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Unexpected H_2O-Induced Ar−X Activation with Trifluoromethylpalladium(II) Aryls†

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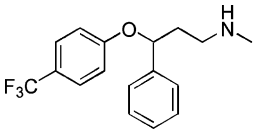
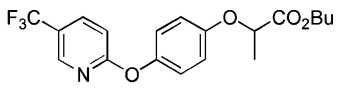
Abstract: A series of new complexes [(L−L)Pd(Ar)(CF_3)] (L−L = dppe, dppp, tmeda; Ar = Ph, p-Tol, C_6D_5) have been synthesized and fully characterized in solution and in the solid state. Remarkable Ph−X activation (X = I, Cl) by [(dppe)Pd(Ph)(CF_3)] (**1**) has been found to come about to cleanly produce biphenyl and [(dppe)Pd(Ph)(X)]. This reaction does not take place under rigorously anhydrous conditions but in the presence of traces of water it readily occurs, exhibiting an induction period and being zero order in PhI. As shown by mechanistic studies, the role of water is to promote reduction of small quantities of the Pd(II) complex to Pd(0) which activates the Ph−X bond. Subsequent transmetalation to give diphenyl Pd complexes, followed by Ph−Ph reductive elimination give rise to the observed products. The water-induced reduction to catalytically active Pd(0) has been demonstrated to proceed via both the Pd(II)/P(III) to Pd(0)/P(V) redox mechanism and α-F transfer, followed by facile hydrolysis of the difluorocarbene to carbonyl, migratory insertion, and reductive elimination of PhC(X)O (X = F, OH, or OOCPh). In the absence of H_2O and ArX, the diphosphine-stabilized trifluoromethyl Pd phenyl complexes undergo slow Ph−CF_3 reductive elimination under reinforcing conditions (xylenes, 145 °C).

Introduction

Selectively fluorinated organic compounds commonly exhibit biological activity.[1,2] "At present, up to 30−40% of agrochemicals and 20−30% of pharmaceuticals contain at least one fluorine atom".[3] Aromatics containing a CF_3 group constitute one of the most important classes of such compounds, including the highly commercially successful antidepressant Prozac and herbicide Fusilade.[4] There are, however, only a limited number of methods for the introduction of a perfluoroalkyl group into the aromatic ring.



Prozac



Fusilade

Some progress has been made in the development of alternatives to the classical Swarts reaction,[5] such as metal-mediated Ar−CF_3 coupling[1,2,6,7] which commonly employs ArI and *stoichiometric* amounts of in situ generated, reactive "$CuCF_3$". The only reported *catalytic* reductive coupling reaction of this type utilizes iodoarenes, perfluoroalkyl iodides (R_fI), Zn metal, and a Pd catalyst under sonication (eq 1).[8]

$$R_f\text{-I} + \text{Ar-I} + \text{Zn} \xrightarrow[\text{ultrasound}]{\text{Pd cat.}} R_f\text{-Ar} + ZnI_2 \qquad (1)$$

Perfluoroalkyl palladium aryls are likely to mediate reaction 1, undergoing Ar−R_f reductive elimination from the metal center.[8] Considering the importance of aromatic perfluoroalkylation, it is surprising that the chemistry of complexes containing both a σ-aryl and a perfluoroalkyl on Pd remains largely unexplored. Among several Pd perfluoroalkyls reported[9−14] there is only one such species, [(dppbz)Pd(CF_3)(*o*-Tol)], where dppbz = 1,2-bis(diphenylphosphino)benzene, which is reluctant to undergo C−C reductive elimination for days at 130 °C.[13] Herein, we describe the synthesis, full characterization, and unexpected striking reactivity of the new complexes [L_nPd(Ar)(CF_3)].

† Contribution No. 8662.

(1) For a recent monograph, see: Kirsch, P *Modern Fluoroorganic Chemistry*; Wiley-VCH: Weinheim, 2004.
(2) For a monograph on fluorinated aromatic compounds, see: Clark, J. H.; Wails, D.; Bastock, T. W. *Aromatic Fluorination*; CRC Press: Boca Raton, FL, 1996.
(3) Large, S.; Roques, N.; Langlois, B. R. *J. Org. Chem.* **2000**, *65*, 8848.
(4) Quadbeck-Seeger, H.-J.; Faust, R.; Knaus, G.; Siemeling, U. *World Records in Chemistry*; Wiley-VCH: Weinheim, 1999.
(5) The Swarts reaction (displacement of aliphatic Cl with F in the presence of antimony fluorides) has been known for over a century: Swarts, F. *Acad. R. Belg.* **1892**, *24*, 309.
(6) For reviews, see: Dolbier, W. R., Jr. *Chim. Oggi* **2003**, *21*, 66. Furin, G. G. *Russ. Chem. Rev.* **2000**, *69*, 491.
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10.1021/ja0602389 CCC: $33.50

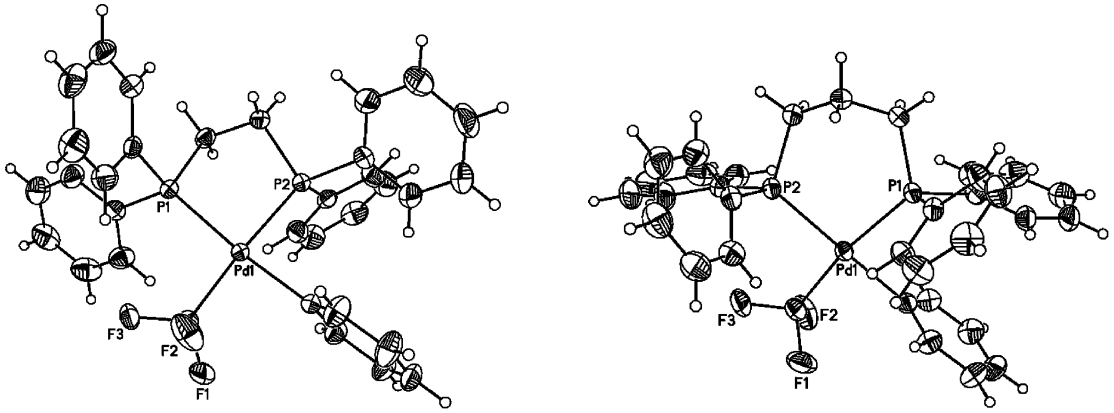
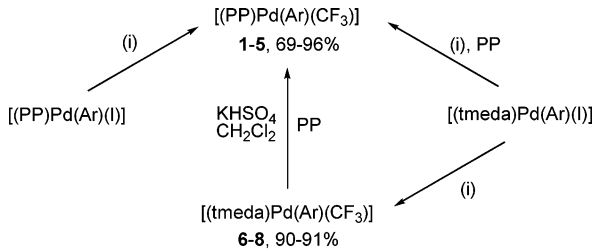


Figure 1. ORTEP drawings of **1** (left) and **4** (right) with thermal ellipsoids shown at the 50% probability level.

Scheme 1



1: PP = dppe, Ar = Ph; **2**: PP = dppe, Ar = *p*-Tol; **3**: PP = dppe, Ar = C_6D_5; **4**: PP = dppp, Ar = Ph; **5**: PP = dppp, Ar = *p*-Tol; **6**: Ar = Ph; **7**: Ar = *p*-Tol; **8**: Ar = C_6D_5

(i) = Me_3SiCF_3/CsF

Results and Discussion

Synthesis and Characterization. New trifluoromethyl palladium aryls were prepared using Ruppert's reagent, Me_3SiCF_3, in the presence of CsF (Scheme 1). The Me_3SiCF_3/F^- system has been widely used to make CF_3-derivatives of various metals, including Pd.[13,14] The reaction of [(dppe)Pd(I)Ph] with excess Me_3SiCF_3/CsF cleanly produced [(dppe)Pd(CF_3)Ph] (**1**) which was isolated spectroscopically and analytically pure in 69% yield. Similarly, [(tmeda)Pd(CF_3)Ph] (**6**) was prepared in 91% yield from [(tmeda)Pd(I)Ph].[15] An alternative route was developed to **1** by reacting **6** with dppe in the presence of $KHSO_4$ as a scavenger for the tmeda released upon P,P/N,N ligand exchange. Such ligand exchange could also be performed in situ, i.e., by running the reaction of [(tmeda)Pd(I)Ph] with Me_3SiCF_3/CsF in the presence of a bidentate phosphine. This technique was found most convenient for the preparation of [(dppp)Pd(CF_3)Ph] (**4**). The aforementioned methods were also used for the synthesis of analogous complexes containing σ-*p*-Tol and σ-C_6D_5 ligands (Scheme 1). An attempt to prepare [(tmeda)Pd(CF_3)$_2$] from [(tmeda)PdCl_2] failed due to the poor solubility of the latter. However, more easily soluble [(teeda)PdCl_2] (teeda = tetraethylethylenediamine) and [(dippp)PdCl_2] (dippp = bis(1,3-diisopropylphosphinopropane) were readily converted to [(teeda)Pd(CF_3)$_2$] (**9**) and [(dippp)Pd(CF_3)$_2$] (**10**), respectively, upon treatment with Me_3SiCF_3/CsF.

New complexes **1**−**10** were characterized by elemental analysis and ^{1}H, ^{19}F, and ^{31}P NMR data (see the Experimental Section). Complexes **1**, **4**, **6**, **9**, and **10** were also studied by single-crystal X-ray diffraction (e.g., Figure 1). Selected geometry parameters for these structures and for [(dppe)Pd(CF_3)I] (**11**) and [(dppe)Pd(CF_3)Cl] (**12**) (see below) are presented in Table 1.

The data in Table 1 complement the recent detailed structural studies of a series of R_fPd complexes by Hughes' group and Rheingold and Zakharov.[11,12] Our structural data confirms the conclusion[11,12] that a CF_3 group has a much stronger trans influence than I and Cl, as can be judged by the Pd−P bond distances in complexes **11** and **12** (Table 1). This difference is particularly significant for the chloro complex **12**, in which the Pd−P bond trans to CF_3 is 0.10 Å longer than the one trans to Cl. Considering the fact that the trans influence might be governed exclusively by inductive/field effects[16] and that the field parameters for Cl and CF_3 are very similar,[17] the difference of 0.10 Å is remarkable. Indeed, the values[17] of σ_m (Hammett), *F* (Swain−Lupton, modified), and σ_F (Taft) for Cl vs CF_3 are $\sigma_m = 0.37$ vs 0.43, $F = 0.42$ vs 0.38, and $\sigma_F = 0.43$ vs 0.46. Even more astounding is the fact that in the nonfluorinated analogue of **12**, [(dppe)Pd(CH_3)Cl], the Pd−P bond distances[18] of 2.339(1) Å (trans to C) and 2.231(1) Å (trans to Cl) are approximately the same as those in **12** (Tables 1 and 2). Unlike the strongly electron-withdrawing CF_3 (see above), a methyl group is almost electroneutral ($\sigma_m = -0.07$; $F = 0.01$; $\sigma_F = 0.01$).[17]

The previously obtained data on the trans influence of perfluoroalkyl groups vs methyl are not without controversy.[11,12] Nonetheless, the almost identical coordination geometry in the structures of [(dppe)Pd(CF_3)Cl] (**12**) and [(dppe)Pd(CH_3)Cl] (Table 2; Figure 2) is unexpected. The chlorine/methyl disorder of 8% was determined from the refined occupancies and is too small to affect substantially the real values for the geometry parameters. Furthermore, the structure of [(dcpe)Pd(CH_3)Cl][18] (dcpe = 1,2-bis(dicyclohexylphosphino)ethane) that is devoid of disorder, displays essentially the same parameters (Table 2). Therefore, we conclude that for this series of complexes, the trans and cis influence of the electronically and sterically different CH_3 and CF_3 groups are strikingly similar.[19] In contrast,

(15) The reaction of [(Ph_3P)$_2$Pd(I)Ph] with Me_3SiCF_3/CsF was poorly selective, leading to inseparable reaction mixtures due to facile phosphine displacement. The formation of a mixture of *trans*-[(Ph_3P)$_2$Pd(CF_3)Ph], *cis*- and *trans*-[(Ph_3P)Pd(CF_3)$_2$Ph]$^-$, and free PPh_3 was observed by ^{19}F and ^{31}P NMR even at <50% conversion. This result is consistent with the recent report[14] demonstrating facile displacement of PPh_3 on Pd and Pt with CF_3 upon treatment with Me_3SiCF_3/[Me_4N]F.

(16) Landis, C. R.; Firman, T. K.; Root, D. M.; Cleveland, T. *J. Am. Chem. Soc.* **1998**, *120*, 1842.
(17) Hansch, H.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *97*, 165.
(18) Calabrese, J. C. Unpublished results (DuPont Crystallographic Database, 1996).

Table 1. Selected Geometry Parameters for **1**, **4**, **6**, and **9**−**12**

geometry params (Å or deg)	complex						
	[(dppe)-Pd(Ph)CF_3]·hexane **1**	[(dppp)-Pd(Ph)CF_3]·1/2CH_2Cl_2 **4**	[(tmeda)-Pd(Ph)CF_3] **6**	[(teeda)-Pd$(CF_3)_2$] **9**	[(dippp)-Pd$(CF_3)_2$] **10**	[(dppe)-Pd(CF_3)I] **11**[a]	[(dppe)-Pd(CF_3)Cl]·1/2PhCl **12**
Pd−Ph	2.056(2)	2.055(2)	1.996(1)				
Pd−CF_3	2.067(2)	2.071(2)	1.993(1)	2.025(1)	2.070(4) 2.090(4)	2.157(8)	2.084(3)
Pd−I						2.646(1)	
Pd−Cl							2.354(1)
Pd−P (trans to Ph or X)	2.341(1)	2.356(1)				2.255(1)	2.246(1)
Pd−P (trans to CF_3)	2.298(1)	2.310(1)			2.342(1) 2.343(1)	2.302(1)	2.345(1)
Pd−N (trans to Ph)			2.198(1)				
Pd−N (trans to CF_3)			2.169(1)	2.193(1)			
CF_3−Pd−Ph (or X)	86.73(6)	84.85(7)	85.28(6)			92.0(2)	88.71(8)
CF_3−Pd−CF_3				85.90(7)	86.1(2)		
Ph−Pd−P (cis)	89.04(5)	85.57(5)					
CF_3−Pd−P (cis)	99.14(5)	96.21(5)			89.6(1) 90.1(1)	93.9(2)	91.01(8)
P−Pd−P	85.10(2)	93.36(2)				84.42(5)	85.37(3)
N−Pd−N			82.77(5)	83.06(5)			
Ph−Pd−N (cis)			93.76(6)				
CF_3−Pd−N (cis)			98.27(6)	95.54(5)			
X−Pd−P (cis)						89.68(4)	94.77(3)

[a] The iodine and CF_3 groups are disordered (0.87/0.13), and hence the presented Pd−CF_3 bond distance for **11** may be artificially lengthened.

Table 2. Selected Geometry Parameters for [(dppe)Pd(CF_3)Cl], [(dppe)Pd(CH_3)Cl], and [(dcpe)Pd(CH_3)Cl]

geometry parameter (Å or deg)	[(dppe)Pd(CF_3)Cl] (**12**) (this work)	[(dppe)Pd(CH_3)Cl][a] (ref 18)	[(dcpe)Pd(CH_3)Cl] (ref 18)
Pd−C	2.084(3)	2.135(4)	2.130(6)
Pd−Cl	2.354(1)	2.376(1)	2.381(2)
Pd−P (trans to C)	2.345(1)	2.339(1)	2.320(2)
Pd−P (trans to Cl)	2.246(1)	2.231(1)	2.222(2)
C−Pd−Cl	88.71(8)	87.0(2)	89.22(2)
P−Pd−P	85.37(3)	86.26(4)	87.74(6)
C−Pd−P	91.01(8); 176.06(8)	91.1(2); 177.4(2)	91.0(2); 175.8(2)
Cl−Pd−P	94.77(3); 175.36(3)	95.68(4); 174.86(5)	92.38(6); 175.08(6)

[a] There is a minor 8% chlorine/methyl disorder as determined from the refined occupancies.

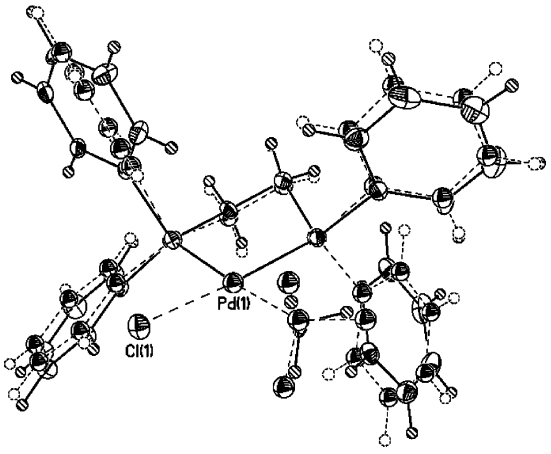


Figure 2. Superimposed molecules of [(dppe)Pd(CF_3)Cl] (**12**) and its nonfluorinated congener [(dppe)Pd(CH_3)Cl], showing essentially identical coordination geometry around Pd.

the Pd−N bond distances trans to C in [(tmeda)Pd(*i*-C_3F_7)I] and [(tmeda)Pd(CH_3)I] have been measured[11] at 2.137(18) and 2.204(7) Å, respectively, clearly indicating that CH_3 is a stronger trans influencing ligand than perfluoroalkyl (*i*-C_3F_7). The Pd−P(N) bond distances trans to the Ph ligands are less than 0.05 Å longer than those trans to the CF_3 groups (Table 1), despite the fact that a phenyl group is a much weaker acceptor (σ_m = 0.06; F = 0.12; σ_F = 0.14).[17] The Pd−Ph and Pd−CF_3 bond distances are almost the same within the molecules of **1** (2.056(2) and 2.067(2) Å), **4** (2.055(2) and 2.071(2) Å), and **6** (1.996(1) and 1.993(1) Å).

Ar−X Activation. To model catalytic formation of $PhCF_3$, reductive elimination from **1** was studied in the presence of PhI. It was reasoned that, if the Ph−CF_3 bond formed, the resulting Pd(0) would be trapped by in situ Ph−I oxidative addition to give [(dppe)Pd(I)Ph]. Against this expectation, however, the reaction took a completely different path, leading cleanly to [(dppe)Pd(CF_3)I] (**11**) and biphenyl (eq 2). Similarly, heating **1** in neat PhCl for 2 h at 135 °C did not produce $PhCF_3$, but full conversion of **1** was observed to Ph_2 and [(dppe)Pd(CF_3)-

(19) (a) As early as 1972, Clark and co-workers[19b] reported that the trans influence of a CF_3 group in a series of Pt complexes is almost as strong as that of a methyl group. Bennett et al.[19c] have observed both smaller and larger trans influence for CF_3 as compared to that for CH_3. For a detailed discussion, see refs 11 and 12. (b) Appleton, T. G.; Chisholm, M. H.; Clark, H. C.; Manzer, L. E. *Inorg. Chem.* **1972**, *11*, 1786. (c) Bennett, M. A.; Chee, H.-K.; Robertson, G. B. *Inorg. Chem.* **1979**, *18*, 1061. Bennett, M. A.; Chee, H.-K.; Jeffery, J. C.; Robertson, G. B. *Inorg. Chem.* **1979**, *18*, 1071.

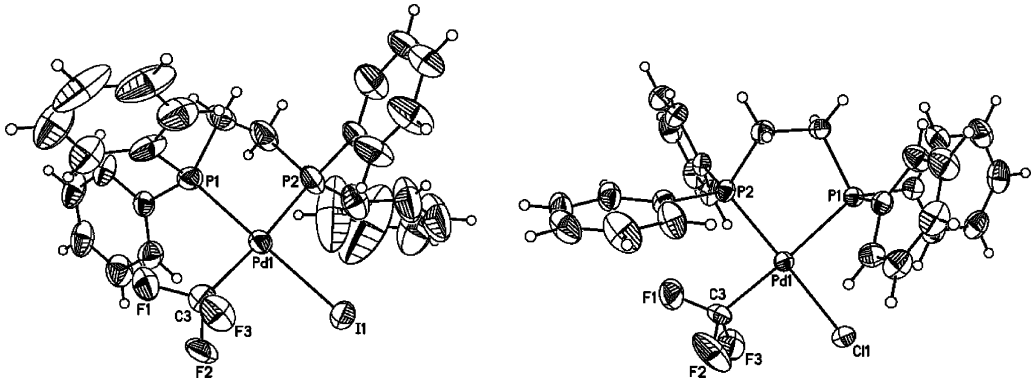
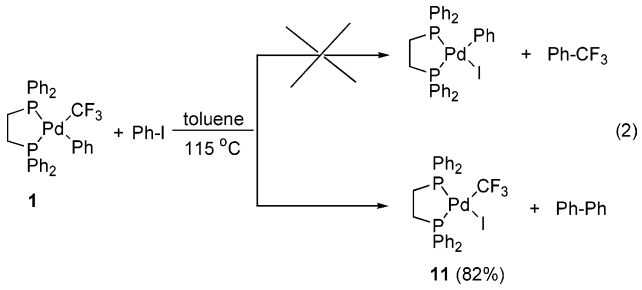


Figure 3. ORTEP drawings of **11** (left) and **12** (right) with thermal ellipsoids shown at the 50% probability level.

Cl] (**12**) at ca. 90% selectivity. Both **11** and **12**[20] were fully characterized, including X-ray diffraction (Figure 3).



(2)

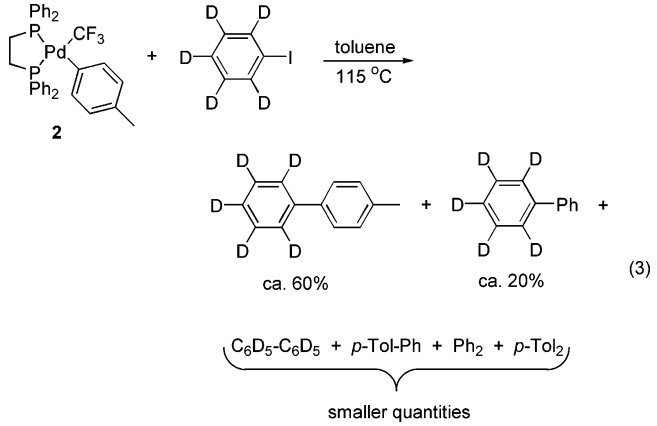
The reactivity of **1** toward PhCl and PhI (eq 2) was striking. Although PhX oxidative addition to the Pd(II) center, followed by Ph−Ph reductive elimination from Pd(IV) would rationalize the observed results, this path is highly unlikely,[21] especially given the particular inertness of the Ph−Cl bond.[22] To gain insight into the mechanism of this remarkable ArX activation with a Pd(II) complex, a series of experiments were carried out and observations made, as follows.

(1) A free radical mechanism proposed[23] for the formally similar reactivity of a PCP Pd pincer complex can be ruled out since reaction 2 in toluene did not produce bibenzyl (GC−MS).

(2) Reaction 2 is promoted by adventitious water. No reaction was observed under rigorously anhydrous conditions commonly used in our laboratories.[24] Upon deliberate addition of minute quantities of water, an induction period (0.5−1 h) was observed, after which the reaction proceeded with acceleration, displaying complex kinetics and being zero order in PhI.

(3) The H_2O-induced reaction of [(dppe)Pd(CF_3)(*p*-Tol)] (**2**) with C_6D_5I gave rise (GC−MS) to *p*-Tol−C_6D_5 (ca. 60%), Ph−C_6D_5 (ca. 20%), and smaller quantities of $(C_6D_5)_2$, *p*-Tol−Ph, Ph_2 and *p*-Tol_2 (eq 3). The aryl scrambling was also observed by ^{19}F NMR, especially toward the end of the reaction.

(4) No aryl−aryl exchange was detected (NMR) after heating [(dppe)Pd(CF_3)(*p*-Tol)] (**2**), [(dppp)Pd(CF_3)(*p*-Tol)] (**5**), or



(3)

[(dppe)Pd(CF_3)(C_6D_5)] (**3**) at 115 °C in toluene in the presence or absence of H_2O for 6 h.

(5) Complex **4**, the dppp analogue of **1**, reacted with PhI similarly, except that faster kinetics and lower selectivities were observed.

(6) The iodo congener of **1**, [(dppe)Pd(Ph)(I)], appeared unreactive toward PhI under similar conditions.

(7) Reaction 2 shares some features with the arylation of PhI with [L_2PdPh_2] (L = Et_2PPh) to give Ph_2 and [$L_2Pd(I)Ph$].[25a] Both exhibit an induction period and are zero order in PhI. Unlike the reaction of [L_2PdPh_2] with PhI, which is catalyzed by its product, [$L_2Pd(I)Ph$],[25a] reaction 2 is not autocatalytic in **11**. However, reaction 2 was found to be catalyzed by [(dppe)-Pd(Ph)(I)] (7 mol %) under anhydrous conditions.[26] Even in the presence of catalytic quantities of [(dppe)Pd(Ph)(I)], reaction 2 was slow at the beginning, accelerating upon formation of **11**, with the conversion being ca. 1% and 30% after 2 and 4 h at 115 °C, respectively.

On the basis of the above data, a mechanism is presented (Scheme 2) that involves an in situ transformation of a small quantity of **1** to a reactive, phosphine-stabilized Pd(0) species which undergoes facile oxidative addition of PhI. The resulting [LPd(I)Ph] then reacts with **1** via transmetalation,[25,27] with the iodo ligand providing critical nucleophilic assistance to the S_E-Ar-type process.[28] The promoting but *not* catalytic effect of the

(20) Strukul, G.; Ros, R.; Michelin, R. A. *Inorg. Chem.* **1982**, *21*, 495.
(21) See, for example: Böhm, V. P. W.; Herrmann, W. A. *Chem. Eur. J.* **2001**, *7*, 4191. Canty, A. J.; Patel, J.; Rodemann, T.; Ryan, J. H.; Skelton, B. W.; White, A. H. *Organometallics* **2004**, *23*, 3466. Consorti, C. S.; Flores, F. R.; Dupont, J. *J. Am. Chem. Soc.* **2005**, *127*, 12054 and references therein.
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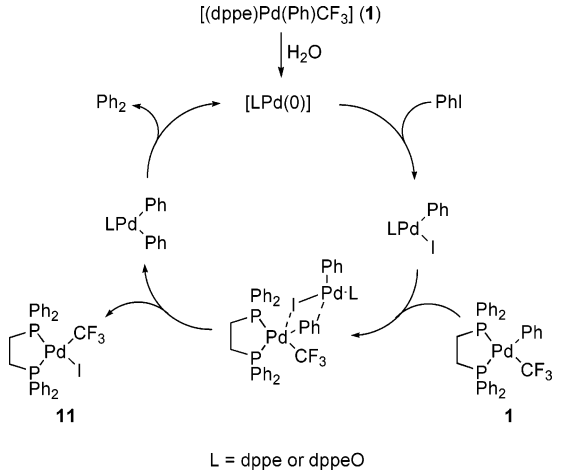
(24) Macgregor, S. A.; Roe, D. C.; Marshall, W. J.; Bloch, K. M.; Bakhmutov, V. I.; Grushin, V. V. *J. Am. Chem. Soc.* **2005**, *127*, 15304 and references therein.
(25) (a) Ozawa, F.; Hidaka, T.; Yamamoto, T.; Yamamoto, A. *J. Organomet. Chem.* **1987**, *330*, 253. (b) Ozawa, F.; Fujimori, M.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1986**, *5*, 2144.
(26) Insufficiently purified samples of **1**−**3** were found to react with PhI in the absence of added water, likely due to contamination with small quantities of the catalytically active starting materials [(dppe)Pd(Ar)(I)].
(27) For a recent report, see: Albeniz, A. C.; Espinet, P.; López-Cimas, O.; Martín-Ruiz, B. *Chem. Eur. J.* **2005**, *11*, 242 and references therein.

Scheme 2

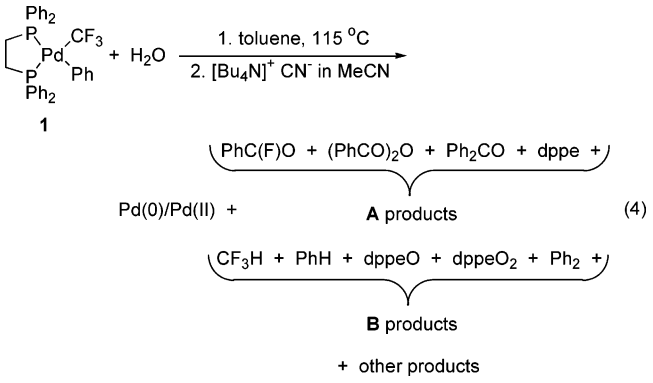


product (**11**) might deal with extra nucleophilic assistance from its I ligand, i.e. [LPd(I)Ph] interacts with **1** only via Ph, with iodide for coordination to **1** provided by **11**.[28b] Reductive elimination of biphenyl completes the catalytic cycle (Scheme 2).

The catalytic loop presented in Scheme 2 is similar to the Ozawa−Yamamoto mechanism,[25] although the origin of the Pd(0) is unclear. There are at least a few pathways that might produce Pd(0) from **1** and H_2O. The water-induced Pd(II)/P(III) to Pd(0)/P(V) process would conceivably lead to "[(dppeO)Pd]".[29,30] Stoichiometry considerations suggest that the reaction of **1** with water should give "[(dppeO)Pd]", PhH, and CF_3H. In fact, monitoring reaction 2 by ^{31}P NMR often revealed the presence of a small amount (1−5%) of a species exhibiting two doublets at 43.4 and 58.3 ppm (J_{P-P} = 26.7 Hz) which is consistent with a Pd−dppeO moiety (but not free dppeO[29]). Alternatively, Pd(0) might be generated from **1** via α-F transfer,[31,32] followed by coupling of the (F)Pd=CF_2 with the Ph ligand[33] or facile hydrolysis of the difluorocarbene to carbonyl,[31] migratory insertion to Pd benzoyl, and reductive elimination of PhC(X)O, where X = F[34] or OOCPh[35] if the Pd−F bond is hydrolyzed.

The Key First Step: Pd(II) Reduction. To elucidate the reduction mechanism, **1** was decomposed with water in toluene in a sealed high-pressure NMR sapphire tube at 115 °C. After ca. 1 h the solution turned light tan, and several hours later Pd(0) was produced in the form of palladium metal, along with reddish-brown viscous oil, poorly soluble in toluene. After 24 h, full conversion of **1** was observed. The ^{19}F NMR spectrum displayed several resonances from the decomposition products, of which two were reliably identified by their characteristic chemical shifts and coupling constant, PhC(F)O (+16 ppm, s) and CF_3H (−79.8 ppm, d, J_{F-H} = 80 Hz). Only few signals of very low intensity were found in the ^{31}P NMR spectrum of the same sample, indicating that almost all P-containing species were located in the red-brown oily precipitate, rather than in the toluene phase. The tube was then unsealed under N_2 in a drybox, and the toluene solution was decanted off the brown oil. GC−MS analysis of the toluene fraction confirmed the formation of PhC(F)O and revealed the presence of benzene, biphenyl, benzophenone, and benzoic anhydride, among other products. The toluene-insoluble red-brown oil was dissolved in MeCN and analyzed by ^{31}P NMR. A number of broad resonances were observed, along with two sharp lines from $[(dppe)_2Pd]^{2+}$ (58.0 ppm) and $dppeO_2$ (30.8 ppm). To release all P-ligands coordinated to palladium, the solution was treated with excess $[Bu_4N]^+$ CN^-. After this treatment, ^{31}P NMR analysis of the sample indicated the presence of free dppe (singlet, −12.8 ppm), dppeO (two doublets, −12.0 and 29.5 ppm, J_{P-P} = 48.3 Hz),[29] and $dppeO_2$ (singlet, 30.8 ppm), in a ca. 6:3:2 ratio.

Apart from the Pd(0) produced, all of the identified products of the reaction of **1** with H_2O in toluene can be divided into two groups, **A** and **B** (eq 4). The **A** group products, dppe and



aromatic carbonyl compounds, point to the Pd reduction path involving α-F transfer[31,32] leading to a fluoro difluorocarbene σ-phenyl palladium complex. At this point, the dppe ligand may be coordinated to the metal in a monodentate fashion. The difluorocarbene ligand is fully expected[31] to be highly susceptible to hydrolysis leading to a carbonyl species. The latter undergoes facile migratory insertion to produce a Pd benzoyl, followed by reductive elimination (Scheme 3). If the Pd−F bond is hydrolyzed prior to that, benzoic anhydride rather than PhC-

(28) (a) Reutov, O. A.; Beletskaya, I. P. *Reaction Mechanisms of Organometallic Compounds*; Wiley-Interscience: New York, 1968. (b) A reviewer proposed that the transmetalation step (Scheme 2) might involve more reactive[28c] Pd species produced upon ionization of the Pd−I bond. Such Pd−I ionization is certainly a possibility, which would give rise to a cationic Pd species of enhanced electrophilicity. The critical[28a] nucleophilic assistance might then come from the I^- formed upon Pd−I bond ionization or be provided by **11**. (c) See, for example: Kawataka, F.; Kayaki, Y.; Shimizu, I.; Yamamoto, A. *Organometallics* **1994**, *13*, 3517. Yamamoto, A. *J. Organomet. Chem.* **1995**, *500*, 337. Kayaki, Y.; Shimizu, I.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 917.

(29) For a recent review, see: Grushin, V. V. *Chem. Rev.* **2004**, *104*, 1629.

(30) For original research papers reporting the Pd(II)/P(III) to Pd(0)/P(V) redox transformation, induced by hard nucelophiles, such as F^-, AcO^-, OH^-, and H_2O, see: (a) Mason, M. R.; Verkade, J. G. *Organometallics* **1990**, *9*, 864 and **1992**, *11*, 2212. (b) Ioele, M.; Ortaggi, G.; Scarsella, M.; Sleiter, G. *Polyhedron* **1991**, *10*, 2475. (c) Amatore, C.; Jutand, A.; M'Barki, M. A. *Organometallics* **1992**, *11*, 3009. (d) Ozawa, F.; Kubo, A.; Hayashi, T. *Chem. Lett.* **1992**, 2177. (e) Grushin, V. V.; Alper, H. *Organometallics* **1993**, *12*, 1890. (f) Mandai, T.; Matsumoto, T.; Tsuji, J.; Saito, S. *Tetrahedron Lett.* **199**3, *34*, 2513. (g) Ozawa, F.; Kubo, A.; Matsumoto, Y.; Hayashi, T.; Nishioka, E.; Yanagi, K.; Moriguchi, K. *Organometallics* **1993**, *12*, 4188. (h) Grushin, V. V.; Bensimon, C.; Alper, H. *Inorg. Chem.* **1994**, *33*, 4804. (i) Monteil, F.; Kalck, P. *J. Organomet. Chem.* **1994**, *482*, 45. (j) Amatore, C.; Carré, E.; Jutand, A.; M'Barki, M. A. *Organometallics* **1995**, *14*, 1818. (k) Amatore, C.; Blart, E.; Genêt, J. P.; Jutand, A.; Lemaire-Audoire, S.; Savignac, M. *J. Org. Chem.* **1995**, *60*, 6929. (l) Papadogianakis, G.; Peters, J. A.; Maat, L.; Sheldon, R. A. *J. Chem. Soc., Chem. Commun.* **1995**, 1105.

(31) For a review, see: Brothers, P. J.; Roper, W. R. *Chem. Rev.* **1988**, *88*, 1293.

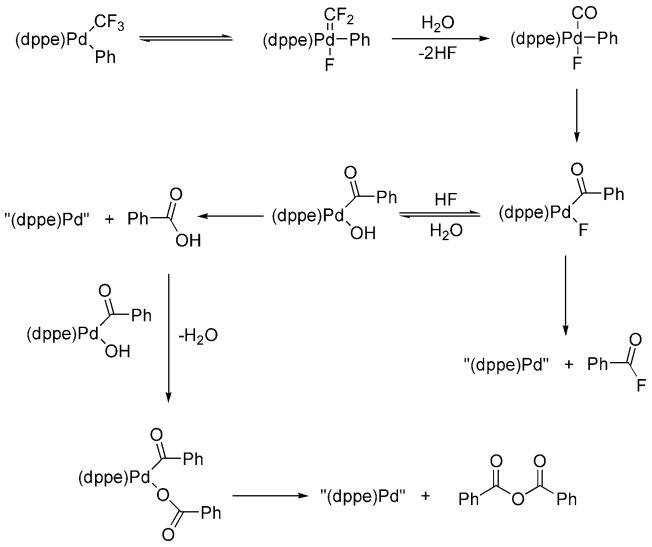
(32) Huang, D.; Caulton, K. G. *J. Am. Chem. Soc.* **1997**, *119*, 3185. Huang, D.; Koren, P. R.; Folting, K.; Davidson, E. R.; Caulton, K. G. *J. Am. Chem. Soc.* **2000**, *122*, 8916.

(33) van der Boom, M. E.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.* **1999**, *121*, 6652.

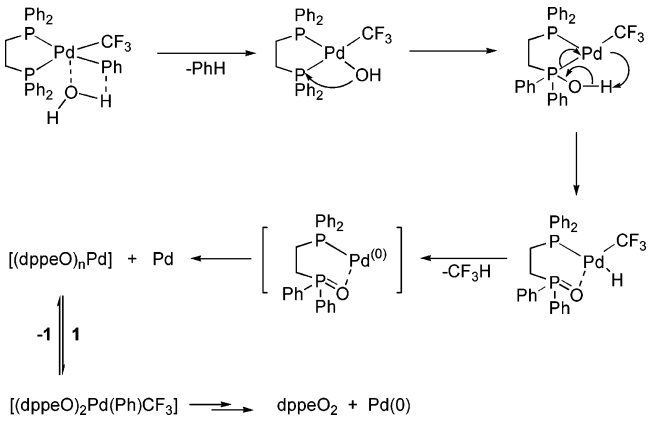
(34) Fraser, S. L.; Antipin, M. Yu.; Khroustalyov, V. N.; Grushin, V. V. *J. Am. Chem. Soc.* **1997**, *119*, 4769.

(35) Grushin, V. V.; Alper, H. *J. Am. Chem. Soc.* **1995**, *117*, 4305.

Scheme 3



Scheme 4



(F)O is the final product. The formation of $(PhCO)_2O$ upon reaction of $[(Ph_3P)_2Pd_2(Ph)_2(OH)_2]$ with CO has been demonstrated[35] to occur via initial reductive elimination of PhCOOH. The acid reacts instantaneously with the as yet unreacted hydroxo complex to produce a Pd benzoyl benzoate which reductively eliminates the anhydride.[35] As for the formation of benzophenone, it would take place via transmetalation giving rise to a σ-phenyl Pd benzoyl.

The **B**-group products come from the reduction of Pd(II) to Pd(0) at the expense of dppe oxidation[29,30] (Scheme 4). The first step likely involves coordination of H_2O to the metal center and protonolysis of the Pd−Ph bond. Intramolecular nucleophilic attack of the OH ligand on a phosphorus atom[24] followed by H transfer[36] and H−CF_3 reductive elimination should lead to Pd(0) stabilized by only one dppeO ligand. Disproportionation of the "(dppeO)Pd" then gives rise to Pd metal and $[(dppeO)_nPd]$.[37] P-ligand exchange between the dppeO Pd(0) species produced and the starting complex **1** would yield $[(dppeO)_2Pd(Ph)CF_3]$ which can also undergo the Pd(II)/P(III) to Pd(0)/P(V) transformation, to give $dppeO_2$ (Scheme 4). Although the sequence of events is not precisely known, it is clear that the formation of Pd(0) from **1** is due to at least two well-documented reactions, α-F transfer[31,32] (Scheme 3) and the Pd(II)/P(III) to Pd(0)/P(V) redox process[29,30] (Scheme 4) which might proceed via a metallophosphorane, as has been recently demonstrated by Macgregor.[24,36]

The two reduction mechanisms may be symbiotic. For instance, the HF produced upon hydrolysis of the CF_2 ligand (Scheme 3) might facilitate protonolysis of the Pd−Ph bond (Scheme 4). It is also conceivable that the formation of dppeO (Scheme 4) may accelerate the hydrolysis of the C−F bonds (Scheme 3) due to the basicity of the oxygen center of dppeO.

The overall mechanism (Scheme 2) is fully consistent with the lack of reactivity of $[(dippp)Pd(CF_3)_2]$ (**10**) that is devoid of a σ-aryl ligand, toward PhI and PhCl in the temperature range of 115−145 °C.

The Ar/Ar exchange accompanying the reaction (e.g., eq 3) likely occurs via reversible P−C reductive elimination,[39−45] although a metallophosphorane path[24,36] cannot be completely ruled out. Commonly, P−C reductive elimination from a σ-aryl Pd(II) tertiary phosphine complex requires coordinative unsaturation,[39−43] whereas the metallophosphorane path does not,[24] and sometimes both can be observed simultaneously.[24,43] The complexity of the water-induced reduction of **1** to zero-valent palladium (Schemes 3 and 4) prevents a conclusive study of the Ar/Ar exchange during the reaction (eq 3). Nonetheless, the fact that the Ar/Ar exchange does occur during the reaction (eqs 2 and 3) but not upon heating four-coordinate **2**, **3**, or **5** at the same temperature (see above) supports the P−C reductive elimination path which involves *coordinatively unsaturated* Pd aryls.

The lack of reactivity of [(dppe)Pd(I)Ph] toward PhI under conditions employed for reaction 2 indicates that the CF_3 group in **1** facilitates the transmetalation, apparently by lowering the accessible LUMO on Pd and thus increasing the efficiency of nucleophilic assistance to S_EAr via $(CF_3)Pd\cdots I-Pd$ interaction. In accord with the mechanism shown in Scheme 2, $[(dippp)Pd(CF_3)_2]$ and $[(teeda)Pd(CF_3)_2]$ remained unreactive toward ArI under the standard conditions (eq 2).

Although a detailed study of Ar−CF_3 reductive elimination is beyond the scope of this work, we would like to disclose some of our preliminary results in this article. Like $[(dppbz)Pd(CF_3)(o\text{-Tol})]$,[13] our trifluoromethyl palladium aryls did not undergo Ar−CF_3 reductive elimination at 130 °C. The formation

(36) Macgregor, S. A.; Neave, G. W. *Organometallics* **2004**, *23*, 891.

(37) We attempted the synthesis and isolation of [(dppeO)Pd(Ph)I] to demonstrate that this complex, like [(dppe)Pd(Ph)I], can catalyze reaction 2. For that, a 1:2 mixture of $[Pd_2(dba)_3]$ and dppeO in benzene was treated with excess PhI. In this way we had earlier prepared and successfully isolated [(dppmO)Pd(Ph)I].[29] Unlike the latter, however, its dppeO congener was not isolable, probably due to poor stability. We believe that the weak dppeO chelation (seven-membered ring) makes the complex more prone to oligomerization[38] and/or P−C reductive elimination (see below), as compared to the much more stable six-membered dppmO chelate.[29] Nonetheless, the in situ generated [(dppeO)Pd(Ph)I], a stronger electrophile than [(dppe)Pd(Ph)I], is expected (Scheme 2) to contribute to the catalysis of reaction 2.

(38) Coyle, R. J.; Slovokhotov, Yu. L.; Antipin, M. Yu.; Grushin, V. V. *Polyhedron* **1998**, *17*, 3059.

(39) Kong, K.-C.; Cheng, C.-H. *J. Am. Chem. Soc.* **1991**, *113*, 6313.

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(42) Goodson, F. E.; Wallow, T. I.; Novak, B. M. *J. Am. Chem. Soc.* **1997**, *119*, 12441.

(43) Grushin, V. V. *Organometallics* **2000**, *19*, 1888.

(44) For Ar/Ar exchange in dppe Pd aryls, see, for example: Baranano, D.; Hartwig, J. F. *J. Am. Chem. Soc.* **1995**, *117*, 2937. Mann, G.; Baranano, D.; Hartwig, J. F.; Rheingold, A. L.; Guzei, I. A. *J. Am. Chem. Soc.* **1998**, *120*, 9205.

(45) For examples of facile P−C reductive elimination from cyclopalladated complexes, see: (a) Vicente, J.; Arcas, A.; Bautista, D.; Tiripicchio, A.; Tiripicchio-Camellini, M. *New J. Chem.* **1996**, *20*, 345. (b) Vicente, J.; Arcas, A.; Bautista, D.; Jones, P. G. *Organometallics* **1997**, *16*, 2127. (c) Vicente, J.; Abad, J.-A.; Frankland, A. D.; Ramírez de Arellano, M. C. *Chem. Eur. J.* **1999**, *5*, 3066.

of $PhCF_3$, however, was observed after heating **1** or **4** in the presence of dppe and dppp, respectively, in xylenes at 145 °C (oil bath). The reaction of **1** was very sluggish and poorly selective, producing $PhCF_3$ in only ca. 10% yield (^{19}F NMR) after 64 h. The decomposition of **4** in the presence of dppp under similar conditions was at least an order of magnitude faster, with the selectivity toward $PhCF_3$ being ca. 60%. Complex **6** produced only traces of $PhCF_3$ under such conditions.

Conclusions

We have conducted the first systematic study of trifluoromethylpalladium aryls, including high-yield synthesis and full characterization of a series of new complexes of that type. Some of these complexes can undergo Ar−CF_3 reductive elimination under reinforcing conditions. It has been found that the new CF_3Pd(II) aryl complexes are surprisingly capable of activating the inert Ar−X (X = I, Cl) bonds of nonactivated haloarenes. This reaction is induced by traces of water and involves the formation of minute quantities of Pd(0) species which serve as a catalyst for the process. The reaction then involves Ar−X oxidative addition to the Pd(0) catalyst, followed by transmetalation to give biaryl Pd complexes and their Ar−Ar reductive elimination reaction. The water-induced reduction to catalytically active Pd(0) has been demonstrated to occur via both the Pd(II)/P(III) to Pd(0)/P(V) redox process and α-F transfer, followed by facile hydrolysis of the difluorocarbene to carbonyl, migratory insertion, and reductive elimination of PhC(X)O, where X = F, OH, or OOCPh.

The Ar−X activation chemistry described in this article points, once again, to the inability of Pd(II) species to oxidatively add the C−X bond of nonactivated haloarenes.[21] The new "hidden" pathway (Schemes 2−4), as elucidated by mechanistic studies, involves H_2O-induced reduction of the Pd(II) complex to a small quantity of Pd(0) which, in tandem with the initial Pd(II) aryl, provides an easy path for activation and coupling of the ArX substrate.

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. dppeO,[46] [(tmeda)Pd(Ar)I],[47] and [(dippp)-$PdCl_2$],[48] were prepared as described in the literature. 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, Delaware.

[(dppe)Pd(Ph)I]. A mixture of [(tmeda)Pd(Ph)I] (0.30 g; 0.70 mmol), dppe (0.305 g; 0.77 mmol), and toluene (10 mL) was stirred under N_2 at room temperature for 3 h. The pale-yellow precipitate was separated, washed with hexanes, and dried under vacuum. The product was recrystallized by dissolving in ca. 8 mL of 1,2-dichloroethane (note: CH_2Cl_2 seemed to slowly decompose the complex) and adding hexanes (ca. 60 mL). After 1.5 h at +5 °C, the yellow crystals were separated from the almost colorless mother liquor, washed with hexanes, and dried under vacuum. The yield of >95% pure (^{31}P NMR) [(dppe)-Pd(Ph)I] was 0.49 g (99%).

[(dppp)Pd(Ph)I]. A mixture of [(tmeda)Pd(Ph)I] (0.30 g; 0.70 mmol), dppp (0.33 g; 0.80 mmol), and toluene (5 mL) was stirred under N_2 at room temperature for 4 h. The originally formed amorphous-looking precipitate first turned oily, and then a crystalline solid formed. Ether (12 mL) was added, and the mixture was stirred overnight. The yellow solid was separated from the purple mother liquor, washed with ether, and recrystallized from 1,2-dichloroethane−ether to produce orange crystalline [(dppp)Pd(Ph)I] in 0.41 g (81%) yield.

[(tmeda)Pd(Ph)CF_3]. In a glovebox, a 25-mL round-bottom flask with a magnetic stir-bar was charged with [(tmeda)Pd(Ph)I] (0.62 g; 1.45 mmol), freshly dried, finely ground CsF (0.66 g; 4.34 mmol), and THF (10 mL). The flask was capped with a rubber septum and brought out. At stirring, CF_3SiMe_3 (0.40 mL; 2.71 mmol) was syringed in, and the mixture was vigorously stirred at room temperature until decolorization (2 h) and then for an additional 0.5 h. The product was isolated in air. The solution was evaporated and the residue extracted with CH_2Cl_2 (10 mL, then 3 × 3 mL). The combined extracts were filtered through Celite, evaporated to ca. 1 mL, and treated with ether (40 mL). After standing at +5 °C overnight, the white crystals were collected, washed with ether, and dried under vacuum. The yield was 0.47 g. Evaporation of the combined mother liquor and the washings produced a residue which gave additional 0.02 g of the pure product upon washing with ether and drying. Total yield: 0.49 g (91%). Anal. Calcd for $C_{13}H_{21}F_3N_2Pd$, %: C, 42.3; H, 5.7; N, 7.6. Found, %: C, 42.1; H, 5.6; N, 7.4. ^1H NMR (CD_2Cl_2, 20 °C), δ: 2.2 (s, 6H, CH_3), 2.6 (br, 4H, CH_2), 2.7 (s, 6H, CH_3), 6.9 (m, 1H, p-Ph), 7.0 (m, 2H, m-Ph), 7.5 (m, 2H, o-Ph). ^{19}F NMR (CD_2Cl_2, 20 °C), δ: −21.2 (s).

[(tmeda)Pd(Tol)CF_3]. In a glovebox, a 50-mL flask with a magnetic stir-bar was charged with [(tmeda)Pd(Tol)I] (1.00 g; 2.34 mmol), freshly dried, finely ground CsF (0.95 g; 6.25 mmol), and THF (20 mL). The flask was capped with a rubber septum and brought out. At stirring, CF_3SiMe_3 (0.70 mL; 4.74 mmol) was syringed in, and the mixture was vigorously stirred at room temperature for 1.5 h, until the original orange color was gone. The product was isolated in air. The solution was evaporated and the residue extracted with CH_2Cl_2 (20 mL, then 3 × 5 mL). The combined extracts were filtered through Celite, evaporated to ca. 2 mL, and treated with ether (30 mL). After standing at +5 °C for 6 h, the white crystals were collected, washed with ether, and dried under vacuum. The yield was 0.785 g (90%). Anal. Calcd for $C_{14}H_{23}F_3N_2Pd$, %: C, 43.9; H, 6.1; N, 7.3. Found, %: C, 43.6; H, 5.9; N, 7.0. ^1H NMR (CD_2Cl_2, 20 °C), δ: 2.2 (s, 6H, NCH_3), 2.3 (s, 3H, CCH_3), 2.6 (m, 4H, CH_2), 2.7 (s, 6H, NCH_3), 6.8 (d, 2H, J = 7.9 Hz, C_6H_4), 7.3 (d, 2H, J = 7.9 Hz, C_6H_4). ^{19}F NMR (CD_2Cl_2, 20 °C), δ: −21.2 (s).

[(dppe)Pd(Ph)CF_3]. (a) In a glovebox, a 25-mL round-bottom flask with a magnetic stir-bar was charged with [(dppe)Pd(Ph)I] (0.30 g; 0.42 mmol), freshly dried, finely ground CsF (0.20 g; 1.32 mmol), and THF (8 mL). The flask was capped with a rubber septum and brought out. At stirring, CF_3SiMe_3 (0.12 mL; 0.81 mmol) was syringed in, and the mixture was vigorously stirred at room temperature until the yellow color was gone (1 h). Stirring the milky-white suspension for an additional 10 min resulted in the appearance of a light tan color. The reaction mixture was worked up in air. After all volatiles were removed under vacuum, the solid residue was extracted with CH_2Cl_2 (first 5 mL, then 3 × 2 mL). The combined extracts were filtered through Celite, evaporated to ca. 1 mL, and treated with 10 mL of MeOH (portion-wise). After 24 h at +5 °C, the solid was separated, washed with MeOH, and recrystallized by dissolving in boiling benzene (ca. 3 mL), cooling to room temperature, and adding ether (3 mL). After 12 h, the white crystals were separated, washed with ether, and dried under vacuum. The yield of [(dppe)Pd(Ph)CF_3]·0.5C_6H_6 was 0.20 g (69%). Anal. Calcd for $C_{33}H_{29}F_3P_2Pd$, %: C, 62.7; H, 4.7. Found, %: C, 62.5; H, 4.7. ^1H NMR (CD_2Cl_2, 20 °C), δ: 2.3 (m, 4H, CH_2), 6.8−7.8

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(48) Portnoy, M.; Ben-David, Y.; Rousso, I.; Milstein, D. *Organometallics* **1994**, *13*, 3465.

(multiplets, 25H, Ph). ^{19}F NMR (toluene, 20 °C), δ: −18.0 (dd, *cis*-J_{F-P} = 19.5 Hz, *trans*-J_{F-P} = 52.8 Hz). ^{31}P NMR (toluene, 20 °C), δ: 40.1 (dq, 1P, *cis*-J_{P-P} = 15.8 Hz, *trans*-J_{F-P} = 52.8 Hz, P trans to CF_3); 41.8 (dq, 1P, *cis*-J_{P-P} = 15.8 Hz, *cis*-J_{F-P} = 19.5 Hz, P cis to CF_3).

(b) A mixture of [(tmeda)Pd(Ph)CF_3] (0.10 g; 0.27 mmol), dppe (0.115 g; 0.29 mmol), CH_2Cl_2 (3 mL), and $KHSO_4$ (0.20 g) was vigorously stirred under N_2 for 3 days. Isolation of the product was performed in air. ^{19}F NMR analysis of the reaction mixture indicated >99% conversion. The reaction mixture was filtered through cotton wool, evaporated to ca. 1 mL, and treated with MeOH (5 mL). After standing at +5 °C overnight, the white crystals of [(dppe)Pd(Ph)CF_3] were separated, washed with MeOH and ether, dried, and then recrystallized from benzene−ether. The yield was 0.155 g (85%).

[(dppe)Pd(Ph-d_5)CF_3]. This complex was prepared from [(tmeda)-Pd(Ph-d_5)CF_3] and dppe, as described above.

[(dppp)Pd(Ph)CF_3]. In a glovebox, a 15-mL round-bottom flask with a magnetic stir-bar was charged with [(tmeda)Pd(Ph)I] (0.17 g; 0.40 mmol), dppp (0.17 g; 0.41 mmol), freshly dried, finely ground CsF (0.18 g; 1.18 mmol), and THF (6 mL). The flask was capped with a rubber septum and brought out; the mixture was stirred for 1−2 min until all solids, except CsF had dissolved. At stirring, CF_3SiMe_3 (0.10 mL; 0.68 mmol) was syringed in, and the mixture was vigorously stirred at room temperature for 1.5 h. More CF_3SiMe_3 (0.10 mL; 0.68 mmol) was added, and stirring continued for another 1 h and 20 min until the orange-yellow color was gone and a light tan color of the liquid phase developed. The reaction mixture was worked up in air. After all volatiles were removed under vacuum, the oily residue was extracted with CH_2Cl_2 (3 × 3 mL). The combined extracts were filtered through cotton wool and evaporated to give an oil. After drying under vacuum and stirring with 2 mL of ether for a minute, the oil solidified. After evaporation of the ether, the residue was dried under vacuum and dissolved in 3 mL of warm benzene. The benzene solution was filtered warm through Celite, evaporated to ca. 1 mL, and treated with 10 mL of ether. Briefly scratching the inner glass wall under the cloudy solution with a spatula prompted crystallization. After 1 h, the slightly yellow crystals were separated, washed with ether, and dried. The complex was recrystallized once again by adding ether (15 mL) to its solution in ca. 1 mL of benzene. The yield of [(dppp)Pd(Ph)CF_3]·0.5Et_2O as pale-yellow crystals was 0.20 g (71%). Anal. Calcd for $C_{36}H_{36}F_3O_{0.5}P_2$-Pd, %: C, 61.6; H, 5.2. Found, %: C, 61.3; H, 5.3. ^{1}H NMR (CD_2Cl_2, 20 °C), δ: 1.2 (t, 3H, CH_3 of Et_2O), 1.8 (m, 2H, CH_2), 2.45 (m, 4H, CH_2), 3.5 (q, 2H, CH_2 of Et_2O), 6.6−7.8 (multiplets, 25H, Ph). ^{19}F NMR (toluene, 20 °C), δ: −19.3 (dd, *cis*-J_{F-P} = 17.8 Hz, *trans*-J_{F-P} = 49.9 Hz). ^{31}P NMR (toluene, 20 °C), δ: 1.1 (dq, 1P, *cis*-J_{P-P} = 37.5 Hz, *trans*-J_{F-P} = 49.9 Hz, P trans to CF_3); 9.1 (dq, 1P, *cis*-J_{P-P} = 37.5 Hz, *cis*-J_{F-P} = 17.8 Hz, P cis to CF_3).

[(dppe)Pd(Tol)CF_3]. A mixture of [(tmeda)Pd(Tol)CF_3] (0.15 g; 0.39 mmol), dppe (0.20 g; 0.50 mmol), CH_2Cl_2 (5 mL), and $KHSO_4$ (0.5 g) was vigorously stirred under N_2 for 5 h. ^{19}F NMR analysis of the reaction mixture indicated >99% conversion. Isolation of the product was performed in air. The reaction mixture was filtered through cotton wool, evaporated to ca. 2 mL, and treated with MeOH (first 1 mL, after 30 min 5 more mL). The white crystals were separated, thoroughly washed with MeOH and ether, and dried under vacuum. After recrystallization from CH_2Cl_2−ether and drying under vacuum, the yield of [(dppe)Pd(Tol)CF_3] was 0.25 g (96%). Anal. Calcd for $C_{34}H_{31}F_3P_2$-Pd, %: C, 61.4; H, 4.7. Found, %: C, 60.0; H, 4.8. ^{1}H NMR (CD_2Cl_2, 20 °C), δ: 2.2 (s, 3H, CH_3), 2.3 (m, 4H, CH_2), 6.7 (dd, J_{H-H} = 7.6 Hz, J_{H-P} = 1.5 Hz, 2H, arom Tol), 7.05 (t-looking dd, J_{H-H} = 7.6 Hz, J_{H-P} = ca. 7.6 Hz, 2H, arom Tol), 7.3−7.9 (multiplets, 20H, Ph). ^{19}F NMR (CD_2Cl_2, 20 °C), δ: −18.0 (dd, *cis*-J_{F-P} = 18.9 Hz, *trans*-J_{F-P} = 51.1 Hz). ^{31}P NMR (CD_2Cl_2, 20 °C), δ: 40.0 (dq, J_{P-P} = 15.8 Hz, J_{F-P} = 18.9 Hz, 1P, P cis to CF_3), 41.4 (dq, J_{P-P} = 15.8 Hz, J_{F-P} = 51.1 Hz, 1P, P trans to CF_3). ^{1}H NMR (toluene-d_8, 20 °C), δ: 1.85 (m, 4H, CH_2), 2.2 (s, 3H, CH_3), 6.8 (dd, J_{H-H} = 7.8 Hz, J_{H-P} = 1.5 Hz, 2H, arom. Tol), 6.9−7.3 (multiplets, 16H, Ph), 7.5 (t-looking dd, J_{H-H} = 7.8 Hz, J_{H-P} = ca. 7.8 Hz, 2H, arom Tol), 7.8 (m, 4H, Ph). ^{19}F NMR (toluene-d_8, 20 °C), δ: −16.2 (dd, *cis*-J_{F-P} = 19.5 Hz, *trans*-J_{F-P} = 52.3 Hz). ^{31}P NMR (toluene-d_8, 20 °C), δ: 38.6 (dq, J_{P-P} = 15.8 Hz, J_{F-P} = 19.5 Hz, 1P, P cis to CF_3), 40.3 (dq, J_{P-P} = 15.8 Hz, J_{F-P} = 52.3 Hz, 1P, P trans to CF_3).

[(dppp)Pd(Tol)CF_3]. A mixture of [(tmeda)Pd(Tol)CF_3] (0.21 g; 0.55 mmol), dppp (0.30 g; 0.73 mmol), CH_2Cl_2 (8 mL), and $KHSO_4$ (0.7 g) was vigorously stirred under N_2 for 18 h. ^{19}F NMR analysis of the reaction mixture indicated 99% conversion. Isolation of the product was performed in air. The reaction mixture was filtered through cotton wool, evaporated to ca. 2 mL, and treated with MeOH (5 mL). A few oily droplets formed, which quickly crystallized on gentle swirling. After 20 min, more MeOH (20 mL) was added. After 1 h at room temperature and then 3 h at +5 °C the white crystals were separated, thoroughly washed with MeOH and ether, and dried under vacuum. The yield of [(dppe)Pd(Tol)CF_3] was 0.325 g (87%). Anal. Calcd for $C_{35}H_{33}F_3P_2Pd$, %: C, 61.9; H, 4.9. Found, %: C, 61.4; H, 5.0. ^{1}H NMR (CD_2Cl_2, 20 °C), δ: 1.8 (m, 2H, central CH_2), 2.1 (s, 3H, CH_3), 2.45 (m, 4H, side CH_2), 6.45 (d, J_{H-H} = 7.3 Hz, 2H, arom Tol), 6.9 (t-looking dd, J_{H-H} = 7.3 Hz, J_{H-P} = ca. 7.3 Hz, 2H, arom Tol), 7.1−7.8 (multiplets, 20H, Ph). ^{19}F NMR (CD_2Cl_2, 20 °C), δ: −19.3 (dd, *cis*-J_{F-P} = 17.2 Hz, *trans*-J_{F-P} = 48.2 Hz). ^{31}P NMR (CD_2Cl_2, 20 °C), δ: 1.1 (dq, J_{P-P} = 41.5 Hz, J_{F-P} = 17.2 Hz, 1P, P cis to CF_3), 8.8 (dq, J_{P-P} = 41.5 Hz, J_{F-P} = 48.2 Hz, 1P, P trans to CF_3). ^{1}H NMR (toluene-d_8, 20 °C), δ: 1.3 (m, 2H, central CH_2), 1.9 (m, 4H, side CH_2), 2.1 (s, 3H, CH_3), 6.6 (dd, J_{H-H} = 7.9 Hz, 2H, arom Tol), 6.8−7.2 (multiplets, 16H, Ph), 7.75 (t-looking dd, J_{H-H} = 7.9 Hz, J_{H-P} = ca. 7.9 Hz, 2H, arom Tol), 7.75 (m, 4H, Ph). ^{19}F NMR (toluene-d_8, 20 °C), δ: −17.5 (dd, *cis*-J_{F-P} = 18.0 Hz, *trans*-J_{F-P} = 50.0 Hz). ^{31}P NMR (toluene-d_8, 20 °C), δ: 0.8 (dq, J_{P-P} = 39.5 Hz, J_{F-P} = 18.0 Hz, 1P, P cis to CF_3), 8.7 (dq, J_{P-P} = 39.5 Hz, J_{F-P} = 50.0 Hz, 1P, P trans to CF_3).

Reaction of [(dppe)Pd(Ph)CF_3] with PhI. A mixture of [(dppe)-Pd(Ph)CF_3] (90 mg), PhI (0.2 mL), and N_2-saturated (*but not anhydrous*) toluene (3 mL) was sealed under nitrogen and heated at 115 °C (oil bath). The starting complex had quickly dissolved, and yellow crystals were noticed after 2.5 h. The heating was continued for additional 2.5 h, after which the mixture was allowed to cool to room temperature and then kept at +5 °C overnight. The yellow crystals were separated, washed with ether, and dried under vacuum. The yield of [(dppe)Pd-(I)CF_3] was 80 mg (82%). ^{1}H NMR (CD_2Cl_2, 20 °C), δ: 2.3 (m, 4H, CH_2), 7.5−8.0 (multiplets, 20H, Ph). ^{19}F NMR (CD_2Cl_2, 20 °C), δ: −11.9 (dd, *cis*-J_{F-P} = 26.4 Hz, *trans*-J_{F-P} = 64.2 Hz). ^{31}P NMR (CD_2-Cl_2, 20 °C), δ: 46.2 (dq, 1P, *trans*-J_{F-P} = 64.2 Hz, J_{P-P} = 21.7 Hz, P trans to CF_3); 56.2 (br m, 1P, P cis to CF_3). The mother liquor was filtered through silica gel and analyzed by GC−MS. The analysis indicated the formation of biphenyl and no bibenzyl.

Reaction of [(dppe)Pd(Ph)CF_3] with PhCl. A 5-mm NMR tube was charged with [(dppe)Pd(Ph)CF_3] (20 mg) and N_2-saturated (*but not anhydrous*) PhCl (0.6 mL), sealed under N_2, and heated at 140 °C (oil bath) for 2 h to produce [(dppe)Pd(Cl)CF_3] in ca. 90% yield at 100% conversion. The reaction mixture remained colorless and solid-free during the reaction. Layering the solution with hexanes resulted in crystal formation, some of which were of X-ray quality. ^{19}F NMR (CD_2Cl_2, 20 °C), δ: −19.8 (dd, *cis*-J_{F-P} = 27.0 Hz, *trans*-J_{F-P} = 67.1 Hz). ^{31}P NMR (CD_2Cl_2, 20 °C), δ: 42.3 (dq, 1P, *trans*-J_{F-P} = 67.1 Hz, J_{P-P} = 27.7 Hz, P trans to CF_3); 58.5 (m, 1P, P cis to CF_3). The mother liquor was filtered through silica gel and analyzed by GC−MS to indicate the formation of biphenyl.

Reaction of [(dppe)Pd(Tol)CF_3] with C_6D_5I in toluene. In a glovebox, two 5-mm NMR tubes were charged with [(dppe)Pd(Tol)-CF_3] (13 mg), C_6D_5I (5 μL), and anhydrous toluene-d_8 (0.8 mL), and sealed with rubber septa. Both tubes were brought out. Degassed H_2O (0.2 μL) was microsyringed in one of the tubes, and both samples were placed in an oil bath at 115 °C. The H_2O-free sample remained colorless, and no reaction was observed (NMR) after 6 h. The H_2O containing

Table 3. Selected Crystallographic Data for **1**, **4**, **6**, and **9**−**12**

	1	**4**	**6**	**9**
empirical formula	$C_{36}H_{36}F_3P_2Pd$	$C_{34}H_{31}F_3P_2Pd$	$C_{13}H_{21}F_3N_2Pd$	$C_{12}H_{24}F_6N_2Pd$
FW	693.99	664.93	368.72	416.73
cryst color, form	colorless, irreg. block	colorless, irreg. block	colorless, irreg. block	colorless, prism
cryst system	monoclinic	monoclinic	monoclinic	monoclinic
space group	P2(1)/n	P2(1)/c	P2(1)/n	Cc
a (Å)	12.214(5)	11.265(4)	8.361(3)	15.702(5)
b (Å)	15.812(7)	22.727(9)	16.466(6)	8.550(3)
c (Å)	16.782(7)	13.333(5)	11.389(4)	11.809(3)
α (deg)	90	90	90	90
β (deg)	98.318(6)	111.946(7)	110.163(5)	94.882(5)
γ (deg)	90	90	90	90
V (Å^3)	3207(2)	3166(2)	1471.8(9)	1579.6(8)
Z	4	4	4	4
density (g/cm^3)	1.437	1.395	1.664	1.752
abs. *μ*(mm^{-1})	0.72	0.726	1.282	1.231
F(000)	1420	1352	744	840
cryst size (mm)	0.34 × 0.22 × 0.22	0.38 × 0.32 × 0.32	0.28 × 0.28 × 0.19	0.18 × 0.18 × 0.16
temp (°C)	-100	-100	-100	-100
scan mode	*ω*	*ω*	*ω*	*ω*
detector	Bruker-CCD	Bruker-CCD	Bruker-CCD	Bruker-CCD
θ_{max} (deg)	28.3	28.29	29.22	28.31
no. obsrvd reflns	27962	31729	27438	13683
no. unique reflns	7956	7843	3973	1952
R_{merge}	0.0322	0.0323	0.0278	0.0299
no. params	352	361	176	98
R indices [$I > 2\sigma(I)$][a]	wR2=0.059, R1=0.025	wR2=0.073, R1=0.027	wR2=0.047, R1=0.018	wR2=0.035, R1=0.014
R indices (all data)[a]	wR2=0.061, R1=0.029	wR2=0.076, R1=0.031	wR2=0.047, R1=0.019	wR2=0.036, R1=0.014
S[b]	1.075	1.06	1.068	1.066
max diff peak, hole (e/Å^3)	0.40,−0.36	0.61,−0.48	0.72,−0.52	0.31,−0.40

	10	**11**	**12**
empirical formula	$C_{17}H_{34}F_6P_2Pd$	$C_{27}H_{24}F_3IP_2$ Pd	$C_{30}H_{29}Cl_{1.5}F_3P_2Pd$
FW	520.78	700.7	668.05
cryst.color, form	colorless, rod	gold, prism	colorless, irreg. block
cryst system	monoclinic	orthorhombic	monoclinic
space group	P2(1)	P2(1)2(1)2(1)	P2(1)/n
a (Å)	8.0634(6)	8.625(4)	9.215(2)
b (Å)	14.7398(12)	13.616(6)	26.278(7)
c (Å)	19.8663(14)	22.834(10)	12.097(3)
α (deg)	90	90	90
β (deg)	110.509(3)	90	101.897(4)
γ (deg)	90	90	90
V (Å^3)	2211.5(3)	2682(2)	2866.3(13)
Z	4	4	4
density (g/cm^3)	1.564	1.736	1.548
abs. *μ*(mm^{-1})	1.032	1.997	0.937
F(000)	1064	1368	1350
cryst size(mm)	0.48 × 0.18 × 0.15	0.37 × 0.13 × 0.10	0.26 × 0.18 × 0.13
temp (°C)	−100	−100	−100
scan mode	*ω*	*ω*	*ω*
detector	Bruker-CCD	Bruker-CCD	Bruker-CCD
θ_{max} (deg)	28.49	28.32	28.33
no. obsrvd reflns	17164	47171	26290
no. unique reflns	5576	6646	7102
R_{merge}	0.0316	0.0557	0.0401
no. params	243	314	361
R indices [$I > 2\sigma(I)$][a]	wR2=0.105, R1=0.043	wR2=0.081, R1=0.028	wR2=0.087, R1=0.035
R indices (all data)[a]	wR2=0.113, R1=0.056	wR2=0.082, R1=0.030	wR2=0.094, R1=0.047
S[b]	1.037	1.091	1.035
max diff peak, hole (e/Å^3)	1.50,−1.20	1.02,−0.57	0.77,−0.44

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = \{\sum [w(F_o^2 - F_c^2)^2]/\sum [w(F_o^2)^2]\}^{1/2}$ (sometimes denoted as R_w2). [b] GooF $= S = \{\sum [w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where *n* is the number of reflections, and *p* is the total number of refined parameters.

sample turned yellow after 3 h. After 5 and 8 h since the beginning of the reaction, ^{19}F NMR analysis indicated 50% and ca. 100% conversion, respectively. The ^{19}F NMR spectra recorded during the reaction indicated partial Ar/Ar scrambling in both the starting material and the product. After cooling the sample to room temperature, the pale-yellow liquid phase was separated and filtered through a short silica plug; the colorless filtrate was analyzed by GC−MS to indicate the formation of Tol−C_6D_5 (ca. 60%), Ph−C_6D_5 (ca. 20%), and smaller quantities of $(C_6D_5)_2$, *p*-Tol−Ph, Ph_2 and *p*-Tol_2.

[(teeda)PdCl$_2$]. In air, $PdCl_2$ (1.0 g) was dissolved in 100 mL of boiling MeCN. To the hot solution, teeda (3 mL) was added at stirring. Yellow crystals of the product began to precipitate. After cooling to room temperature and keeping the mixture at +5 °C overnight, the yellow crystalline product was separated by filtration, washed with ether (4 × 30 mL), and dried under vacuum. The yield was 1.85 g (94%).

[(teeda)Pd(CF$_3$)$_2$]. In a glovebox, a 10-mL round-bottom flask with a magnetic stir-bar was charged with [(teeda)$PdCl_2$] (0.10 g; 0.29 mmol), freshly dried, finely ground CsF (0.46 g; 3.03 mmol), and CH_2-

Cl_2 (5 mL). The flask was capped with a rubber septum and brought out. At stirring, CF_3SiMe_3 (0.25 mL; 1.70 mmol) was syringed in, and the mixture was vigorously stirred at room temperature for 68 h, at which point the starting yellow complex had disappeared. The product was isolated in air. The solution was filtered through Celite, evaporated to ca. 2 mL, treated with ether (10 mL), and kept at +5 °C for 2 h. The precipitate was recrystallized by adding 12 mL of ether to its warm solution in ca. 2 mL of boiling CH_2Cl_2 and then keeping the mixture at +5 °C for 2 h. The yield was 0.07 g (59%). Anal. Calcd for $C_{12}H_{24}F_6N_2Pd$, %: C, 34.6; H, 5.8; N, 6.7. Found, %: C, 34.7; H, 5.6; N, 6.7. ^{1}H NMR (CD_2Cl_2, 20 °C), δ: 1.4 (t, 12H, J = 7 Hz, CH_3), 2.7 (s, 4H, CH_2), 2.85 (m, 4H, CH_2), 3.15 (m, 4H, CH_2). ^{19}F NMR (CD_2Cl_2, 20 °C), δ: −26.5 (s).

[(dippp)Pd(CF_3)$_2$]. In a glovebox, a 30-mL round-bottom flask with a magnetic stir-bar was charged with [(dippp)$PdCl_2$] (0.30 g; 0.66 mmol), freshly dried, finely ground CsF (1.10 g; 7.24 mmol), and CH_2Cl_2 (10 mL). The flask was capped with a rubber septum and brought out. At stirring, CF_3SiMe_3 (0.75 mL; 5.08 mmol) was syringed in, and the mixture was vigorously stirred at room temperature for 40 h. ^{19}F NMR analysis of the brown liquid phase indicated 100% conversion to [(dippp)Pd(CF_3)$_2$]. The mixture was evaporated, and the residue was extracted with benzene (4 × 5 mL). The combined extracts were filtered through Celite, evaporated to ca. 2 mL, and treated with hexanes (20 mL). The product (0.32 g; 94% yield) was recrystallized from CH_2Cl_2−hexanes three times without losses and appeared pure by NMR, although was tannish in color. To obtain the complex as a white solid it was recrystallized by adding ether (7 mL) to its solution in a minimal volume of CH_2Cl_2 and keeping the mixture at +5 °C overnight. The white crystals were separated cold, washed with cold ether, and dried under vacuum. The yield was 0.29 g (85%). Anal. Calcd for $C_{17}H_{34}F_6P_2Pd$, %: C, 39.2; H, 6.6. Found, %: C, 39.1; H, 6.3. ^{1}H NMR (CD_2Cl_2, 20 °C), δ: 1.2 (dd, 12H, J = 7.1 and 11.6 Hz, CH_3), 1.35 (dd, 12H, J = 7.4 and 18.6 Hz, CH_3), 1.6 (m, 4H, CH_2), 1.9 (m, 2H, CH_2), 2.4 (m, 4H, CH). ^{19}F NMR (CD_2Cl_2, 20 °C), δ: −20.5 (m). ^{31}P NMR (CD_2Cl_2, 20 °C), δ: 23.3 (m).

Water-Induced Decomposition of 1. A high-pressure NMR sapphire tube was charged with **1** (40 mg), toluene (0.4 mL), and water (5 μL), sealed, and heated at 115 °C. After ca. 1 h the solution turned light tan, and several hours later precipitation of palladium metal and reddish-brown viscous oil was observed. After 24 h, full conversion of **1** was detected. The ^{19}F NMR spectrum displayed several resonances from the decomposition products. Two of them were identified as PhC(F)O (+16 ppm, s) and CF_3H (−79.8 ppm, d, J_{F-H} = 80 Hz). A few resonances of very low intensity were found in the ^{31}P NMR spectrum of the sample, indicating that almost all P-containing species were located in the red-brown oily precipitate, rather than in the toluene phase. The tube was then unsealed under N_2 in a glovebox, and the toluene solution was decanted off the brown oil. GC−MS analysis of the toluene fraction confirmed the formation of PhC(F)O and revealed the presence of benzene, biphenyl, benzophenone, and benzoic anhydride, among other products. The toluene-insoluble red-brown oil was dissolved in MeCN and analyzed by ^{31}P NMR. A number of broad resonances were observed, along with two sharp lines from [(dppe)$_2$Pd]$^{2+}$ (58.0 ppm) and $dppeO_2$ (30.8 ppm). To release all coordinated P-ligands, the solution was treated with $[Bu_4N]^+$ CN^- (65 mg). After this treatment, ^{31}P NMR analysis of the sample indicated the presence of free dppe (s, −12.8 ppm), dppeO (d, −12.0; d, 29.5 ppm; J_{P-P} = 48.3 Hz),[29] and $dppeO_2$ (s, 30.8 ppm) in a 6:3:2 molar ratio.

X-ray Crystallographic studies. A summary of crystallographic data for new complexes **1**, **4**, **6**, and **9**−**12** is presented in Table 3. The CIF files for these complexes and also for [(dppe)Pd(Cl)CH_3][18] and [(dcpe)Pd(Cl)CH_3][18] are presented in the Supporting Information.

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Supporting Information Available: Full details of the crystallographic data (CIF) for new complexes **1**, **4**, **6**, **9**−**12** and for previously analyzed[18] [(dppe)Pd(Cl)CH_3] and [(dcpe)-Pd(Cl)CH_3]. This material is available free of charge via the Internet at http://pubs.acs.org.

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