Synthesis and Characterization of Organopalladium Complexes Containing a Fluoro Ligand

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The synthesis of organopalladium complexes containing a fluoro ligand, $[(Ph_3P)_2Pd(F)R]$, is described. Two general synthetic strategies have been developed: (i) neutralization of hydroxo palladium dimers, $[(Ph_3P)_2Pd_2(R)_2(\mu\text{-}OH)_2]$ (R = Me or Ph), with TREAT HF ($[(HF)_3{\cdot}NEt_3]$) in the presence of PPh_3 and (ii) the ultrasound-promoted exchange between $[(Ph_3P)_2Pd(I)R]$ and AgF in benzene. It is essential for the synthesis with TREAT HF that no excess of the HF source is used; otherwise, the corresponding bifluorides, $[(Ph_3P)_2Pd(FHF)R]$, are formed instead. Conducting the I/F exchange in the presence of 5−10% of the corresponding organic iodide, RI, is beneficial for purity of the desired fluoro complexes. All complexes **1**−**10** have been fully characterized by a variety of methods. The fluoro ligand in $[(Ph_3P)_2Pd(F)R]$ is inert in anhydrous media of low polarity. However, in the presence of trace amounts of water, F ligand exchange is observed. No irreversible hydrolysis of the Pd−F bond takes place as $[(Ph_3P)_2Pd(F)R]$ remains the only observable (NMR) species in the system. VT NMR studies of various $[(Ph_3P)_2Pd(F)R]$ in CH_2Cl_2 saturated with water have been conducted, revealing a push/pull-type, "ambiphilic" mechanism of the H_2O-promoted F ligand-exchange process. The Pd−F bond cleavage likely involves nucleophilic attack of water on the metal center, concomitantly occurring with the formation of a hydrogen bond between the fluoro ligand and H_2O.

Introduction

Late transition metal complexes containing a fluoro ligand are of considerable interest in modern research due to their relevance to contemporary concepts of bonding in coordination chemistry, C−F bond activation and formation, and catalysis.[1−4] The latter makes fluoro complexes of the platinum group metals especially attractive. However, surprisingly little is known about fluoro palladium compounds, despite the fact that palladium is one of the most important catalytic metals whose complexes are capable of promoting a wide variety of reactions,[5] including important industrial processes.[6] Although some inorganic solid-state palladium fluorides have been synthesized,[7] no reports have appeared in the literature describing the isolation and reliable characterization of molecular palladium fluorides. Two compounds have been formulated as $[(Ph_3P)_4Pd_2(\mu\text{-}F)_2]F_2$[8] and $[(Ph_3P)_2Pd(H)F]$[9] only on the basis of elemental analysis data, with no evidence for the presence of a Pd−F bond. A cationic Pd(II) fluoro complex $[(Et_3P)_3PdF]^+$ has been characterized by ^{19}F NMR in solution but never isolated.[10] In light of the recent studies by Mason and Verkade,[11] one might expect the cation, $[(Et_3P)_3PdF]^+$, to be very unstable, readily decomposing to a mixture of Pd(0) and P(V) compounds.

Organometallic complexes of palladium containing a fluoro ligand are of special interest due to their potential role in organofluorine chemistry. In this paper, we report the synthesis and characterization of a series of novel organopalladium fluoro complexes of the type $[(Ph_3P)_2Pd(R)F]$, where R = Ar or Me. Part of this work has been recently published as a preliminary communication.[12] Two synthetic techniques will be described: (i) neutralization of organopalladium hydroxides with TREAT HF, a 3:1 complex of HF with

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Table 1. Isolated Yields and Analytical Data for the Complexes $[(Ph_3P)_2Pd(R)(X)]$ (X = F or HF_2), 1−10

					analysis, calcd (found)	
complex	R	X	fluorinating agent	yield, %	% C	% H
1	C_6H_5	F	TREAT HF or AgF	90−98	69.4 (69.5)	4.9 (4.9)
2	CH_3	F	TREAT HF or AgF	60−85	66.8 (67.1)	5.0 (5.1)
3	C_6H_5	HF_2	TREAT HF	95−99	67.5 (67.6)	4.9 (4.9)
4	CH_3	HF_2	TREAT HF	85−90	64.9 (64.7)	5.0 (4.9)
5	4-$CH_3C_6H_4$	F	AgF	71−92	69.7 (69.5)	5.0 (5.1)
6	4-$CH_3OC_6H_4$	F	AgF	80−96	68.2 (68.0)	4.9 (5.1)
7	1-$C_{10}H_7$	F	AgF	92−98	71.1 (71.0)	4.8 (4.9)
8	4-ClC_6H_4	F	AgF	71−87	66.2 (66.1)	4.5 (4.7)
9[a]	4-$CF_3C_6H_4$	F	AgF	80−86	62.4 (62.4)	4.2 (4.5)
10	4-$O_2NC_6H_4$	F	AgF	86−90	65.3 (65.1)	4.4 (4.6)

[a] Complex **9** was isolated as a 2:1 dichloromethane adduct, $[(Ph_3P)_2Pd(4\text{-}CF_3C_6H_4)(F)]\cdot{}^1/_2CH_2Cl_2$.

triethylamine, and (ii) ultrasound-promoted I/F exchange between iodo organopalladium complexes and silver(I) fluoride. Both methods seem to be general and, therefore, might be applicable to the preparation of otherwise unobtainable fluoro complexes of other transition metals.

Results and Discussion

Neutralization of Palladium Hydroxo Complexes with TREAT HF. In a number of cases, HF has been used for the preparation of fluoro complexes of Fe, Mo, Tc, Ru, W, Re, Ir, and Pt.[1] An efficient substitute for anhydrous hydrogen fluoride, "TREAT HF" ($Et_3N\cdot 3HF$), is a new, versatile fluorinating agent which has already been widely used in organic synthesis[13a] but only recently applied in organometallic chemistry.[12,13b] We found that the reaction between TREAT HF, a hydroxo palladium dimer, $[(Ph_3P)_2Pd_2(R)_2(\mu\text{-}OH)_2]$, where R = Ph[14a] or Me,[14b] and PPh_3 in a 2:3:6 molar ratio furnished the corresponding fluorides, *trans*-$[(Ph_3P)_2Pd(R)(F)]$ (R = Ph, **1**, and Me, **2**), in high yield (eq 1). Each molecule of $Et_3N\cdot 3HF$ "neutralizes"

$$3[(Ph_3P)_2Pd_2(R)_2(\mu\text{-}OH)_2] + 2[Et_3N(HF)_3] + 6PPh_3 \xrightarrow{\text{benzene}} 6[(Ph_3P)_2Pd(R)(F)] + 2Et_3N + 6H_2O \quad \begin{matrix}\mathbf{1},\ R = Ph\\ \mathbf{2},\ R = Me\end{matrix} \qquad (1)$$

three hydroxo ligands on the metal. Any excess of TREAT HF must be avoided for the synthesis of **1** and **2** because, like their platinum counterparts[15a,b] and some other transition metal fluorides,[13b,15c,d] the desired fluorides are prone to forming stable adducts with HF, *trans*-$[(Ph_3P)_2Pd(R)(HF_2)]$ (R = Ph, **3**, and Me, **4**; eq 2).

$$[(Ph_3P)_2Pd_2(R)_2(\mu\text{-}OH)_2] + 2PPh_3 \xrightarrow[-2H_2O]{\text{TREAT HF (excess)}} 2[(Ph_3P)_2Pd(R)(FHF)] \quad \begin{matrix}\mathbf{3},\ R = Ph\\ \mathbf{4},\ R = Me\end{matrix} \qquad (2)$$

Reactions 1 and 2 as well as the subsequent isolation of the products were conducted in air, affording complexes **1**−**4** as white or pale cream-yellow, well-shaped crystals. The "neutralization" method is simple and efficient. Its major limitation, however, stems from the fact that hydroxo palladium dimers of the type $[(Ph_3P)_2Pd_2(Ar)_2(\mu\text{-}OH)_2]$ are difficult to synthesize when Ar = σ-aryls other than phenyl. For instance, pure $[(Ph_3P)_2Pd_2(4\text{-}CH_3C_6H_4)_2(\mu\text{-}OH)_2]$ cannot be obtained by the procedure developed for $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}OH)_2]$,[14a] most likely due to the σ-aryl/phosphine aryl exchange[16] occurring in the course of the reaction between $[(Ph_3P)_2PdCl_2]$, *p*-iodotoluene, and alkali. On the other hand, it is thought that our neutralization method employing TREAT HF could be successfully used for the preparation of fluoro complexes of other transition metals from various readily accessible[17−19] hydroxo derivatives.

Ultrasound-Promoted Exchange between AgF and Organopalladium Iodides. The other synthetic method for the preparation of organopalladium fluorides is based upon the ultrasound-promoted halide exchange between readily available organopalladium iodides, $[(Ph_3P)_2Pd(Ar)(I)]$,[20] and silver fluoride in benzene (eq 3). All fluoro palladium complexes obtained by both

$$[(Ph_3P)_2Pd(Ar)I] + AgF \xrightarrow[\text{benzene}]{\text{ultrasound}} [(Ph_3P)_2Pd(Ar)F] + AgI \qquad (3)$$

$\mathbf{1}$, Ar = Ph
$\mathbf{5}$, Ar = 4-$CH_3C_6H_4$
$\mathbf{6}$, Ar = 4-$CH_3OC_6H_4$
$\mathbf{7}$, Ar = 1-$C_{10}H_7$
$\mathbf{8}$, Ar = 4-ClC_6H_4
$\mathbf{9}$, Ar = 4-$CF_3C_6H_4$
$\mathbf{10}$, Ar = 4-$NO_2C_6H_4$

techniques, their yields, and analytical data are summarized in Table 1.

Silver fluoride has been used for the preparation of various fluoro complexes.[1] These reactions are normally conducted in polar solvents, such as methanol, acetonitrile, and acetone, in which AgF is somewhat soluble.

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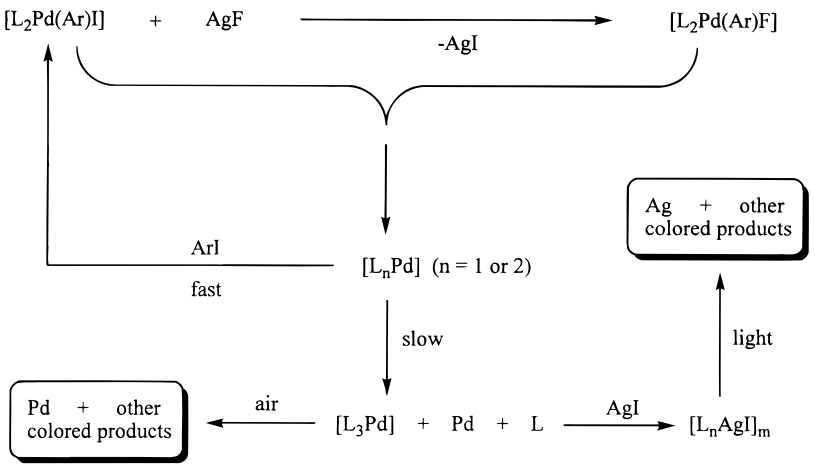
Scheme 1



Using these solvents for the synthesis of the palladium fluoro complexes, **1**, **2**, **5**−**10**, would be futile as the target products are insoluble in acetonitrile while being reactive toward acetone and, especially, methanol (see below). Simply stirring the iodo palladium complex, $[(Ph_3P)_2Pd(Ph)(I)]$, with AgF in benzene resulted in poor conversions and yields. Under sonication, however, this reaction smoothly occurred, furnishing the desired fluoride in 80−98% isolated yield at 100% conversion. We believe that this method might be successfully extended to the preparation of a large variety of transition metal fluoro complexes from their much more readily available iodo derivatives. For this reason, a very detailed description of the synthetic procedure developed for the F/I exchange under sonication is presented in the Experimental Section.

Reaction 3 is heterogeneous in nature. We have noticed that even under similar conditions the reaction time may vary in a broad range, sometimes from 1 to 10 h, depending on the size of the AgF granules used as well as the stirring and sonication efficiency. When a bromo complex, $[(Ph_3P)_2Pd(Ph)(Br)]$, was used for the synthesis instead of its iodo analogue, the reaction was sluggish, taking over 1 day for just ca. 70−80% conversion. This observation suggests that the mechanism of the exchange likely involves the interface formation of a bimetallic complex, e.g., $[(Ph_3P)_2Pd(Ph)(\mu\text{-}I)(\mu\text{-}F)Ag]$, which eliminated AgI to give the palladium fluoride. As the ΔH_f° values for crystalline AgF and AgI are −48.5 and −14.91 kcal/mol, respectively,[21] the driving force for the PdI/AgF exchange might be the superior stability of the palladium fluoride product. Indeed, it was recently established[22] that for anhydrous media of low polarity (CH_2Cl_2 and $CHCl_3$), the affinity of the metal center in $[(Ph_3P)_2Pd(Ph)(X)]$ for various halogens, X, decreases in the order F > Cl > Br > I. Similar observations were previously made for a series of Rh(I) complexes.[23]

When duplicating the I/F exchange reactions described in this paper, one should not rely completely on the reaction times specified in the Experimental Section but rather frequently monitor the process (e.g., by ^{31}P NMR).[24] In some cases, the Pd fluorides isolated from the I/F exchange experiments were yellow or even brown, although complexes of the type $[(Ph_3P)_2Pd(R)F]$ are white in nature. However, no side products were detected by ^{31}P NMR analysis of the reaction mixtures, and all fluoro complexes isolated were found to be *spectroscopically pure*, regardless of their color. The high yields (Table 1) of the fluoro complexes also suggested that the side reactions were minor, producing just trace amounts of deeply colored impurities. Interestingly, once quantitative conversion was achieved, filtration of the reaction suspension would sometimes produce virtually colorless, clear solutions which darkened upon isolation of the product. It was also noticed that while remaining spectroscopically pure, the products became deeper in color upon prolonged exposure to light. At the same time, the reaction between a bromo complex, $[(Ph_3P)_2Pd(Ph)(Br)]$, and AgF always gave white products, albeit the conversion never reached 100% (see above).

We found that the formation of the colored impurities can be suppressed by conducting the I/F exchange in the presence of small amounts of the corresponding iodoarene. For instance, the reaction between $[(Ph_3P)_2Pd(4\text{-}CH_3C_6H_4)(I)]$ and AgF was conducted several times, always affording spectroscopically pure **5** in high yield. However, the exchange in the absence of $4\text{-}CH_3C_6H_4I$ gave the desired product as a brownish-grey solid, whereas *white* crystals of **5** were isolated from the exchange carried out in the presence of 5−10

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(24) (a) Following the I/F exchange reactions by ^{31}P NMR is convenient because the signals of the starting iodo complexes are 3−5 ppm downfield from those of the corresponding fluorides. It is worth noting that because the I/F exchange reactions were run in the presence of small amounts of water,[24b] the ^{31}P NMR spectra of the reaction mixtures exhibited slightly broadened *singlet* resonances for the fluoro complexes (see text). (b) Silver(I) fluoride originating from aqueous solutions *always* contains some amounts of water which is virtually impossible to remove, see: Horn, E.; Snow, M. R. *Aust. J. Chem.* **1980**, *33*, 2369.

mol % of *p*-iodotoluene. Scheme 1 readily accounts for the beneficial effect of iodoarenes. In the course of the I/F exchange, a small amount of the palladium(II) complexes possibly decomposed to give Pd(0), e.g., via the fluoride-induced intramolecular redox process, [Pd(II)−P(III)/Pd(0)−P(V)].[11] The resulting coordinatively unsaturated zerovalent complexes, $[(Ph_3P)_nPd]$ (n = 1 or 2), are known to be unstable, disproportionating rapidly to Pd metal, $[(Ph_3P)_3Pd]$, and $[(Ph_3P)_4Pd]$.[14b] The latter is completely dissociated in solution to $[(Ph_3P)_3Pd]$ and free triphenylphosphine,[25] which easily forms soluble complexes with silver halides.[26] The Pd(0) side products and iodotriphenylphosphinesilver species contaminated the fluoro palladium complexes, subsequently staining them upon air- and light-induced decomposition. In the presence of ArI, however, the C−I bond would oxidatively add to $[(Ph_3P)_nPd]$ (n = 1 or 2) prior to its disproportionation,[14b] thus terminating the formation of free PPh_3 and its soluble silver complexes. The oxidative addition of Ar−I to the Pd(0) should produce the starting σ-aryl iodo Pd complex, which would eventually be converted, in situ, to the desired Pd fluoride because an excess of AgF was always used for the synthesis.

Characterization of Fluoro Palladium Complexes. Complexes **1**−**10** are air-stable compounds. If pure, they can be stored in air at room temperature for weeks and even a few months without decomposition. All palladium fluorides are easily soluble in dichloromethane and chloroform, moderately soluble in benzene, but insoluble in alkanes, acetonitrile, acetone, and methanol. However, adding MeOH to a benzene solution of **1** does not result in precipitation of the complex but rather its slow (hours at room temperature) decomposition to Pd(0), Ph_3PO, and other products.

The nature of the Pd−F bond in **1**−**10** is an important issue from the perspective of potential use of such complexes in synthesis and catalysis. Since the fluoride anion is the hardest base known (orbital electronegativity in water is −12.18 eV) while Pd^{2+} is a soft acid, the interaction between them is expected to be neither charge- nor orbital-controlled.[27] Although one might anticipate a Pd−F bond to be rather weak and easily ionized, this is not true for organopalladium fluorides **1**−**10**. The X-ray structure of almost ideally square-planar **1** suggests that the Pd−F bond (2.085(3) Å) is covalent.[12] The ^{19}F and ^{31}P NMR spectral characteristics for the fluoro complexes are summarized in Table 2. In anhydrous[28] solvents of low polarity, such as benzene, chloroform, and dichloromethane, all ligands on the Pd atom in **1** are inert on the NMR time scale. For solutions of **1** in *dry* CD_2Cl_2, a doublet at 19.5 ppm and a triplet at −274 ppm with the same coupling constant (J_{P-F} = 13.3 Hz) are observed in the ^{31}P and ^{19}F NMR spectra, respectively.[12]

Table 2. ^{31}P and ^{19}F NMR Data for Organopalladium Fluoro Complexes, *trans*-$[(Ph_3P)_2Pd(F)(R)]$, in Dichloromethane

complex	^{31}P NMR, δ^a	^{19}F NMR, δ^b	J_{F-P}, Hz
$[(Ph_3P)_2Pd(C_6H_5)F]$, **1**	19.5	−274	13.3
$[(Ph_3P)_2Pd(CH_3)F]$, **2**	24.5	−268	12.5
$[(Ph_3P)_2Pd(4-C_6H_4CH_3)F]$, **5**	18.9	−274	12.0
$[(Ph_3P)_2Pd(4-C_6H_4OCH_3)F]$, **6**	19.7	−276	11.8
$[(Ph_3P)_2Pd(1-C_{10}H_7)F]$, **7**	19.7	−275	12.5
$[(Ph_3P)_2Pd(4-C_6H_4Cl)F]$, **8**	19.2	−279	13.0
$[(Ph_3P)_2Pd(4-C_6H_4CF_3)F]$, **9**	19.7	−280; −63[c]	10.8
$[(Ph_3P)_2Pd(4-C_6H_4NO_2)F]$, **10**	19.3	−283	10.4

[a] External standard: 85% H_3PO_4. [b] External standard: $CFCl_3$. [c] The singlet resonance at −63 ppm is due to the CF_3 group.

In the presence of trace amounts of water, however, the ^{31}P and ^{19}F NMR signals from **1** appear as broadened *singlets* with similar chemical shifts and $\Delta\nu_{1/2}$ = 5−20 (^{31}P) and 50−150 Hz (^{19}F). The loss of P−F coupling was indicative of exchange processes occurring in moist solutions of **1**. Processes involving Pd−F ionization (eq 4) and/or Pd−F···HOH hydrogen bond formation (eq 5) were conceivable.

$$[(Ph_3P)_2Pd(Ph)F] \overset{H_2O}{\rightleftharpoons} [(Ph_3P)_2Pd(Ph)]^+ + F^- \quad (4)$$

$$[(Ph_3P)_2Pd(Ph)F] + H_2O \rightleftharpoons [(Ph_3P)_2Pd(Ph)F\text{---}HOH] \quad (5)$$

Thermodynamic considerations predict that as the sample is being cooled the formation of **1** should be favored by equilibrium 4, which will shift to the left, but disfavored by equilibrium 5 due to its shift to the right. The room-temperature ^{31}P NMR spectrum of **1** in CH_2Cl_2 (stock bottle; water content <0.1%) exhibited a singlet at 19.7 ppm with $\Delta\nu_{1/2}$ = 7.5 Hz ($< J_{PF}$ = 13.3 Hz). Upon slowly cooling the sample to +5 °C, this singlet resonance resolved into a doublet identical with that observed for anhydrous solutions of **1** at 20 °C. At coalescence (ca. +10 °C), $\Delta G^{\ddagger}$ for Pd−F ionization was calculated[29] to be 14.6 kcal/mol. The VT NMR data obtained was indicative of Pd−F ionization (eq 4), i.e., in the presence of small amounts of H_2O, the fluoro ligand in complex **1**, at ambient temperature, became labile on the NMR time scale. Evidence has been reported for facile ionization of the palladium−halogen bond in closely related complexes $[L_2Pd(X)Ar]$ (L = tertiary phosphine, X = halogen) of both trans[16b,22] and cis[30] geometry, under mild conditions.

Equilibrium 5 *alone* fails to account for the VT NMR behavior observed. Clearly, the formation of **1** via loss of water from $[(Ph_3P)_2Pd(Ph)(F\cdots HOH)]$ would be favored at higher rather than lower temperatures. By no means does this imply, however, that no hydrogen bond formation between **1** and water takes place. Moreover, the Pd−F···HOH hydrogen bond likely plays an important role in the Pd−F ionization process (see below).

Because no other resonances were observed in the low-temperature ^{31}P NMR spectrum of **1**, all the equi-

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(28) Samples for the NMR studies of complexes **1**−**10** were prepared by vacuum transfer of the dry solvent to a solid complex placed in a standard 5-mm NMR tube. The tube was then filled with nitrogen and sealed. The prepurified solvent was stirred with P_2O_5 under nitrogen for at least 24 h prior to use.

(29) (a) $k = \pi J/\sqrt{2} = 30\ s^{-1}$, where J = coupling constant in hertz; $\Delta G^{\ddagger} = RT\{\ln(k_B/h) - \ln(k/T)\} = 14.6$ kcal/mol, where k_B is Boltzmann's constant, h is Planck's constant, and R is the universal gas constant.[29b] (b) Harris, R. K. *Nuclear Magnetic Resonance Spectroscopy: A Physicochemical View*; Longman Scientific & Technical: Harlow, 1986.

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Scheme 2

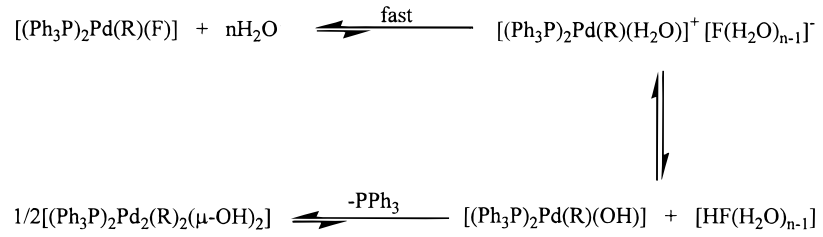


Table 3. Temperature of Coalescence and $\Delta G^{\ddagger}$ Values Obtained from VT ^{31}P NMR Studies of Solutions of *trans*-[$(Ph_3P)_2Pd(F)(R)$] (0.0185 mmol) in CH_2Cl_2 (0.5 mL) Containing Water (0.037 mmol)

complex	temp of coalescence, K	$\Delta G^{\ddagger}$, kcal/mol
$[(Ph_3P)_2Pd(C_6H_5)F]$, **1**	253	13.0
$[(Ph_3P)_2Pd(CH_3)F]$, **2**	233	12.0
$[(Ph_3P)_2Pd(4\text{-}C_6H_4CH_3)F]$, **5**	253	13.1
$[(Ph_3P)_2Pd(4\text{-}C_6H_4OCH_3)F]$, **6**	253	13.1
$[(Ph_3P)_2Pd(1\text{-}C_{10}H_7)F]$, **7**	273	14.1
$[(Ph_3P)_2Pd(4\text{-}C_6H_4Cl)F]$, **8**	288	14.9
$[(Ph_3P)_2Pd(4\text{-}C_6H_4CF_3)F]$, **9**	248	12.9
$[(Ph_3P)_2Pd(4\text{-}C_6H_4NO_2)F]$, **10**	258	13.4

libria between the fluoro complexes and products of Pd−F ionization were obviously shifted almost entirely toward the fluoro complex. This is consistent with the fact that the synthesis, isolation, and recrystallization[31] of the fluoro complexes were successfully carried out with solvents which had not been dried. The spectral parameters, reactivity, and color of **1** were different from those of the cationic complex, $[(Ph_3P)_2Pd(Ph)]^+$,[32] which would form upon complete loss of F^- from **1**. The hydrolysis of **1** (Scheme 2) is the reverse of its formation from the Pd hydroxo dimer and HF in the form of TREAT HF (compare eq 1 and Scheme 2).[33,34] Obviously, in the presence of water, the Pd−F bond is not inert, albeit certainly favored by thermodynamics.

In an attempt to reveal mechanistic features of the water-induced Pd−F ionization, we undertook VT NMR studies of various arylpalladium fluorides in wet CH_2Cl_2 (Table 3). For each of the samples studied ($[(Ph_3P)_2Pd(R)F] = 3.7 \times 10^{-2}$ mol/L) the molar ratio of water to the Pd fluoride was 2:1.[35] All room-temperature ^{31}P NMR spectra of these samples exhibited singlet resonances which resolved into doublets upon cooling. As seen from Table 3, there was no correlation between the electronic effects of the substituents on the benzene ring and the temperature of coalescence. Both strong electron-withdrawing and electron-releasing substituents facilitated the exchange, whereas the slowest ionization was observed for **7** and **8** containing relatively "neutral" 1-naphthyl and 4-chlorophenyl ligands.[36]

The lack of correlation may be rationalized in terms of both electrophilic and nucleophilic attack of H_2O on the fluoro complex. Water may cause the ionization of the Pd−F bond by coordinating to the metal center (**A**; nucleophilic cleavage)[37] or by forming a hydrogen bond with the F ligand (**B**; electrophilic cleavage).[38−40] It is also conceivable that the Pd−F bond ionizes via both nucleophilic and electrophilic paths concomitantly, as shown in structures **C** and **D** ("ambiphilic" or push/pull-type mechanisms).

Depending on the nature of group X (structures **A**−**D**), the $Pd^{\delta+}-F^{\delta-}$ bond is polarized to a different extent. Electron-withdrawing substituents on the ring

(31) The fluoro complexes are convenient to recrystallize by adding pentane or hexane to their concentrated solutions in benzene or, preferentially, dichloromethane. Precipitating the complexes with ether instead of pentane or hexane normally results in substantial losses, especially for compound **9** which is slightly soluble in ether, perhaps due to the lipophilic CF_3 group. Complexes **1**−**10** can also be successfully recrystallized by adding toluene to their concentrated dichloromethane solution, followed by removal of the CH_2Cl_2 by rotary evaporation (15−30 min at ambient temperature) and keeping the resulting solution at ca. −15 to −20 °C overnight.

(32) Amatore, C.; Carré, E.; Jutand, A.; M'Barki, M. A.; Meyer, G. *Organometallics* **1995**, *14*, 5605.

(33) The hydroxo palladium complexes are obviously more basic than triethylamine since the reaction between $[(Ph_3P)_2Pd_2(R)_2(\mu\text{-}OH)_2]$ (3 equiv) and $[(HF)_3{\cdot}NEt_3]$ (2 equiv) in the presence of PPh_3 occurs quantitatively, resulting in the formation of the corresponding fluoro complex and free Et_3N.

(34) (a) Although it has been established[34b] that the equilibrium between $[(Ph_3P)_2Pd(R)(OH)]$ and $[(Ph_3P)_2Pd_2(R)_2(\mu\text{-}OH)_2]$ (R = Ph or Me) is shifted almost entirely toward the dimer, the palladium fluoride remains the only thermodynamically favored species when dissolved in dichloromethane saturated with water (Scheme 2). (b) Grushin, V. V.; Alper, H. *Organometallics* **1996**, *15*, 5242.

(35) (a) All samples were made up by dissolving 0.0185 mmol of each fluoro complex in 0.5 mL of CH_2Cl_2 saturated with water (0.198% by weight at 20 °C).[40b] (b) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents. Physical Properties and Methods of Purification*, 4th ed.; Wiley: New York, 1986; p 490−491.

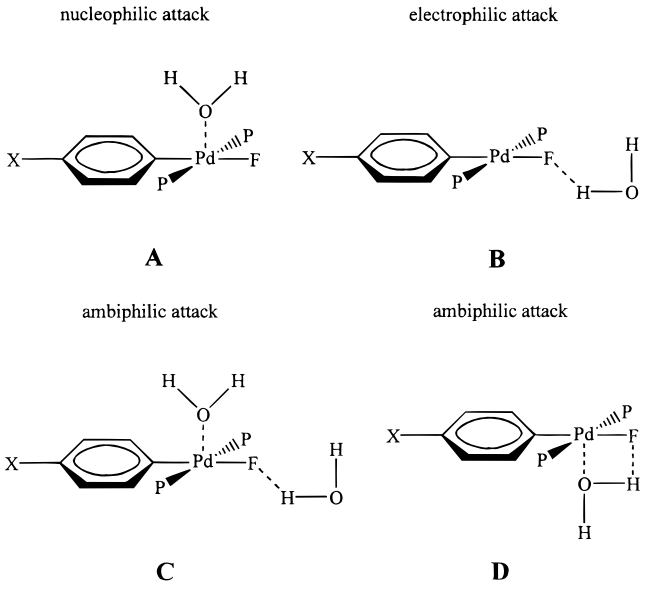
(36) The lack of correlation cannot be accounted for by impurities in the fluoro complexes used for the VT NMR studies. Two recrystallizations of **7** from dichloromethane−hexane did not affect the temperature of coalescence. No difference in the VT NMR behavior was observed for similarly prepared wet dichloromethane solutions of **1** originating from the TREAT HF and AgF reactions.

(37) Alkaline hydrolysis of $[(Ph_3P)_2Pd(Ph)I]$ to $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}OH)_2]$ in the presence of 18-crown-6 likely involves nucleophilic attack of OH^- on the metal center, see: Grushin, V. V.; Alper, H. *J. Am. Chem. Soc.* **1995**, *117*, 4305. Adding solid KOH to a dichloromethane solution of **1** resulted, within hours, in the formation of PPh_3 and the hydroxo palladium dimer,[14a] which were identified by ^{31}P NMR.

(38) For examples of hydrogen bonds to fluoro ligands in transition metal complexes, see: Richmond, T. G. *Coord. Chem. Rev.* **1990**, *105*, 221.

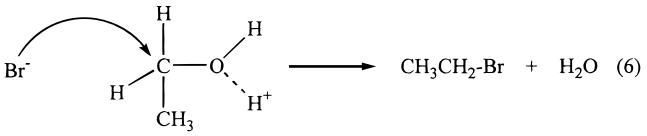
(39) (a) Veltheer, J. E.; Burger, P.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 12478. (b) Mechanism **B** may govern ionization of the Ir−F bond in the 18e complex, $[Cp^*Ir(PMe_3)(Ph)F]$, whose hydrolysis is "likely aided by hydrogen bonding",[39a] whereas direct coordination of H_2O to the electronically saturated Ir center is unlikely. The Pd fluorides are 16e complexes which may undergo facile ligand exchange via the associative mechanism. In aqueous THF, $[Cp^*Ir(PMe_3)(Ph)F]$ exists in equilibrium with a species formulated as $[Cp^*Ir(PMe_3)(Ph)(H_2O)]^+[F{\cdot}xH_2O]^-$.[39a] Depending on the amount of water added, the equilibrium can be shifted toward the covalent fluoride or the cationic aqua complex. Nonetheless, the fluoro ligand on the Ir atom remains *inert* on the NMR time scale, regardless of the position of the equilibrium. In contrast, the Pd−F bond is labile on the NMR time scale (at room temperature) when complexes of the type $[(Ph_3P)_2Pd(R)F]$ are dissolved in solvents containing even small amounts of H_2O.

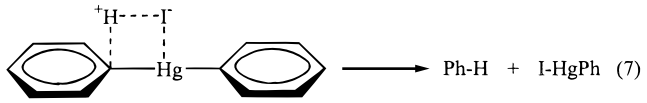
(40) Intermediate **B**, $[(Ph_3P)_2Pd(R)(F{\cdots}HOH)]$, contains the already "hydrated" fluoride as a ligand which is an incomparably better leaving group than the F^-. There is much similarity between this intermediate and bifluoride complexes **3** and **4**, in which the FHF ligand is *labile under rigorously dry conditions*. The ^{1}H NMR spectra of **3** and **4** are almost indistinguishable from those of their fluoro counterparts, **1** and **2**, respectively, except for the presence of broad downfield resonances at ca. 12.5 ppm arising from the FHF ligand. At room temperature, ^{19}F NMR signals of **3** and **4** were too broad to be observed and only singlet resonances were found in the ^{31}P NMR spectra of **3** and **4** in dry dichloromethane (see Experimental Section), obviously due to fluorine exchange processes. Upon cooling a dichloromethane solution of **4** to −85 °C, the ^{31}P NMR singlet resonance transformed to a broad, poorly resolved doublet (δ = 27 ppm; J_{P-F} = 8.3 Hz).



would increase the partial positive charge on the palladium,[41] thus facilitating Pd−F ionization via the *nucleophilic* path involving coordination of water to the metal center (**A**). Hydrogen bonding between the F ligand and an H atom of another (**C**) or the same (**D**) water molecule provides electrophilic aid to the process. To the contrary, when X is an electron-donating group, the *electrophilic* path (**B**) may be dominant due to stronger filled/filled repulsions,[42] with nucleophilic support coming from the oxygen coordinated to the metal (**C** and/or **D**). As a result, both relatively electron-deficient and electron-rich *σ*-organic ligands in $[(Ph_3P)_2Pd(R)F]$ speed up the water-induced Pd−F ionization.[43]

In concluding this article, we would like to remark on conceptual analogies to mechanistic models **C** and **D**, which can be found in various areas of chemistry. In many instances, electrophiles provide aid to nucleophilic reactions, whereas the presence of a nucleophile is crucial for a number of electrophilic processes. For example, S_N2-type reactions between primary alcohols and anionic nucleophiles (e.g., Br^-) readily occur only in the presence of a strong protic acid[44] because protonation of the OH function changes it into a much better leaving group (eq 6). Similarly, electrophilic substitution in organomercury compounds is orders of magnitude faster in the presence of nucleophiles.[45] Although the reaction between diphenylmercury and sulfuric acid is sluggish, the C−Hg bond is cleaved very rapidly when I^- is added (eq 7).





Experimental Section

General Considerations. A Varian VXR-200 NMR spectrometer was used for measuring ^1H, ^{19}F, and ^{31}P NMR spectra. Elemental analyses were carried out by M-H-W Laboratories (Phoenix, AZ). Silver fluoride, TREAT HF, and other chemicals were purchased from Aldrich Chemical Co. and used as received. The organopalladium hydroxo complexes, $[(Ph_3P)_2Pd_2(R)_2(\mu\text{-}OH)_2]$, where R = Ph or Me, were prepared as described in the literature.[14] Organopalladium iodo complexes of the type $[(Ph_3P)_2Pd(I)Ar]$ were obtained in the following manner. A mixture of 40% NaOH (20 g), PPh_3 (2.4 g, 9.2 mmol), benzene (65 mL), $[(Ph_3P)_2PdCl_2]$ (2.0 g, 2.9 mmol), and benzyltriethylammonium chloride (0.1 g, 0.04 mmol) was vigorously stirred under N_2 at room temperature for 24 h. The mixture was then stirred at 65−75 °C until the zerovalent palladium complex[46] generated dissolved in the organic phase. The bottom aqueous layer was carefully separated by a pipette. After the yellow benzene solution was allowed to cool to room temperature, powdered sodium iodide (5−7 g)[47] and an aryl iodide (3.5−5 mmol) were added and the mixture was stirred under nitrogen for 15−30 min. The arylpalladium iodo complexes were isolated in air. The mixture was filtered, the solids were thoroughly extracted with benzene,[48] and the combined clear organic solutions were reduced in volume and treated with excess ethanol. White or yellowish crystals of the product were separated, washed with ethanol and ether, and dried under vacuum. The yield of the spectroscopically pure[20] organopalladium iodo complexes was in the range of 75−97%.

The I/F exchange was performed under nitrogen in a Schlenk-type flask immersed in a Branson 1200 ultrasonic bath filled with water. Using flasks with a broad and desirably flat bottom surface was found to be crucial for the synthesis, as it prevented the dense silver salts from amassing in a thick,

(41) (a) In palladium complexes of the type $[L_2Pd(X)(4\text{-}C_6H_4Y)]$, where L is a tertiary phosphine, X is a halogen, and Y is a *π*-acceptor (e.g., NO_2), both polar and *resonance*[41b] effects may be responsible for an increase in the positive charge on the metal center. (b) Manna, J.; Kuehl, C. J.; Whiteford, J. A; Stang, P. J. *Organometallics* **1997**, *16*, 1897.

(42) Caulton, K. G. *New J. Chem.* **1994**, *18*, 25.

(43) Among complexes of the type $[(Ph_3P)_2Pd(4\text{-}XC_6H_4)F]$, the slowest exchange was observed for **8** (X = Cl) in which the Pd−F bond is polarized to the degree that is least favorable for hydrolysis via **C**- or **D**-type path. Replacing the *p*-chlorophenyl ligand with a more electron-donating one (**1**, **2**, **5**, or **6**) facilitates the hydrogen bond formation, whereas more electron-withdrawing groups (**9** and **10**) increase the rate of nucleophilic attack on the metal. Both effects eventually result in the elimination of the hydrated F^- from the palladium. It is believed that synergism of the two mechanisms, as shown in structures **C** or **D**, is essential for efficient Pd−F ionization. The 1-naphthyl ligand in **7** is too remote from the F to impede its hydrogen bonding to water but bulky enough to limit access of H_2O to the metal center. As a result, the water-induced ligand exchange in **7** is noticeably slower than in **1**.

(44) March, J. *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, 4th ed.; Wiley: NewYork, 1992. Bunton, C. A. *Nucleophilic Substitution at a Saturated Carbon Atom*; Elsevier: New York, 1963.

(45) Reutov, O. A.; Beletskaya, I. P. *Reaction Mechanisms of Organometallic Compounds*; North-Holland: Amsterdam, 1968. Makarova, L. G.; Nesmeyanov, A. N. *The Organic Compounds of Mercury*; North-Holland: Amsterdam, 1967.

(46) Ioele, M.; Ortaggi, G.; Scarsella, M.; Sleiter, G. *Polyhedron* **1991**, *10*, 2475.

(47) The addition of NaI suppressed the formation of small amounts (1−3%) of the corresponding organopalladium chloride, $[(Ph_3P)_2Pd(Cl)Ar]$. The latter apparently arose from ligand exchange between the $[(Ph_3P)_2Pd(I)Ar]$ formed and the Cl^- present in droplets of the aqueous phase, always remaining in the flask after the aqueous layer is separated. Alternatively, to make the system Cl^--free, the benzene solution of the Pd(0) complex can be washed with a few portions of water. However, because the washing must be done under nitrogen, we found this less convenient than simply adding solid NaI to the mixture.

(48) Unlike other $[(Ph_3P)_2Pd(I)Ar]$ prepared in this work, the *p*-chlorophenyl complex, $[(Ph_3P)_2Pd(I)(4\text{-}C_6H_4Cl)]$, is only moderately soluble in benzene and, hence, partially precipitates upon formation. To assure a good isolated yield, the solid mixture of NaI and $[(Ph_3P)_2Pd(I)(4\text{-}C_6H_4Cl)]$ should be thoroughly extracted with dichloromethane and/or hot benzene.

stationary layer under the liquid phase. The reactions were run in benzene, which had not been dried before the reaction, at 10−25 °C in the dark. At lower temperatures the reaction was slow, whereas at higher temperatures side reactions occurred, resulting in lower yields and contamination of the product. Occasional exposure of the reaction mixtures to light for 5−10 min did not ruin or terminate the process. The exchange was normally conducted with a 30−100% excess of AgF, which was stored and handled under nitrogen in the dark. Satisfactory results were obtained when the AgF reagent had been briefly exposed to air for obtaining an accurate weighing before the reaction. The fluorination of the iodo complexes with AgF was monitored by ^{31}P NMR analysis of the liquid phase. Once the exchange process was complete, the sonication was immediately stopped to avoid decomposition of the desired fluorides.

[(Ph$_3$P)$_2$Pd(F)Ph], 1. (a) A mixture of [(Ph$_3$P)$_2$Pd(I)Ph] (162 mg, 0.19 mmol) and AgF (39 mg, 0.31 mmol) in benzene (6 mL) was sonicated under N_2 in the dark at 15−18 °C until the iodo complex disappeared (2 h; ^{31}P NMR control). The solution was filtered through Celite, reduced in volume to ca. 2 mL, and treated with pentane to give 135 mg (96%) of **1** as white crystals, which were separated, washed with pentane, and dried under vacuum.

(b) A mixture of [(Ph$_3$P)$_2$Pd(I)Ph] (450 mg, 0.62 mmol), AgF (118 mg, 0.93 mmol), and iodobenzene (7 μL, 0.06 mmol) in benzene (10 mL) was sonicated under N_2 in the dark at 18−25 °C until the iodo complex disappeared (2.5 h; ^{31}P NMR control). The liquid phase was separated, and the solid was extracted first with benzene (4 × 10 mL) and then with dichloromethane (3 × 10 mL). The combined organic solutions were filtered through a Celite plug, which was then washed with dichloromethane (10 mL). The combined filtrates were reduced in volume to ca. 5 mL and treated with hexane to give 385 mg (98%) of **1** as white crystals, which were separated, washed with pentane, and dried under vacuum. ^{1}H NMR (CDCl$_3$, 20 °C)[49] δ: 6.2 (t, 2H, J = 7.3 Hz, 3,5-C$_6$H$_5$Pd), 6.35 (t, 1H, J = 7.0 Hz, 4-C$_6$H$_5$Pd), 6.55 (d, 2H, J = 7.3 Hz, 2,6-C$_6$H$_5$Pd), 7.1−7.6 (m, 30H, C$_6$H$_5$P).

[(Ph$_3$P)$_2$Pd(F)Me], 2. TREAT HF (27.5 μL, 0.17 mmol) was added to a suspension of [(Ph$_3$P)$_2$Pd$_2$(Me)$_2$(μ-OH)$_2$] (202 mg, 0.25 mmol), PPh$_3$ (140 mg, 0.53 mmol), and benzene (10 mL), and the mixture was stirred for 1 h. The benzene solution was filtered through a short Celite plug, reduced in volume, and treated with pentane to give 283 mg (84%) of spectroscopically pure **2** as a yellowish solid. Colorless crystals of **2** were obtained by adding toluene (5 mL) to a saturated solution of the yellowish material in dichloromethane, slowly evaporating the mixture on a rotary evaporator at room temperature until most of the dichloromethane was removed, and keeping the resulting oversaturated toluene solution of **2** at −17 °C overnight. ^{1}H NMR (CDCl$_3$, 20 °C) δ: −0.1 (t, 3H, J_{P-H} = 5.8 Hz, CH$_3$Pd), 7.2−7.8 (m, 30H, C$_6$H$_5$P).

[(Ph$_3$P)$_2$Pd(HF$_2$)Ph], 3. TREAT HF (215 μL, 1.32 mmol) was added to a stirred mixture of [(Ph$_3$P)$_2$Pd$_2$(Ph)$_2$(μ-OH)$_2$] (620 mg, 0.66 mmol), PPh$_3$ (390 mg, 1.49 mmol), and benzene (35 mL), and the mixture was vigorously stirred until the solids dissolved and then stirred for another 5 min. The solution was filtered through a short Celite plug, which was then washed with benzene (3 × 5 mL). The combined benzene solutions were reduced in volume to ca. 10 mL, at which point crystals of **3** started to deposit. To complete precipitation, pentane (25 mL) was slowly added portionwise and the mixture was left at room temperature for 2 h. The crystals were separated, washed with pentane, and dried under vacuum. The yield of **3** was 984 mg (98%). ^{1}H NMR (CDCl$_3$, 20 °C) δ 6.2 (t, 2H, J = 7.3 Hz, 3,5-C$_6$H$_5$Pd), 6.35 (t, 1H, J = 7.0 Hz, 4-C$_6$H$_5$Pd), 6.55 (d, 2H, J = 7.3 Hz, 2,6-C$_6$H$_5$Pd), 7.1−7.6 (m, 30H, C$_6$H$_5$P), 12.4 (br s, 1H, FHF). ^{31}P NMR (CH$_2$Cl$_2$, 20 °C) δ: 20.2 (s).

[(Ph$_3$P)$_2$Pd(HF$_2$)Me], 4. TREAT HF (200 μL, 1.24 mmol) was added to a stirred mixture of [(Ph$_3$P)$_2$Pd$_2$(Me)$_2$(μ-OH)$_2$] (515 mg, 0.64 mmol), PPh$_3$ (380 mg, 1.45 mmol), and benzene (15 mL), and the mixture was vigorously stirred until the solids dissolved and then stirred for 5 more min. The solution was filtered through cotton wool, reduced in volume to ca. 3 mL, and treated with ether (15 mL). The crystals were separated, washed with ether, and dried under vacuum. The yield of yellowish **4** was 760 mg (86%). Colorless crystals of the spectroscopically pure **4** were obtained by recrystallization from dichloromethane−toluene, as described in ref 31. ^{1}H NMR (CDCl$_3$, 20 °C) δ: −0.1 (t, 3H, J_{P-H} = 5.8 Hz, CH$_3$Pd), 7.2−7.8 (m, 30H, C$_6$H$_5$P), 12.4 (br s, 1H, FHF). ^{31}P NMR (CH$_2$Cl$_2$, 20 °C) δ: 25.6 (s).

[(Ph$_3$P)$_2$Pd(F)(4-C$_6$H$_4$CH$_3$)], 5. A mixture of [(Ph$_3$P)$_2$Pd(I)(4-C$_6$H$_4$CH$_3$)] (335 mg, 0.39 mmol), AgF (109 mg, 0.85 mmol), *p*-iodotoluene (6 mg, 0.03 mmol), and benzene (10 mL) was sonicated under N_2 in the dark at 15−20 °C until the iodo complex disappeared (5 h; ^{31}P NMR control). The reaction mixture was filtered through a Celite plug, which was thoroughly washed with benzene. The combined filtrates were reduced in volume to ca. 5 mL and treated with excess pentane to give white crystals of **5**, which were washed with pentane and dried under vacuum. The yield of **5** was 270 mg (92%). ^{1}H NMR (CDCl$_3$, 20 °C) δ: 1.9 (s, 3H, CH$_3$), 6.1 (d, 2H, J_{H-H} = 8.0 Hz, 3,5-C$_6$H$_4$Pd), 6.4 (dt, 2H, J_{H-H} = 8.0 Hz, H_{H-P} = 1.7 Hz, 2,6-C$_6$H$_4$Pd), 7.2−7.7 (m, 30H, C$_6$H$_5$P).

[(Ph$_3$P)$_2$Pd(F)(4-C$_6$H$_4$OCH$_3$)], 6. A mixture of [(Ph$_3$P)$_2$Pd(I)(4-C$_6$H$_4$OCH$_3$)] (476 mg, 0.55 mmol) and AgF (130 mg, 1.02 mmol) in benzene (15 mL) was sonicated under N_2 in the dark at 15−20 °C until the iodo complex disappeared (3 h; ^{31}P NMR control). The reaction mixture was filtered through a Celite plug, which was thoroughly washed with benzene. The combined filtrates were reduced in volume to ca. 5 mL and treated with pentane to give yellowish crystals of **6**, which were washed with pentane and dried under vacuum. The yield of **6** was 399 mg (96%). ^{1}H NMR (CDCl$_3$, 20 °C) δ: 3.5 (s, 3H, CH$_3$), 5.9 (d, 2H, J_{H-H} = 8.5 Hz, 3,5-C$_6$H$_4$Pd), 6.4 (dt, 2H, J_{H-H} = 8.5 Hz, H_{H-P} = 1.5 Hz, 2,6-C$_6$H$_4$Pd), 7.1−7.6 (m, 30H, C$_6$H$_5$P).

[(Ph$_3$P)$_2$Pd(F)(1-C$_{10}$H$_7$)], 7. A mixture of [(Ph$_3$P)$_2$Pd(I)(1-C$_{10}$H$_7$)] (224 mg, 0.25 mmol) and AgF (86 mg, 0.68 mmol) in benzene (7 mL) was sonicated under N_2 in the dark at 15−20 °C until the iodo complex disappeared (4 h; ^{31}P NMR control). The solution was filtered through a Celite plug, which was then thoroughly washed first with benzene and then with dichloromethane. The combined filtrates were reduced in volume to ca. 5 mL and treated with pentane to give 193 mg (98%) of **7** as pale-yellow crystals, which were separated, washed with pentane, and dried under vacuum. ^{1}H NMR (CDCl$_3$, 20 °C) δ: 6.4 (t, 1H J_{H-H} = 7.6 Hz, C$_{10}$H$_7$), 6.8−7.0 (m, 5H C$_{10}$H$_7$), 7.1−7.6 (m, 30H, C$_6$H$_5$), 8.4 (d, 1H J_{H-H} = 7.6 Hz, C$_{10}$H$_7$).

[(Ph$_3$P)$_2$Pd(F)(4-C$_6$H$_4$Cl)], 8. A mixture of [(Ph$_3$P)$_2$Pd(I)(4-C$_6$H$_4$Cl)] (231 mg, 0.27 mmol) and AgF (70 mg, 0.55 mmol) in benzene (9 mL) was sonicated under N_2 in the dark at 15−20 °C until the iodo complex disappeared (4 h; ^{31}P NMR control). The reaction mixture was transferred onto a Celite plug, which was then thoroughly washed with benzene and dichloromethane. The combined filtrates were reduced in volume to ca. 5 mL and treated with hexane to give 175 mg (86%) of **8** as greyish-white crystals, which were separated, washed with hexane, and dried under vacuum. ^{1}H NMR (CDCl$_3$, 20 °C) δ: 6.2 (d, 2H, J_{H-H} = 8.1 Hz, 3,5-C$_6$H$_4$Pd), 6.5 (d, 2H, J_{H-H} = 8.1 Hz, 2,6-C$_6$H$_4$Pd), 7.1−7.7 (m, 30H, C$_6$H$_5$P).

[(Ph$_3$P)$_2$Pd(F)(4-C$_6$H$_4$CF$_3$)], 9. A mixture of [(Ph$_3$P)$_2$Pd(I)(4-C$_6$H$_4$CF$_3$)] (574 mg, 0.64 mmol) and AgF (116 mg, 0.91 mmol) in benzene (10 mL) was sonicated under N_2 in the dark

(49) Interestingly, all four complexes of the type [(Ph$_3$P)$_2$Pd(Ph)X] (X = F, Cl, Br, and I) exhibit virtually indistinguishable ^{1}H NMR spectral patterns.

at 15−20 °C until the iodo complex disappeared (2 h; ^{31}P NMR control). The reaction mixture was filtered through a Celite plug, which was thoroughly washed with benzene. The combined filtrates were reduced in volume to ca. 5 mL and treated with pentane to give 435 mg (82%) of **9**·$^1/_2CH_2Cl_2$ as yellowish crystals, which were separated, washed with pentane, and dried. ^{1}H NMR ($CDCl_3$, 20 °C) δ: 5.3 (s, 1H, CH_2Cl_2), 6.4 (dq, 2H, J_{H-H} = 8.3 Hz, J_{H-F} = 0.6 Hz, 3,5-C_6H_4Pd), 6.7 (dm, 2H, J_{H-H} = 8.3 Hz, 2,6-C_6H_4Pd), 7.2−7.7 (m, 30H, C_6H_5P).

[(Ph$_3$P)$_2$Pd(F)(4-C$_6$H$_4$NO$_2$)], 10. A mixture of [(Ph$_3$P)$_2$Pd(I)(4-$C_6H_4NO_2$)] (203 mg, 0.23 mmol) and AgF (61 mg, 0.48 mmol) in benzene (9 mL) was sonicated under N_2 in the dark at 15−20 °C until the iodo complex disappeared (4 h; ^{31}P NMR control). The reaction mixture was filtered through a Celite plug, which was then thoroughly washed with benzene. The combined filtrates were reduced in volume to ca. 5 mL and treated with pentane to give 160 mg (90%) of **10** as yellowish crystals, which were separated, washed with pentane, and dried under vacuum. ^{1}H NMR ($CDCl_3$, 20 °C) δ: 6.8 (dt, 2H, J_{H-H} = 9.0 Hz, H_{H-P} = 1.4 Hz, 2,4-C_6H_4Pd), 7.0 (d, 2H, J_{H-H} = 9.0 Hz, 3,5-C_6H_4Pd), 7.2−7.7 (m, 30H, C_6H_5P).

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