Pd}(\text{Ph}_2\text{P})(\text{F})]$, 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 (¹⁹F 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 alleged²⁶ "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

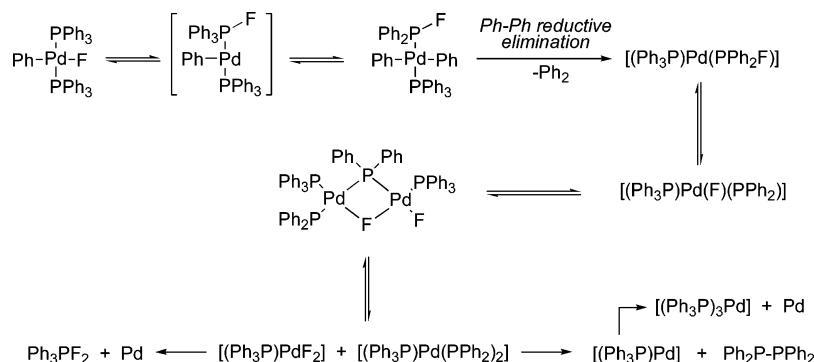
Experimental Section

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*-TolP)₂Pd₂(Ph)₂(μ-F)] (3). Inside a glovebox, a 20 mL vial was charged with $[(\text{o-TolP})_2\text{Pd}_2(\text{Ph})_2(\mu\text{-I})_2]$ ³¹ (0.30 g; 0.24 mmol), AgF (0.12 g; 0.94 mmol), *o*-TolP (5 mg),⁴² and benzene (6 mL). The vial was sealed under N₂, 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 CH₂Cl₂ (6 mL) and filtered through Celite. The Celite was then washed with 4 mL of CH₂Cl₂. 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 C₅₄H₅₂F₂P₂D₂: 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 C₆D₆ at gentle heating to ca. 50 °C and allowing the solution to cool to ambient temperature. ¹⁹F 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). ³¹P NMR (20 °C): δ 31.2 (br m). Under such conditions, the syn–anti ratio was ca. 1.3:1 (¹⁹F NMR). Single crystals were grown by slow diffusion of hexanes into a CH₂Cl₂ solution of **3**.

[(*o*-TolP)₂Pd₂(*p*-Tol)₂(μ-F)] (4). Inside a glovebox, a 20 mL vial was charged with $[(\text{o-TolP})_2\text{Pd}_2(\text{p-Tol})_2(\mu\text{-I})_2]$ ³¹ (0.304 g; 0.24 mmol), AgF (0.12 g; 0.94 mmol), *o*-TolP (5 mg),⁴² and benzene (6 mL). The vial was sealed under N₂, 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 CH₂Cl₂ (6 mL) and filtered through Celite. The Celite was then washed with 5 mL of CH₂Cl₂. 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**·0.5C₆H₆ was 0.23 g (88%). Anal. Calcd for C₅₉H₅₉F₂P₂Pd₂: 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 C₆D₆ at gentle heating to ca. 50 °C and allowing the solution to cool to ambient temperature. ¹H NMR (20 °C): δ 2.1 (br s; CH₃), 2.5 (br s; CH₃), 2.65 (br s; CH₃), 6.6–8.1 (m; aromatic H). ¹⁹F 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). ³¹P NMR (20 °C): δ 34.1 (br m). Under such conditions, the syn–anti ratio was 2:1 (¹⁹F NMR). Single crystals were grown by slow diffusion of hexanes into a CH₂Cl₂ solution of **3**.

[(*o*-Tol₃P)₂Pd₂(*p*-MeOC₆H₄)₂(μ-F)₂] (5**).** Inside a glovebox, a 20 mL vial was charged with [(*o*-Tol₃P)₂Pd₂(*p*-MeOC₆H₄)₂(μ-I)₂]³¹ (0.308 g; 0.24 mmol), AgF (0.12 g; 0.94 mmol), *o*-Tol₃P (5 mg),⁴² and benzene (6 mL). The vial was sealed under N₂, 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 CH₂Cl₂ (6 mL) and filtered through Celite. The Celite was then washed with 2 mL of CH₂Cl₂. 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**·C₆H₆ was 0.17 g (62%). Anal. Calcd for C₆₂H₆₂F₂O₂P₂Pd₂: 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 CD₂Cl₂. ¹H NMR (CD₂Cl₂, 20 °C): δ 2.3 (br s; CH₃), 2.5 (br s; CH₃), 3.6 (s; OCH₃), 6.1–7.8 (m; aromatic H). ¹⁹F NMR (CD₂Cl₂, 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). ³¹P NMR (CD₂Cl₂, 20 °C): δ 32.5 (br m). Under such conditions, the syn–anti ratio was ca. 1.3:1 (¹⁹F NMR). Single crystals were grown by slow diffusion of hexanes into a CH₂Cl₂ 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 ¹⁹F and ³¹P NMR (unlocked) to indicate high conversion. Resonances observed were as follows. For decomposed **3**, ¹⁹F 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). ³¹P NMR: δ –39.8 (t, *J*_{P–F} = 642 Hz) from the major species observed in the ¹⁹F NMR spectrum and other resonances. For decomposed **4**, ¹⁹F 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). ³¹P NMR: δ –40.3 (t, *J*_{P–F} = 641 Hz) from the major species observed in the ¹⁹F NMR spectrum and other resonances. For decomposed **5**, ¹⁹F 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. ³¹P NMR: δ –41.4 (t, *J*_{P–F} = 641 Hz) from the major species observed in the ¹⁹F NMR spectrum and other resonances. As seen from the NMR data, the major ¹⁹F NMR-observable species was a mixed triaryldifluorophosphorane R₂R'PF₂ in all three cases.

Acknowledgment. We thank Dr. Stuart A. Macgregor for discussions.

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>.

OM700469K

(42) As recommended²⁶ for the synthesis of **1**.