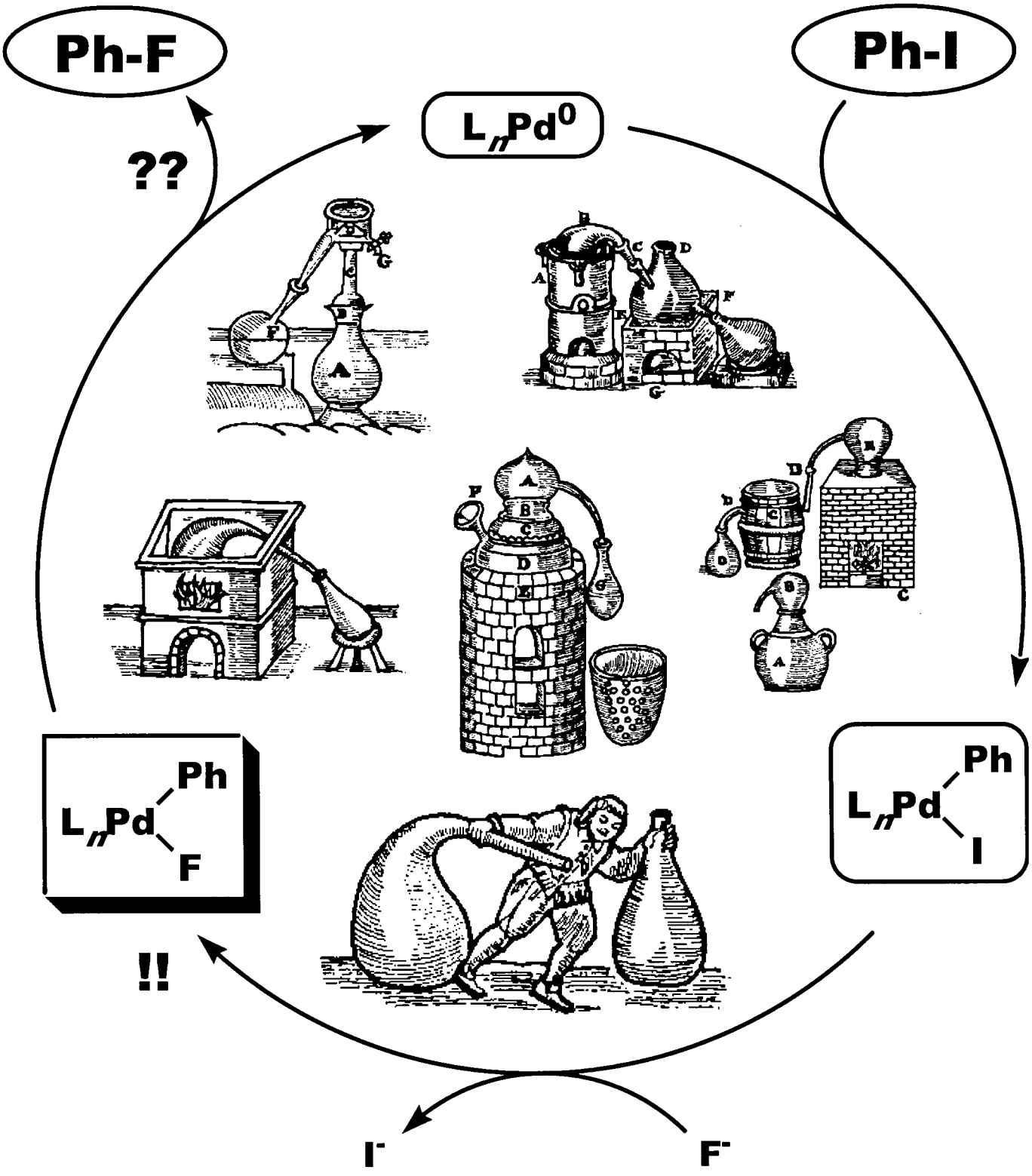
Organopalladium Fluorides**



We have to go step by step, for there is no Philosopher's Stone...

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Palladium Fluoride Complexes: One More Step toward Metal-Mediated C–F Bond Formation**

Vladimir V. Grushin*[a]

Abstract: The first molecular complexes of palladium containing a Pd–F bond, both fluorides and bifluorides, were synthesized and fully characterized in the solid state and in solution. Reactivity studies of the Pd fluoride complexes revealed their unexpected stability and unusual chemical properties, different from the hydroxo, chloro, bromo, and iodo analogues. A novel efficient method to generate "naked fluoride" was developed using $[(Ph_3P)_2Pd(F)Ph]$. The naked fluoride from the Pd source fluorinated dichloromethane, deprotonated chloroform, and catalyzed di- and trimerization of hexafluoropropene under uncommonly mild conditions.

Keywords: fluorination · naked fluoride · palladium · transition metals

Introduction

While considerable progress has been made in the new exciting research area of transition metal fluoride complexes,[1] the closely related field of homogeneous metal-catalyzed fluorination of organic molecules still remains in its early infancy.[2] The importance of C–F bond formation stems from various unique properties of organofluorine compounds, such as the remarkable thermal and chemical stability, good processing properties, but mostly from their biological activity. Numerous fluorinated organic compounds are widely used as pharmaceuticals and agrochemicals,[3] whilst ^{18}F-labelled organic molecules are in considerable demand for the positron-emission tomography (PET) diagnostics technique.[4]

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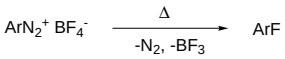
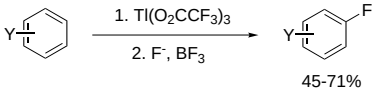
[**] Frontispiece shows woodcuts from: John French, *The Art of Distillation*, London, **1651**. Courtesy of Adam McLean (http://www.levity.com/alchemy/).

There is still only one general practical method for the selective introduction of fluorine into the aromatic ring, that is the Balz–Schiemann reaction [Eq. (1)] first reported as early as 1927.[5]



(1)

While dealing with expensive, toxic and potentially explosive diazonium salts at elevated temperatures, the Balz–Schiemann reaction is still preferred, in both the laboratory and industry, to the few alternative methods which employ either even more toxic thallium, mercury, and lead compounds [Eq. (2)][6] or costly iodonium salts [Eq. (3)].[7]



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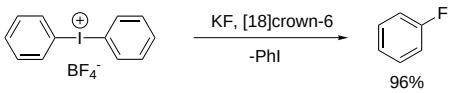
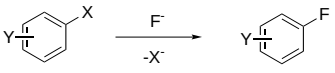


(3)[7c]

With regards to aromatic nucleophilic fluorination, it is also worth mentioning the well-known Meisenheimer chemistry[8] and the closely related Halex process (e.g., the industrial high-temperature synthesis of C_6F_6 from C_6Cl_6 and KF).[9] These methods, however, are limited to only most electron-deficient, strongly electrophilic haloarene substrates which are *activated* toward nucleophilic attack by powerful electron acceptors on the ring. Examples of such reactive substrates include nitro- and cyanoaryl halides, hexa- and pentachlorobenzenes. The Meisenheimer chemistry, however, is not applicable to most common *nonactivated* aryl halides containing electron-donating, neutral, or weakly electron-withdrawing substituents on the aromatic ring.

Realizing the displacement of a halogen in nonactivated aryl halides with fluorine [Eq. (4)] has challenged many



(4)

X = I, Br, Cl
Y = H, electron donor, weak electron acceptor

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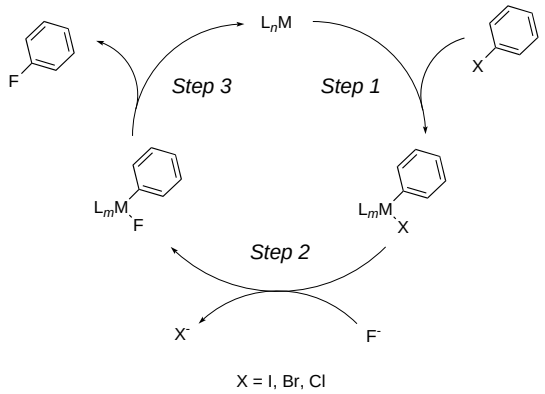
research groups. Being *thermodynamically allowed*, Reaction (4) seems to be an ideally suited candidate for catalysis with a metal complex. Scheme 1 shows a simplified catalytic loop proposed for Reaction (4), involving oxidative addition

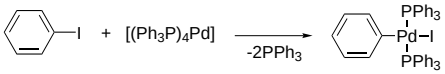


Scheme 1. Simplified catalytic loop proposed for Reaction (4).

of the Ar–X bond to a low-valent transition metal complex, followed by ligand exchange for fluoride and reductive elimination of the desired product, Ar–F, as the final step. With Scheme 1 in mind, we had made numerous attempts to prepare fluoroarenes from corresponding aromatic iodides, bromides, and chlorides in the presence of various Ni, Pd, Pt, Ru, Co, and Rh complexes. Since all those attempts were unsuccessful it became clear that at least one of the steps in the catalytic cycle shown in Scheme 1 flawed.

A project launched in our laboratories at Wilfrid Laurier University, Canada, in the mid 90s was aimed at gaining insight into details of the catalytic loop presented in Scheme 1, with M = Pd. Palladium was the metal of choice due to the remarkable ability of its complexes to catalyze a wide variety of organic reactions,[10] aromatic nucleophilic substitution included.[11] Closely related to this task, the synthesis and studies of then unknown organopalladium fluoride complexes represented a separate considerable challenge in its own right.

Synthesis of organopalladium fluoride complexes: There was little doubt about feasibility of the first step of the catalytic cycle, that is, haloarene activation by oxidative addition of the Ar–X (X = halogen) bond to Pd^0. Tertiary phosphine complexes of zero-valent palladium are well-known[10–12] to smoothly undergo oxidative addition of aryl iodides, bromides, and even much less reactive chlorides to produce σ-aryl palladium(II) halides [e.g., Eq. (5)]. Therefore, it was logical to

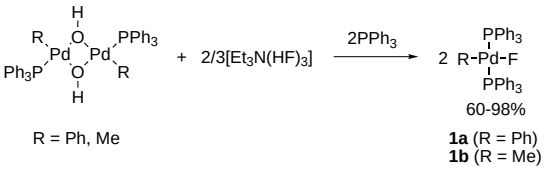


(5)

investigate i) the ability of palladium to form stable organometallic fluoride complexes (Scheme 1, step 2) and ii) the possibility of C–F reductive elimination from organopalladium fluorides (Scheme 1, step 3), should the latter exist at all. Clearly, the key issue to be addressed was the very existence of molecular complexes of palladium containing a Pd–F bond.

At the time our project was launched, there were no reports in the literature, describing an isolable, reliably characterized complex containing a Pd–F bond. Spectroscopic evidence had been reported[13] for the formation of $[(Et_3P)_3PdF]^+$ in solution. This cationic palladium fluoride was never isolated due to its rapid decomposition,[13b] probably by an intramolecular redox process[14] to produce $[(Et_3P)_nPd]$ and Et_3PF_2. Because of this remarkably facile fluoride-induced $Pd^{II}/P^{III} \rightarrow Pd^0/P^V$ reaction,[14] complexes of the type $[(R_3P)_2Pd(F)_2]$ do not exist, whereas their numerous chloro, bromo, and iodo analogues are stable and well-known.

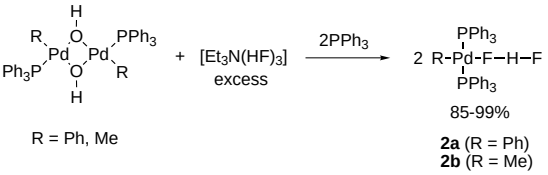
Although the literature data could provide little encouragement for attempting the synthesis of stable palladium fluorides, the very first experiments appeared more successful than we had anticipated. Reacting organopalladium hydroxides with stoichiometric quantities of $Et_3N(HF)_3$ (TREAT HF) in the presence of free phosphine, resulted in the formation of the mononuclear fluoride complexes **1a**, **b** in virtually quantitative yield [Eq. (6)].[15, 16] In the presence of *excess* TREAT HF, the palladium bifluoride complexes **2a**,**b** formed [Eq. (7)].[15]



R = Ph, Me

1a (R = Ph)
1b (R = Me)

(6)

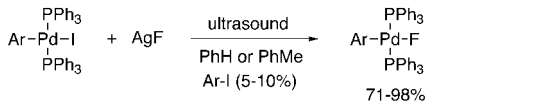


R = Ph, Me

2a (R = Ph)
2b (R = Me)

(7)

Alternatively, palladium fluoride complexes **1a–h** were prepared by the new ultrasound-promoted I/F ligand exchange reaction of $[(Ph_3P)_2Pd(Ar)I]$ with AgF in benzene[15, 16] or toluene[17] [Eq. (8)]. No I/F exchange took place when the reaction was run without sonication. Performing the I/F exchange in the presence of the corresponding aryl iodide (5–10%) was beneficial for the purity of the product.[16] Both the TREAT HF and AgF methods developed in our laboratories have been successfully used by others[18, 19] to prepare fluoro complexes of other transition metals.



(8)

1a (Ar = Ph)
1c (Ar = 4-MeC$_6$H$_4$)
1d (Ar = 4-MeOC$_6$H$_4$)
1e (Ar = 1-naphthyl)
1f (Ar = 4-ClC$_6$H$_4$)
1g (Ar = 4-CF$_3$C$_6$H$_4$)
1h (Ar = 4-O$_2$NC$_6$H$_4$)

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Characterization of organopalladium fluoride complexes: All palladium fluorides and bifluorides [Eqs. (6)–(8)] were characterized by elemental analysis and NMR spectroscopic data. Single-crystal X-ray structures were obtained for two of the fluorides, $[(Ph_3P)_2Pd(Ph)(F)]$ (**1a**)[15, 20] and $[(Ph_3P)_2Pd(4\text{-}NO_2C_6H_4)(F)]$ (**1h**),[17] and one of the bifluorides, $[(Ph_3P)_2Pd(Ph)(FHF)]$ (**2a**).[21] Because the palladium fluoride complexes appeared to be remarkably air- and moisture-stable, X-ray quality crystals of the complexes were grown in air from solvents that had not been dried. Both the structural and solution studies (see below) indicated trans geometry around the palladium atom for all of the fluoride and bifluoride complexes.

X-ray structural studies: The X-ray studies confirmed the presence of a Pd–F bond in the palladium fluoride and bifluoride complexes. The Pd–F bond length of 2.085(3) Å for $[(Ph_3P)_2Pd(Ph)(F)]$ (**1a**),[15] 2.049(2) Å for $[(Ph_3P)_2Pd(4\text{-}NO_2C_6H_4)(F)]$ (**1h**),[17] and 2.098(2) and 2.103(2) Å for $[(Ph_3P)_2Pd(Ph)(FHF)]$ (**2a**; two independent molecules in the asymmetric cell)[21] indicated covalent bonding of the fluoride to the metal atom. The exceptionally strong π basicity of the fluoride ligand[1, 22] is manifested by a number of structural parameters determined for **1a**,[15] **2a**,[21] and also their analogues $[(Ph_3P)_2Pd(Ph)(X)]$ (X = Cl, Br, I).[20] While looking very similar at first sight, these structures exhibit distinct features and interesting trends upon detailed analysis of geometry parameters I–III below.

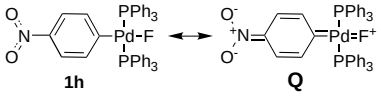
I. The dihedral angle between the σ-aryl ring and the coordination plane CP_2PdX is close to 90° for the weaker π donors (X = I, Br), but deviates considerably from the ideal orthogonal value for X = Cl and F, ligands possessing much stronger π basicity.[1, 22] Optimization of this angle allows for a compromise between destabilization of the Pd–X (X = F, Cl) bond due to $d_\pi - p_\pi$ filled/filled repulsions[22] and perturbation of the aromatic system by push–pull interactions of p_π on X with aromatic π* through filled d orbitals on the palladium atom.

II. The C–C–C *ipso*-angle at the phenyl carbon bound to Pd in the series I (119.2(4)°), Br (117.9(6)°), Cl (117.8(3)°), F (117.0(5)°) suggests[23] that electron-donating properties of the $Pd(PPh_3)_2X$ group *increase* on going from X = I to the lighter, more *electronegative* halogens.[20] The only rationale for this striking observation (so-called "halogen anomaly") could be a considerable increase in π basicity of X = I < Br < Cl < F.

III. Two distinct conformations along the P–Pd–P axis were observed for the structures of $[(Ph_3P)_2Pd(Ph)(X)]$, namely eclipsed (X = F, Cl) and twisted (X = Br, I).[20] The eclipsed conformation apparently favors Pd–F···H–C_6H_4P interactions[15, 17] which alleviate the filled/filled repulsions (see above).

Interestingly, the structure of $[(Ph_3P)_2Pd(Ph)(FHF)]$ (**2a**)[21] exhibited geometry parameters similar to those of $[(Ph_3P)_2Pd(Ph)(I)]$ and $[(Ph_3P)_2Pd(Ph)(Br)]$, rather than of $[(Ph_3P)_2Pd(Ph)(F)]$. All three parameters pointed to considerably diminished π basicity of the FHF ligand as compared with the fluoride ligand, as anticipated.

The *para*-nitrophenyl complex, $[(Ph_3P)_2Pd(4\text{-}NO_2C_6H_4)(F)]$ (**1h**),[17] was studied by single-crystal X-ray diffraction in order to estimate[23] a contribution of the quinoid-type form **Q** to the overall structure [Eq. (9)]. Although spectroscopic evidence was obtained for effects of cross-conjugation in **1h** in



(9)

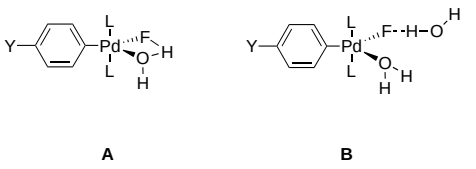
solution,[17] these effects were not strong enough to be observed directly by the X-ray method. Hence, $[Pd(F)(PPh_3)_2]$ is a weaker π donor than NH_2, OR, and NR_2 groups, whose strong π basicity is manifested by the quinoid-type features observed for the X-ray structures of the corresponding *p*-nitrophenyl derivatives.[17, 23]

Characterization of palladium fluorides in solution: A key issue concerning the proposed catalytic loop shown in Scheme 1, was solution behavior of the palladium fluorides. Obviously, synchronous three-center C–F reductive elimination from **1a–h** would be inconceivable if the Pd–F bond was fully ionized in solution.

No chemical evidence of irreversible hydrolysis of the Pd–F bond was observed in chlorinated and aromatic solvents saturated with water. Solution NMR studies,[16] however, revealed a remarkable difference in the behavior of the palladium fluorides in the absence and in the presence of water.

Under rigorously anhydrous conditions, the $^{31}P\{^1H\}$ and ^{19}F NMR spectra of $[(Ph_3P)_2Pd(Ph)(F)]$ (**1a**) in CD_2Cl_2 at 20 °C exhibited a doublet and a triplet, correspondingly, with $J(P–F) = 13.3$ Hz.[15, 16] The ^{13}C NMR signal from the Pd-substituted carbon appeared as a doublet of triplets with $J(C–P) = 6.9$ and $J(C–F) = 50.3$ Hz.[20] Therefore, the structure of **1a** in solution is the same as in the solid state, with the Pd–F bond of **1a** being inert on the NMR time scale.

In sharp contrast, the multiplet resonances described above appeared as broadened singlets in the presence of trace amounts of water.[16] At lower temperatures however, the multiplicity of the $^{31}P\{^1H\}$ NMR signals reappeared for the water-containing samples of **1a**, as well as its aryl-substituted analogues **1c–h**. These NMR experiments suggested that water somehow facilitated cleavage of the Pd–F bond. To gain insight into the mechanism of the Pd–F bond ionization process, solutions of the fluoride complexes **1a–h** in CH_2Cl_2 saturated with water were studied by variable temperature (VT) $^{31}P\{^1H\}$ NMR. Unexpectedly, no correlation was observed between electronic effects of the substituents in the *para*-position of the σ-phenyl ligand and the rate of exchange (temperature of coalescence of the $^{31}P\{^1H\}$ NMR signal). In the series $[(Ph_3P)_2Pd(4\text{-}YC_6H_4)(F)]$, the exchange was slowest for Y = Cl. Both more electron-donating (Y = H, Me, MeO) and electron-withdrawing ($Y = CF_3$, NO_2) groups facilitated the water-induced Pd–F ionization.[16] A plausible rationale for this lack of correlation could be provided by mechanisms **A** and **B** shown in Scheme 2, involving dual-site



A B

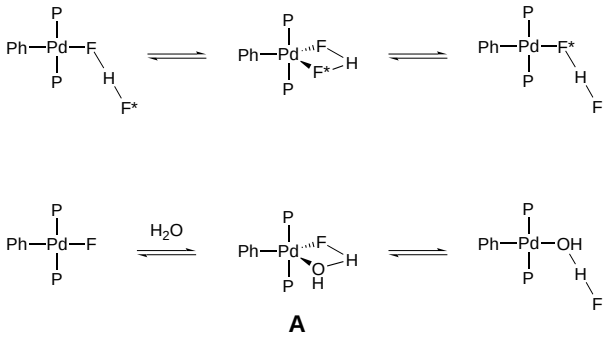
Scheme 2. Dual-site coordination of H_2O to the palladium fluoride molecule ($L = PPh_3$).

coordination of H_2O to the palladium fluoride molecule. As illustrated by Scheme 2, both Pd–O coordination and hydrogen bonding to the F ligand would facilitate ionization of the Pd–F bond. However, nucleophilic attack of H_2O on Pd would be facilitated by electron-withdrawing substituents Y, whereas electron-donating Y would favor hydrogen bonding of the type Pd–F···HOH. An overlap of the two counter-directing effects would result in the lack of correlation observed. Structure **A** of Scheme 2 received strong support from mechanistic studies of solution behavior of the bifluoride analogue of **1a**, $[(Ph_3P)_2Pd(Ph)(FHF)]$ (**2a**).[21]

Even under rigorously anhydrous conditions, **2a** underwent fast F/F exchange (^{19}F NMR) at room temperature. When the exchange was frozen out at $-60\,^{\circ}C$, the ^{1}H, ^{19}F, and $^{31}P\{^{1}H\}$ NMR spectra recorded were in full accord with the structure *trans*-$[(Ph_3P)_2Pd(Ph)(FHF)]$, also observed in the crystalline state.[21] Variable-temperature magnetization transfer studies of **2a** (^{19}F NMR) demonstrated that the rate of F/F exchange was concentration independent. The experiments with samples containing both **2a** and its fluoride analogue **1a** revealed fast exchange between the proximal and distal fluorine atoms of **2a**, much slower exchange involving the metal-bound fluorides of **1a** and **2a**, and no observable exchange between the terminal F of **2a** and the fluoro ligand on **1a** [Eqs. (10)–(12)].

These observations pointed to relatively slow, reversible HF transfer from **2a** to **1a** and back [Eq. (11)] and much faster intramolecular exchange [Eq. (10)] with $\Delta H^{\ddagger} = 33.7$ (2.1) kJ mol^{-1} and $\Delta S^{\ddagger} = -56.1$ (9.6) J mol^{-1} K^{-1}. In agreement with the experimental data, a mechanism for the intramolecular exchange in **2a** involves coordination of the terminal fluorine of the bifluoride ligand to Pd, as shown in Scheme 3. The η^2-FHF species (Scheme 3) clearly resembling complex **A** (Scheme 2) provides strong support for the dual-site coordination mechanism for the hydrolysis of the Pd–F bond (see above).

In concluding this section, solutions of **1a**–**h** in solvents of low polarity are reasonably stable in air, in the absence or presence of water. Under anhydrous conditions at room temperature, the Pd–F bond is inert on the NMR time scale. If water is present, the fluorides undergo reversible hydrolysis which involves dual-site coordination of H_2O to the Pd–F moiety. Although the water-induced Pd–F ionization is fast on the NMR time scale, the equilibrium is shifted to the thermodynamically favored palladium fluoride.

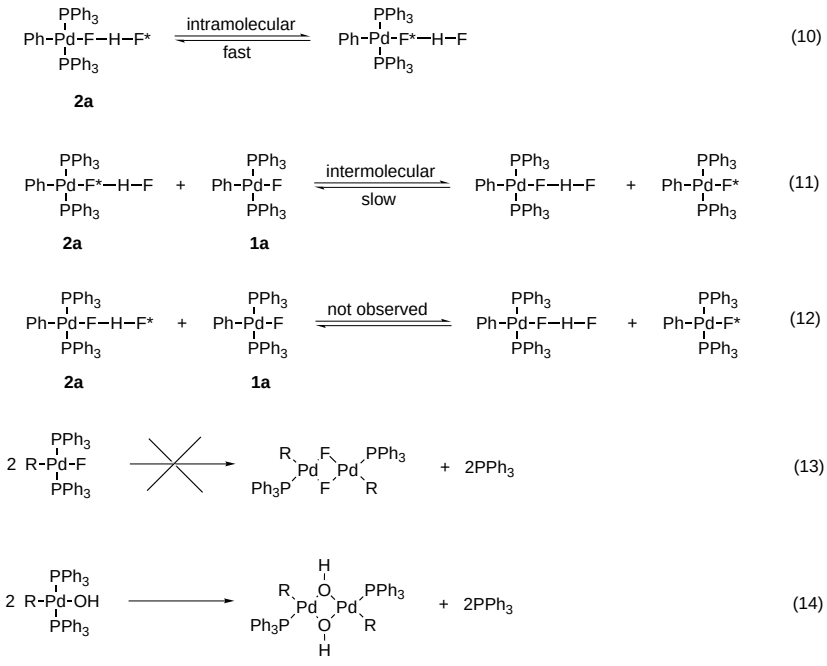


A

Scheme 3. Proposed mechanisms for intramolecular Pd bifluoride exchange (top) and water-induced Pd–F ionization of **1a** (bottom). Compare structures **A** shown in this Scheme and in Scheme 2.

Reactivity of palladium fluoride complexes: Reactivity-wise, the palladium fluorides are remarkably different from their hydroxo, chloro, bromo, and iodo counterparts. Thus, in solution, **1a**–**h** remain monomeric,[15, 16] unlike $[(Ph_3P)_2Pd(R)(OH)]$ which readily dimerize upon loss of one of the phosphines[24] [Eqs. (13), (14)].

Complexes of the type $[(Ph_3P)_2Pd(Ph)X]$ (X = I, Br, Cl) are known[25] to readily react with CO to give $[(Ph_3P)_2Pd(COPh)X]$ which do not undergo reductive elimination even at elevated temperatures. In contrast, $[(Ph_3P)_2Pd(COPh)F]$ formed upon carbonylation of **1a** with CO was stable in solution only below 10 °C, rapidly undergoing reductive elimination of PhCOF at room temperature (Scheme 4).[15] Migratory insertion of CO into the Pd–C



(10)

(11)

(12)

(13)

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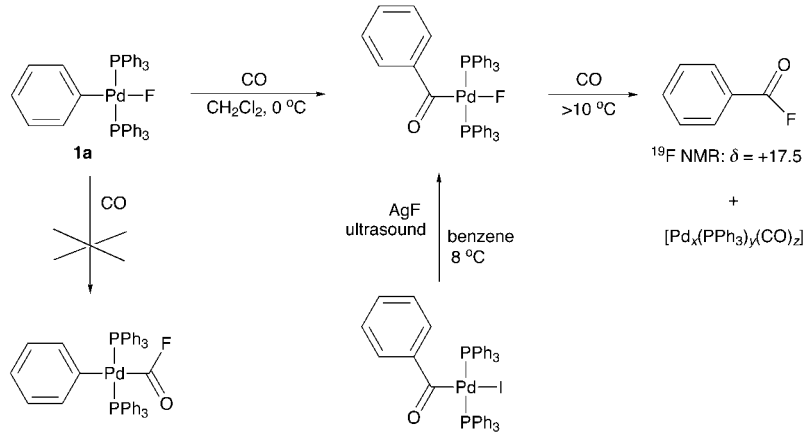


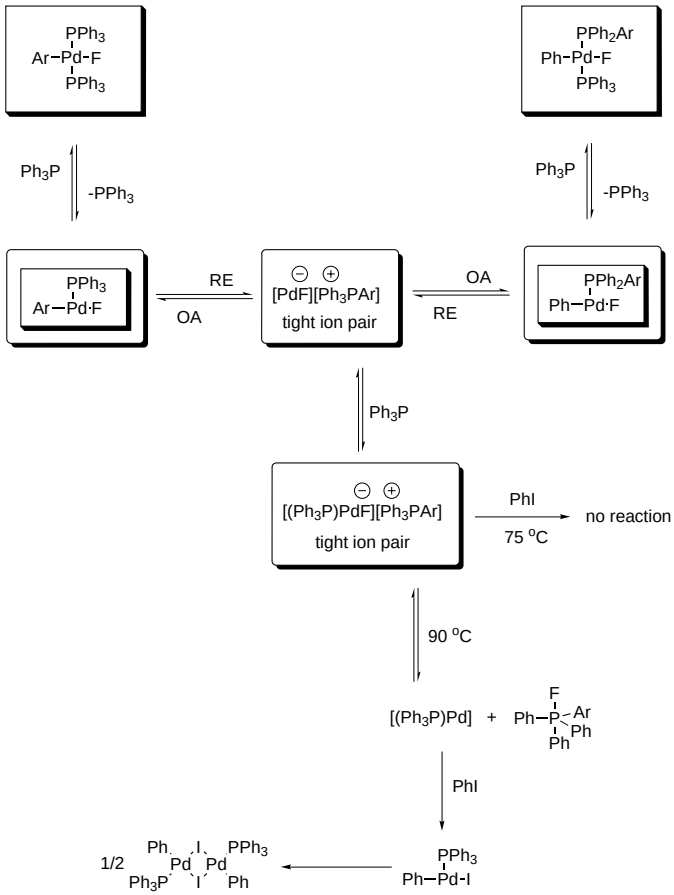
Scheme 4. Carbonylation of **1a** and subsequent reduction elimination of PhCFO.

rather than Pd–F bond of **1a** was confirmed by independent synthesis of $[(Ph_3P)_2Pd(COPh)F]$ from $[(Ph_3P)_2Pd(COPh)I]$ and AgF under sonication. Although attempts to obtain an accurate crystal structure of $[(Ph_3P)_2Pd(COPh)F]$ were unsuccessful, CO insertion into the Pd–C, not Pd–F bond of **1a** was confirmed by X-ray diffraction.

An important issue to be addressed was whether or not the σ-aryl palladium fluoride and bifluoride complexes can reductively eliminate ArF. First, it was found that in rigorously dry benzene or toluene **1a** is considerably more thermally stable than its bifluoride analogue **2a**. The latter was found to decompose within a few hours at 75 °C in toluene to produce Pd^0, benzene, and Ph_3PF_2 [Eq. (15)].[26] This remarkably clean decomposition reaction is proposed to occur by HF dissociation from $[(Ph_3P)_2Pd(Ph)(FHF)]$, followed by HF oxidative addition to form an unstable phenyl Pd^{IV} hydride, $[(Ph_3P)_2Pd(Ph)(F)_2(H)]$. This hydride is expected[27] to undergo fast reductive elimination of benzene, transforming to $[(Ph_3P)_2Pd(F)_2]$ which decomposes[14] to Ph_3PF_2 and $[(Ph_3P)Pd]$. Disproportionation of the latter gives rise to $[(Ph_3P)_3Pd]$ and Pd metal.[26]

The thermal decomposition of **1a–h** in dry toluene at 110 °C was slow, resulting in no C–F reductive elimination products (ArF) but rather P–F bond formation [Eq. (16)]. It was demonstrated[26] that Reaction (16) involves both C–P and P–F reductive elimination from Pd. Mechanistic studies of the thermal decomposition of **1a** and $[(Ph_3P)_2Pd(C_6D_5)(F)]$ revealed that two different processes were involved in the decomposition.

Of the two processes the one shown in Scheme 5 is reversible, occurring even at 75 °C, that is below the actual decomposition temperature (110 °C) of **1a**. Strongly retarded by extra phosphine, this Ph–Pd/Ph–P exchange reaction is similar to those previously observed for analogous iodo, bromo, and chloro palladium aryls (see ref. [24] and references therein). After dissociation of PPh_3 the fluoride complex undergoes reductive elimination to form a tight ion pair, presumably $\{[PdF]^-[Ph_4P]^+\}$ or $\{[(Ph_3P)PdF]^-[Ph_4P]^+\}$, within which the reverse process, P–C oxidative addition occurs. This process is not interrupted by PhI, a scavenger for zero-valent Pd , because in our case the Pd^0 is *anionic* and hence is tightly bound to its counterion reactant. At a higher temperature (90 °C), however, **1a** does react with iodobenzene in toluene to give $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}I)_2]$ and Ph_4PF with > 90 % selectivity [Eq. (17)]. This is due to thermally induced Pd–F dissociation and fluoride transfer to the P atom of the phosphonium cation (Scheme 5). The



Scheme 5. Aryl-aryl exchange reactions and related transformations of **1a** and its deuterated analogue (Ar = Ph or C_6D_5). OA = oxidative addition; RE = reductive elimination.

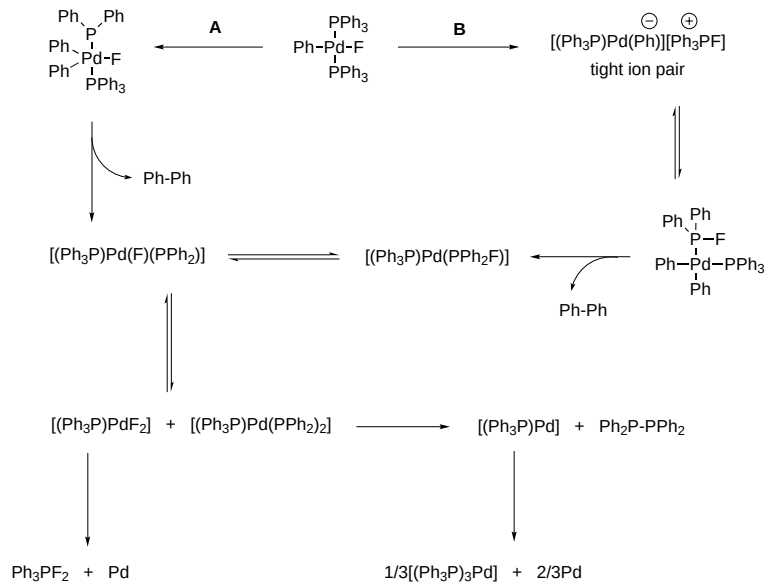
$$3[(Ph_3P)_2Pd(Ph)(FHF)] \xrightarrow[75\ ^oC]{MePh} [(Ph_3P)_3Pd] + 3PhH + 3Ph_3PF_2 + 2Pd \quad (15)$$
2a

$$[(Ph_3P)_2Pd(Ph)F] \xrightarrow[110\text{-}120\ ^oC,\ 16\ h]{toluene,\ N_2} [(Ph_3P)_3Pd] + Pd + Ph\text{-}Ph + Ph_3PF_2 + Ph_2P\text{-}PPh_2 \quad (16)$$
1a

$$[(Ph_3P)_2Pd(Ph)F] + PhI \xrightarrow[90\ ^oC,\ 22\ h]{benzene\text{-}d_6,\ N_2} 1/2\ Ph_3P(Ph)Pd(I)Pd(I)(Ph)PPh_3 + Ph_4PF \quad (17)$$
1a

resulting Pd^0 species is now *neutral* and highly reactive toward the iodobenzene present.

The other process occurring in solutions of the Pd fluoride complexes is less understood mechanistically. It was established that in contrast with the Ph_4P^+ reductive elimination shown in Scheme 5, this second process [Eq. (16)] is *irreversible* and is not shut down in the presence of extra phosphine. Two proposed mechanisms (Scheme 6) account for the formation of all products observed [Eq. (16)], that is α-elimination of a phenyl group from one of the PPh_3 ligands (path **A**) or direct P–F reductive elimination from Pd (path **B**). Both paths are in accord with the fact that *p*-nitrophenyl complex **1h** produced a single biaryl product upon thermal decomposition, 4-nitrobiphenyl.[26] This indicated that the biphenyl produced upon decomposition of **1a** [Eq. (16)] was likely formed from the σ-phenyl ligand and one of the phenyls on the phosphine ligands of the complex.



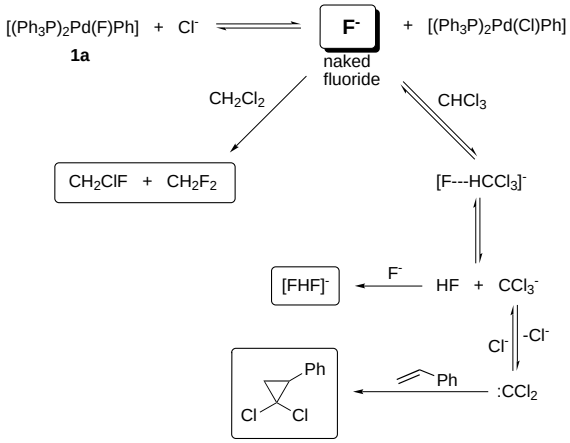
Scheme 6. Two proposed mechanisms for the irreversible thermal decomposition of **1a**.

A number of attempts were made to promote Ph–F reductive elimination from **1a**. The latter was decomposed in the presence of various bidentate phosphines in order to enforce *cis* geometry around palladium to facilitate Ph–F reductive elimination. Nonetheless, only P–F bond formation was observed.[26] Likewise, sonicating a benzene solution of [(dppe)Pd(Ph)(I)] with AgF in benzene produced no PhF but rather $Ph_2P(CH_2)_2P(F)_2Ph_2$ via putative [(dppe)Pd(Ph)(F)] intermediate.

Palladium fluoride complexes as a source of superactive naked fluoride ion: So-called "naked" fluoride ion is the weakly solvated F^- which exhibits uncommonly strong basicity and nucleophilicity. Only a few sources of genuine naked F^- have been reported,[28] all being highly hygroscopic fluorides of onium cations containing no β-hydrogens as to avoid Hofmann elimination. We developed a novel source of naked fluoride using fluoro palladium complexes, for example **1a**.[27]

When studying the relative affinity of Pd in $[(Ph_3P)_2Pd(Ph)]^+$ for halide anions in media of low polarity ($F^- > Cl^- > Br^- > I^-$),[20] it was found that the treatment of **1a** with [PPN]Cl in anhydrous chloroform or dichloromethane gave rise to naked fluoride ions due to ligand exchange [Eq. (18)].[20, 29]

When the F^- was generated in dichloromethane, facile fluorination of the solvent took place, leading to a 5:4 mixture of CH_2ClF and CH_2F_2 (Scheme 7). This nucleophilic fluorination reaction smoothly occurred under uncommonly mild conditions and reached completion within a few hours at room temperature. No other source of naked fluoride has



Scheme 7. Generation and reactions of "naked" fluoride ion from **1a** in CH_2Cl_2 and CH_3Cl.

(18)

been reported to produce the F^- of comparable nucleophilicity. Similarly, dissolving **1a** and [PPN]Cl (1:1.43) in chloroform led to naked fluoride in approximately 60 mM concentration,[29] 30 times greater than ever achieved by any other method.[28] Chloroform solutions of the F^- generated from **1a** were considerably stable, decomposing slowly over the course of days at room temperature. However, the naked fluoride disappeared rapidly upon addition of styrene to the chloroform solution. The reaction produced *gem*-dichlorophenylcyclopropane and FHF^- due to α-elimination by deprotonation of chloroform with the naked fluoride to give dichlorocarbene (Scheme 7). The irreversible trapping of the CCl_2 with styrene shifted all the equilibria in the system toward the formation of the cyclopropane derivative.[29]

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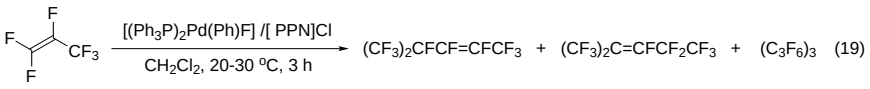
The transformations shown in Scheme 7 demonstrate the exceptional nucleophilicity and basicity of the F^- generated from the palladium fluoride and [PPN]Cl. Two factors contribute to the uncommonly high reactivity of the naked fluoride generated from the Pd complex. First, both compounds employed in the method, namely **1a** and [PPN]Cl are nonhygroscopic. When dissolved in rigorously dry solvents the reagents produce naked fluoride which is H_2O and FHF^--free. Second, the low electrophilicity of $[PPN]^+$ prevents the F^- from coordination to its counterion.

The naked fluoride generated from **1a** and [PPN]Cl was successfully used for catalytic oligomerization of hexafluoropropene [Eq. (19)].[30] Under mild conditions (20–30 °C, 1 atm), 30 g of a mixture of perfluoropropene dimers and trimers was obtained after 3 h with only 0.1 g of **1a** (ca. 0.05 mol %) in the presence of [PPN]Cl (5 equivs) at TOF = $\approx 7.5\ min^{-1}$.



Conclusion

The first soluble palladium fluoride complexes have been synthesized and fully characterized in solution and in the solid state. Chemical properties of these palladium complexes have been studied in detail. The Pd–F bond, covalent in the solid state, remains inert (on the NMR time scale) in solution in low-polar media. The reversible, thermodynamically disfavored ionization of the Pd–F bond is promoted by water. Evidence has been obtained for a dual-site coordination mechanism for the water-induced Pd–F ionization. In dry solvents of low polarity, arylpalladium fluorides undergo F–P and C–P, rather than desired C–F reductive elimination. Nonetheless, both the inertness of the Pd–F bond and the very recently reported reductive elimination of ArX (Ar = bulky aryl,[31] *m*-carboran-9-yl;[32] X = I, Br, Cl) from Pd^{II} suggest that conditions may be found for Ar–F reductive elimination to occur. A novel, simple method has been developed to generate naked fluoride ions from an organopalladium fluoride, in the cleanest way and highest concentration reported to date. The uncommonly high basicity and nucleophilicity of the naked F^- thus produced allowed for mono- and difluorination of dichloromethane, deprotonation of chloroform, and the highly efficient catalytic oligomerization of hexafluoropropene.

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