

Molecular Fluoro Palladium Complexes

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The chemistry of transition metal fluoro complexes^{1,2} is an exciting field which still remains insufficiently explored. Among the intriguing features of organo-transition-metal fluorides are their peculiar reactivity,^{1,2} relevance to metal-mediated C–F bond activation,³ and potential use in catalysis.² Organopalladium complexes containing a fluoro ligand are of special interest for catalysis^{1–5} because Pd–F intermediates likely play a key role in a number of important processes including the cleavage^{3,4} and formation⁵ of C–F bonds. No reports have appeared in the literature describing the isolation and reliable characterization of molecular palladium fluorides.⁶ Considerations of the generalized perturbation theory of the donor–acceptor interaction⁷ do not favor the existence of a stable covalent Pd–F bond. Furthermore, the exceedingly facile fluoride-induced intramolecular reduction, [Pd(II)–P(III)/Pd(0)–P(V)],⁹ seems to be the critical impediment in the synthesis of catalytically important tertiary phosphine Pd fluorides. Because of this redox process, complexes of the type [(R₃P)₂PdF₂] cannot be synthesized, whereas their numerous chloro, bromo, and iodo counterparts are stable and well-studied. In this paper, we report the synthesis and isolation of the first organopalladium tertiary phosphine fluorides, their unexpected reactivity, and the first X-ray structural characterization of a molecular fluoro palladium complex.

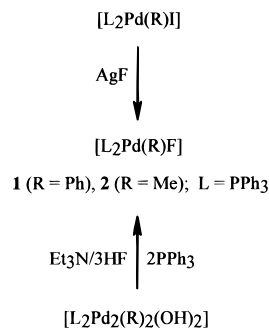
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- (6) (a) Inorganic solid state Pd fluorides have been described, e.g., PdF₂, PdF₄, PdF₂[–], etc. For example, see: Tressaud, A.; Soubeyroux, J. L.; Touhara, H.; Demazeau, G.; Langlais, F. *Mater. Res. Bull.* **1981**, *16*, 207. Bachmann, B.; Mueller, B. G. *Z. Anorg. Allg. Chem.* **1991**, *597*, 9 and references cited therein. (b) A few reports have appeared on Pd phosphine fluorides, all of them being inadequately characterized, e.g., [(Ph₃P)₂Pd(H)F],^{6c} [(Ph₃P)₄Pd₂(μ-F)₂]^{2+,6d} and [(Et₃P)₃PdF]^{+,6e}. The first two have been formulated only on the basis of elemental analysis data, with no evidence for the presence of a Pd–F bond. The third complex has been characterized by ¹⁹F NMR in solution, but never isolated. (c) Doyle, G. J. *Organomet. Chem.* **1982**, *224*, 355. (d) Peacock, R. D.; Kemmitt, R. D. W.; Stocks, J. *J. Chem. Soc. A* **1971**, 846. (e) Dixon, K. R.; McFarland, J. J. *J. Chem. Soc., Chem. Commun.* **1972**, 1274. Cairns, M. A.; Dixon, K. R.; McFarland, J. J. *J. Chem. Soc., Dalton Trans.* **1975**, 1159.
- (7) (a) According to the generalized perturbation theory of chemical reactivity,^{7b} the interaction between “soft” transition metals (Pd²⁺ included) and F[–], the “hardest” base (orbital electronegativity in water = –12.18 eV), is neither charge- nor orbital-controlled and therefore expected to be weak. Although true in general, this prediction is not in line with some experimental observations.^{1,8} (b) Klopman, G. In *Chemical Reactivity and Reaction Paths*; Klopman, G., Ed.; John Wiley and Sons: New York, 1974; p 55.
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Scheme 1



After a mixture of [(Ph₃P)₂Pd(Ph)I] and AgF was sonicated in benzene for 1–6 h (N₂, 20 °C), a new complex, [(Ph₃P)₂Pd(Ph)F] (**1**), was isolated from the solution in over 90% yield.^{10a} These reaction conditions are critical for the synthesis; simply stirring the reagents in benzene resulted in poor conversions and selectivities (³¹P NMR). Attempts to prepare **1** in polar solvents which dissolve AgF, e.g., methanol, acetone, and acetonitrile, were unsuccessful. Complex **1** can also be synthesized (80–97% isolated yield) by the reaction between [(Ph₃P)₂Pd₂(Ph)₂(μ-OH)₂]¹¹ and Et₃N·3HF¹² in the presence of PPh₃ (2.5 equiv) in benzene. The *σ*-methyl derivative, [(Ph₃P)₂Pd(Me)F] (**2**), was prepared similarly (Scheme 1).^{10b} If pure, complexes **1** and **2** can be stored in air for weeks, without any sign of decomposition. Both **1** and **2** are soluble in organic solvents of low polarity, e.g., benzene, chloroform, and dichloromethane, but insoluble in polar solvents, such as acetonitrile or methanol.

The structure of **1** was determined by single-crystal X-ray diffraction (Figure 1).¹³ As no structural studies of molecular fluoro palladium complexes have been reported,^{6,14} the Pd–F bond length might be compared with the Pd–Cl bond distance (2.395(3) Å) in a similar complex, [(Ph₃P)₂Pd(Cl)R], where R = *o*-C₆H₄N(NO)Me.¹⁵ This Pd–Cl bond distance and the difference between the covalent radii of Cl and F (0.99–0.64 = 0.35 Å)¹⁶ suggest that the Pd–F covalent bond length should be around 2.045 Å, close to the experimental value of 2.085(3) Å obtained in this work. This value is also in the range of Pd–F distances (1.89–2.18 Å) determined for solid state Pd fluorides.^{6a} All other structural parameters of the square-planar

(10) (a) A mixture of [(Ph₃P)₂Pd(I)Ph] (162 mg, 0.19 mmol) and AgF (39 mg, 0.31 mmol) in benzene (6 mL) was sonicated under N₂ in the dark at 15–18 °C until the iodo complex disappeared (1–6 h, depending on the size of AgF particles; ³¹P NMR control). The solution was filtered through Celite, reduced in volume, and treated with pentane to give 135 mg (96%) of **1** as white crystals. (b) TREAT HF¹² (27.5 μL, 0.17 mmol) was added to a suspension of [(Ph₃P)₂Pd₂(Me)₂(μ-OH)₂] (202 mg, 0.25 mmol), PPh₃ (140 mg, 0.53 mmol), and benzene (10 mL), and the mixture was stirred for 1 h. The benzene solution was filtered through Celite, reduced in volume, and treated with pentane to give 283 mg (84%) of spectroscopically pure **2** as a yellowish solid. Recrystallization from CH₂Cl₂/toluene gave colorless crystals of **2**.

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(12) (a) Triethylamine tris(hydrogen fluoride), “TREAT HF”, is a new, versatile fluorinating agent which has already been widely used in organic synthesis, but never employed before in the chemistry of transition metals.^{12b} (b) McClinton, M. A. *Aldrichimica Acta* **1995**, 28, 31.

(13) Crystal data: C₄₂H₃₅FP₂Pd, orthorhombic, *Pbca*, Mo Kα radiation, data collection at 163(2) K, *a* = 11.497(2), *b* = 23.932(3), and *c* = 24.811(3) Å, *V* = 6827(2) Å³, *Z* = 8. The structure was solved by direct methods and refined by a full-matrix least-squares technique in an anisotropic approximation for nonhydrogen atoms. The hydrogen atoms were refined in an isotropic approximation with fixed *U*_{iso} = 0.05 Å². For 3694 observed reflections with *I* > 2σ(*I*), the structure was refined to *R* = 0.047 and *R*_w = 0.048.

(14) A structurally characterized complex with a weak Pd···FBF₃ coordination (2.335(5) Å) has been reported: Rheingold, A. L.; Wu, G.; Heck, R. F. *Inorg. Chim. Acta* **1987**, *131*, 147.

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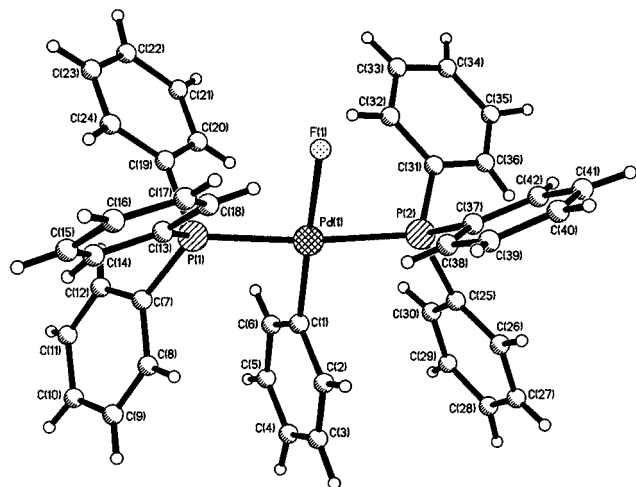


Figure 1. Molecular structure of complex **1**. Selected bond distances (Å) and angles (deg): Pd(1)–F(1) 2.085(3), Pd(1)–C(1) 1.998(5), Pd(1)–P(1) 2.315(1), Pd(1)–P(2) 2.318(1), F(1)–Pd(1)–C(1) 179.0(2), C(1)–Pd(1)–P(1) 91.1(1), C(1)–Pd(1)–P(2) 92.5(1), F(1)–Pd(1)–P(1) 89.90(9), F(1)–Pd(1)–P(2) 86.57(9), P(1)–Pd(1)–P(2) 174.24(5).

complex **1** have expected values;¹⁷ the Pd, F, and two P atoms deviate from the mean least-squares plane by no more than 0.046 Å.

The ¹H, ¹⁹F, and ³¹P NMR spectra¹⁸ of **1** and **2** in rigorously dry solvents, e.g., C₆H₆, CHCl₃, and CH₂Cl₂,¹⁸ indicate that all ligands on the Pd atom are inert. For both fluoro complexes, the ³¹P NMR resonances appeared as doublets at 19.5 and 24.5 ppm with *J*_{PF} = 13.3 and 12.5 Hz, respectively, while triplets with the same coupling constants were found in the ¹⁹F NMR spectra of **1** (*δ* = –274 ppm) and **2** (*δ* = –268 ppm). These data point to covalent character of the Pd–F bond in media of low polarity. Remarkably, in solvents containing small amounts of dissolved water, e.g., CH₂Cl₂, ambient temperature ³¹P and ¹⁹F NMR spectra of **1** and **2** displayed broadened singlets with chemical shifts virtually indistinguishable from those of the corresponding multiplets (see above) and $\Delta\nu_{1/2}$ = 10–20 (³¹P) and 50–100 (¹⁹F) Hz. Cooling these samples to +5 °C resulted in the transformation of the broadened ³¹P NMR singlet peaks into well-resolved doublets identical with those observed for anhydrous solutions of **1** and **2** at 20 °C.¹⁸ Clearly, fluoro ligand exchange takes place in “wet” solutions of **1** and **2**, its rate at coalescence (ca. +10 °C) in CH₂Cl₂ being comparable with the values of the observed P–F coupling constants. No other resonances were found in the low-temperature ³¹P NMR spectra, suggesting that equilibria between the fluoro complexes and products of the Pd–F bond ionization are shifted almost entirely toward the covalent Pd fluorides. Other observations supported this conclusion.

The *o*-phenyl proton resonances of **1**^{18a} are more than 1 ppm upfield from those of the recently reported cationic complex, [(Ph₃P)₂Pd(Ph)]⁺ BF₄[–],¹⁹ both spectra being obtained for CDCl₃

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(18) (a) For complex **1**: ¹H NMR (CDCl₃, 20 °C) *δ* 6.2 (t, 2H, *J* = 7.3 Hz, 3,5-C₆H₃Pd), 6.35 (t, 1H, *J* = 7.0 Hz, 4-C₆H₃Pd), 6.55 (d, 2H, *J* = 7.3 Hz, 2,6-C₆H₃Pd), 7.1–7.6 (m, 30H, C₆H₅P); ¹⁹F NMR (CD₂Cl₂, 20 °C) *δ* –274 (t, *J*_{FP} = 13.3 Hz); ³¹P NMR (CD₂Cl₂, 20 °C) *δ* 19.5 (d, *J*_{PF} = 13.3 Hz). (b) For complex **2**: ¹H NMR (CDCl₃, 20 °C) *δ* –0.1 (t, 3H, *J*_{PH} = 5.8 Hz, CH₃Pd), 7.2–7.8 (m, 30H, C₆H₅P); ¹⁹F NMR (CH₂Cl₂, 20 °C) *δ* –268 (t, *J*_{FP} = 12.5 Hz); ³¹P NMR (CH₂Cl₂, 20 °C) *δ* 24.5 (d, *J*_{PF} = 12.5 Hz).

solutions. Upon addition of Et₂O·BF₃ (1.5 equiv) to **1** in CDCl₃, the originally colorless solution immediately turned red, exhibiting ¹H and ³¹P NMR patterns similar to those described for the orange-pink [(Ph₃P)₂Pd(Ph)]⁺ BF₄[–] and a resonance at –151 ppm in the ¹⁹F NMR spectrum (BF₄[–]). Complex **1** is unreactive toward styrene in the absence of a base, whereas [(Ph₃P)₂Pd(Ph)]⁺ smoothly phenylates styrene under similar conditions.¹⁹ Both fluoro complexes can be quantitatively recrystallized from solvents containing water to yield well-shaped, transparent crystals which do not change upon drying. Redissolving these crystals in anhydrous dichloromethane furnished samples exhibiting the P–F coupling¹⁸ in their ³¹P and ¹⁹F NMR spectra at 20 °C. It is noteworthy that crystals of **1** for the X-ray study were grown in air from benzene/pentane which had not been dried.

The existence, stability, and reactivity of complexes **1** and **2** are surprising. In terms of both steric and electronic (orbital electronegativity) factors,^{7b} the closest analogue of F[–] is hydroxide anion. A few isolable organoplatinum complexes, [(R₃P)₂Pt(X)R’], where X = OH²⁰ and F,²¹ have been reported. However, their hydroxo palladium congeners, [(Ph₃P)₂Pd(OH)R’] (R’ = Me, Ph), cannot be isolated as they are thermodynamically and kinetically unstable, decomposing to free phosphine and the corresponding OH-bridged dimer.²² Unexpectedly, complexes **1** and **2** are stable, exhibiting no sign of decomposition in the solid state or dimerization in solution.²³ The reactivity of **1** and **2** toward CO also differs from that of their well-known analogues containing halogens other than F. Complexes of the type [(Ph₃P)₂Pd(R)X] (X = Cl, Br, and I) readily react with CO to give stable products of CO insertion, [(Ph₃P)₂Pd(COR)X], which do not undergo reductive elimination of RCOX.²⁴ This reaction is a key step for various Pd-catalyzed carbonylation processes.²⁵ In contrast, the carbonylation of **1** in benzene (1 atm, 20 °C) resulted in the formation of PhCOF,²⁶ along with Pd(0) carbonyl phosphine complexes.²⁷ Details of this study will be reported separately.

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Supporting Information Available: Crystallographic details, atomic coordinates, bond lengths and angles, isotropic and anisotropic parameters, and ORTEP drawings for **1** (9 pages). See any current masthead page for ordering and Internet access instructions.

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(23) However, like [(Et₃P)₂Pt(Ph)F],^{21a} **1** and **2** form stable 1:1 adducts with HF, e.g., if their synthesis from the hydroxo dimers^{10b} is conducted in the presence of excess TREAT HF. Satisfactory elemental analyses were obtained for both adducts. The ¹H NMR spectra of **1**·HF and **2**·HF in CDCl₃ display broad singlets at 12.5 ppm (1H) due to the HF₂ ligand, in addition to spectral patterns almost indistinguishable from those of **1** and **2**. Broadened singlets at 20.2 and 25.6 ppm with $\Delta\nu_{1/2}$ = 10–20 Hz are observed in the ³¹P NMR spectra (CH₂Cl₂) of **1**·HF and **2**·HF, respectively. Due to exchange processes, ¹⁹F NMR signals of **1**·HF and **2**·HF in various solvents are too broad to be observed at room temperature.

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(27) Treatment of these Pd(0) complexes with PhI under CO results in the quantitative formation of [(Ph₃P)₂Pd(COPh)]₂.²⁴