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[12] The vesicles were prepared as follows: A small amount of THF (0.3–0.5 mL) and distilled water (10 mL) were added to a vial containing an equimolar ratio (6.9 μmol) of three components: CB[8], viologen with a long alkyl chain ($C_1VC_{12}^{2+}$ or $C_1VC_{16}^{2+}$), and 2,6-dihydroxynaphthalene. The resulting suspension was sonicated at 60°C for 1 h to remove the initially added THF and then kept overnight at room temperature to give a transparent (**2**) or turbid (**3**) solution. The formation of 1:1:1 ternary complexes in **2** and **3** has been confirmed by UV/Vis and ^{1}H NMR spectroscopy as well as ESI mass spectrometry. **2**: ^{1}H NMR (500 MHz, D_2O, 25°C, TMS) $\delta = 8.81$ (2H, brs), 8.54 (2H, brs), 7.73 (2H, brs), 7.25 (2H, brs), 6.87 (3H, brs), 6.64 (3H, brs), 6.45 (2H, brs), 5.89 (2H, brs), 5.75 (16H, d), 5.47 (16H, s), 4.54 (3H, s), 4.17 (16H, d), 2.26 (2H, brs), 1.75–1.15 (18H, brs), 0.86 (3H, brs); UV/Vis (H_2O): $\lambda_{CT} = 552$ nm; ESI-MS: m/z (%): 914.30 (100) [M^{2+}]. **3**: ^{1}H NMR (500 MHz, D_2O, 25°C, TMS) $\delta = 9.02$ (2H, brs), 8.49 (2H, brs), 7.56 (2H, brs), 7.21 (2H, brs), 7.10–6.04 (6H, brs), 5.74 (16H, d), 5.46 (16H, s), 4.16 (16H, d), 2.42–0.65 (34H, brs); UV/Vis (H_2O): $\lambda_{CT} = 548$ nm; ESI-MS: m/z (%): 942.86 (70) [M^{2+}].

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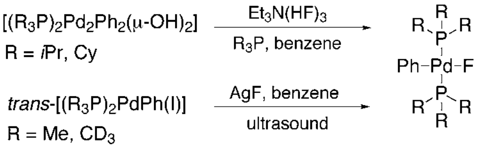
Is Fluoride Bonded to Two Pd Acceptors Still Basic? Three CH_2Cl_2 Molecules Encapsulating a $Pd_2(\mu\text{-}F)_2$ Square and New Implications for Catalysis**

Vladimir V. Grushin* and William J. Marshall

Organotransition-metal fluoro complexes have recently received much attention due to their useful, uncommon properties,[1] and potential use in the synthesis of highly desired, selectively fluorinated organic molecules,[2–4] in catalysis,[5,6] and in C–H activation.[7] Further progress in this new, promising area will depend on firm knowledge of the nature and reactivity of the metal–fluorine bond. As a ligand for the catalytically important platinum group metals, fluoride still remains scantily explored. Thus, being ubiquitous in catalysis, palladium has been shown[6,8] to form isolable fluoro complexes only recently. Here we report on the synthesis, unexpectedly strong basicity, and peculiar reactivity of the first dinuclear organopalladium μ-fluorides and their mononuclear analogues stabilized by (alkyl)$_3$P ligands.

Using our previously developed methods[6,8] we prepared a series of new Pd fluorides **1**–**6** [Eq. (1) and (2)], which were characterized by analytical, spectroscopic, and X-ray diffraction data (see Supporting Information for details).[9]



(1)

64-96%

1 (R = *i*Pr); **2** (R = Cy);
3 (R = Me); **4** (R = CD_3)

$$[(R_3P)_2Pd_2Ph_2(\mu\text{-}I)_2] \xrightarrow[\text{ultrasound}]{\text{AgF, benzene}} [(R_3P)_2Pd_2Ph_2(\mu\text{-}F)_2] \quad (2)$$

60-82%

5 (R = *i*Pr); **6** (R = Cy)

Considering the particularly strong π basicity of coordinated terminal fluoride[1,6,10–12] and the enhanced donating properties of iPr_3P (compared to Ph_3P), Pd–F d_π–p_π filled/filled repulsions in **1** and **3** were expected to be stronger than in their Ph_3P analogue [$(Ph_3P)_2PdPh(F)$],[8] resulting in elongation rather than shortening of the Pd–F bond. Surprisingly, the Pd–F bond lengths in both **1** (Figure 1; 2.050(2) and 2.057(2) Å for two structurally similar molecules in the asymmetric unit), and **3** (Figure 2; 2.057(2) Å) are shorter

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

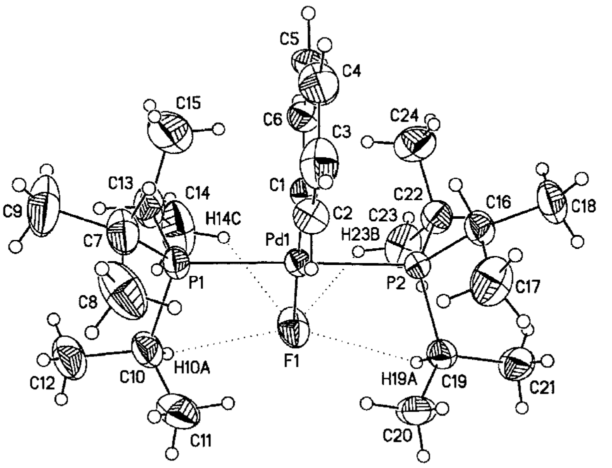

Figure 1. Structure of **1** (ORTEP view; 50% probability ellipsoids), showing C–H···F interactions (2.434–2.575 < 2.67 Å = sum of the van der Waals radii).

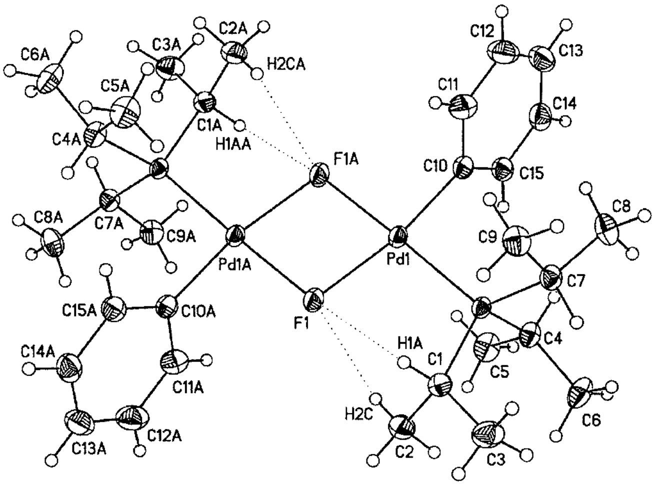

Figure 3. Structure of **5** (ORTEP view; 50% probability ellipsoids), showing PCH···F (2.593 Å) and CCH···F (2.399 Å) contacts.

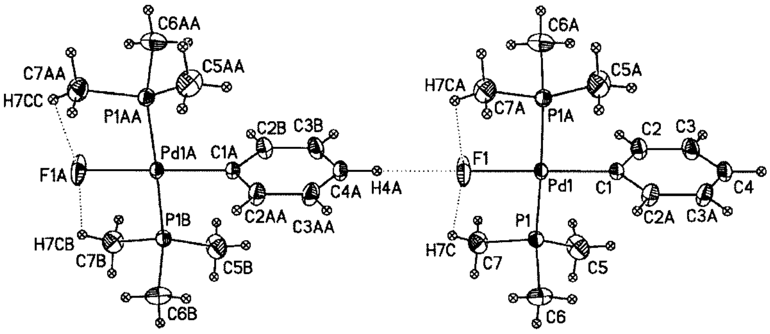

Figure 2. Structure of **3** (ORTEP view; 50% probability ellipsoids), showing intramolecular and intermolecular C–H···F contacts.

than in [$(Ph_3P)_2PdPh(F)$] (2.085(3) Å).[8a] The opposite effect observed could be accounted for only[13] by stronger C–H···F–M interactions[1,6,14] (Figure 1 and 2) efficiently alleviating the Pd–F filled/filled repulsions in **1** and **3**. A previously unobserved combination of both intramolecular[14b–d] and intermolecular[14a] C–H···F–M interactions was found in **3** (Figure 2); the intermolecular CH···F contact to the para-H(sp^{2}C) was surprisingly shorter (2.370 Å) than the intramolecular F···H(sp^{3}C) distance of 2.496 Å.

Homobimetallic μ^2-F complexes of the platinum group metals are extremely rare, especially for Pd and Pt.[11h,15] As a result, little is known about the basicity of μ^2-F bridging two platinum metal Lewis acid centers. It was logical to propose that the binding to two Pd^{II} acceptors would eliminate π-basic properties of the F atoms in **5** and **6**, much like in metal bifluorides.[12] Nonetheless, C–H···F interactions were found in **5** (Figure 3), the first dinuclear organopalladium complex with a fluoride bridge. Therefore, even when coordinated to two Pd centers fluoride retains considerable excessive basicity that requires additional interactions with an electron acceptor for stabilization.[15b,c]

Further manifestation of the striking basicity of fluoride bound to two Pd atoms came from the ability of **6** to form a stable hydrogen-bond adduct with CH_2Cl_2. In pure form, **6** was isolated as a white powder of limited solubility in benzene and toluene. Recrystallization of **6** from CH_2Cl_2/hexane produced clear crystals which, to our surprise, were readily soluble in aromatic solvents. A singlet at $\delta = 4.3$ ppm was observed in the ^1H NMR spectrum ([D$_6$]benzene) of the recrystallized **6**. The difference in the behavior of **6** before (the signal at $\delta = 4.3$ ppm was absent) and after the recrystallization prompted us to analyze the recrystallized material by X-ray diffraction (Figure 4).

As seen from Figure 4, *three* CH_2Cl_2 molecules are hydrogen-bonded to the Pd_2F_2 core of **6**. One of the three CH_2Cl_2 molecules is coordinated to both F ligands through the two hydrogen atoms in a bridging fashion (H···F 2.492 Å). The other two CH_2Cl_2 molecules are "terminal", forming much shorter H···F contacts of 2.083 Å.[16] Owing to the CH_2Cl_2 interactions, the Pd_2F_2 fragment is distorted[15a] from the planar geometry (found in **5**); the fluorides tilt toward the central dichloromethane molecule. The Pd–F bond lengths in **6**·3CH_2Cl_2 are slightly longer than in **5**, that is, 2.119(1) versus 2.098(1) Å *trans* to P and 2.134(1) versus 2.118(1) Å *trans* to Ph.

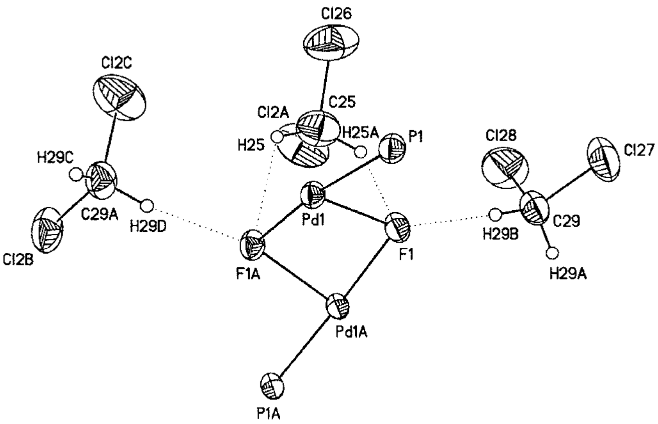

Figure 4. Structure of the Pd_2F_2 core of **6** (ORTEP view; 50% probability ellipsoids) with three CH_2Cl_2 molecules hydrogen-bonded to the fluorine atoms.

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Under anhydrous conditions, the F ligand is inert on the NMR time scale for all **1**–**6** (see Supporting Information). The dimers **5** and **6** exist in PhH or PhMe solution as 2–3:1 mixtures of *anti* and *syn* isomers, for which no fast (NMR) interconversion was observed at 20 °C. Thus, well-resolved multiplets were observed in the ^{19}F NMR spectrum of **6** in [D$_8$]toluene, a doublet at $\delta = -302.3$ ppm with *trans* $J(\mathrm{P,F}) = 142$ Hz (*anti* isomer) and two 1:1 signals (*syn* isomer) at $\delta = -280.0$ ppm (*trans* to P; doublet of triplets, $J(\mathrm{P,F}) = 157$, $J(\mathrm{F,F}) = 60$ Hz), and $\delta = -324.9$ ppm (doublet, $J(\mathrm{F,F}) = 60$ Hz). The ^{31}P NMR spectrum exhibited two doublets at $\delta = 42.2$ (*syn*) and 44.7 ppm (*anti*) with the same *trans* $J(\mathrm{P,F})$ of 157 and 142 Hz, respectively. In contrast, only broad unresolved resonance signals with similar chemical shifts were observed in the NMR spectrum of $\mathbf{6}\cdot 3\,CH_2Cl_2$, suggesting exchange. The latter did not influence substantially the thermodynamics of the *syn*–*anti* isomerization as the same *anti* to *syn* ratio of 3 was observed for **6** and $\mathbf{6}\cdot 3CH_2Cl_2$ in toluene or benzene. ^{1}H NMR studies of $\mathbf{6}\cdot 3CH_2Cl_2$ in [D$_8$]toluene, in the absence or presence of two extra equivalents of CH_2Cl_2, led to the observation of only one singlet ($\delta = 4.3$ ppm) for *all* the dichloromethane in the sample at 20 °C, indicating fast inter- and intramolecular exchange processes. On cooling the sample to −80 °C the singlet from CH_2Cl_2 in exchange did not resolve but shifted upfield to $\delta = 3.9$ ppm. Therefore, the exchange processes could not be frozen out at −80 °C. The $\Delta\delta$ value of 0.4 ppm resulting from the cooling of the sample from 20 °C ($\delta = 4.3$ ppm) to −80 °C ($\delta = 3.9$ ppm) is less significant than the $\Delta\delta$ value of 1.05 ppm (5.35 (free CH_2Cl_2)−4.3 ($\mathbf{6}\cdot n\,CH_2Cl_2$) ppm) at 20 °C. This points to efficient hydrogen bonding of the CH_2Cl_2 molecules to the Pd_2F_2 square in solution even at ambient temperature.

The high π basicity of the F ligand and C−H···FM interactions in **1**–**6** may bear implications for some catalytic reactions involving platinum metal fluoride complexes.[3,5,6] The thermal decomposition of **3** in toluene under rigorously anhydrous conditions (N_2) at 115 °C (> 95 % conversion after 72 h; monitored by ^{19}F and ^{31}P NMR) produced Pd metal, Me_3PF_2, $Me_2(Ph)PF_2$, and $[Me_3PPh]^+FHF^-$. Both difluorophosphoranes (unambiguously identified by their characteristic ^{19}F and ^{31}P NMR spectra[17]) and the phosphonium cation emerged from C−P and P−F reductive elimination reactions similar to those described for $[(Ph_3P)_2PdPh(F)]$.[6] In contrast, the formation of bifluoride (^{19}F NMR spectroscopy: broadened doublet, $\delta = -142.6$ ppm, $J(\mathrm{H,F}) = 121$ Hz)[18] was unexpected. Apparently, the source of hydrogen in the FHF^- was the Me groups of the Me_3P ligands, as was demonstrated by repeating the experiment with **4**, the $(CD_3)_3P$ analogue of **3**. Owing to broadening ($\Delta\nu_{1/2} =$ ca. 50 Hz) the bifluoride ^{19}F resonance signal appeared as an unresolved singlet ($J(\mathrm{D,F}) = 18.8$ Hz)[18] but no H,F coupling of about 120 Hz was observed. While the basic fluoride[3k] might deprotonate the phosphonium salt product, it is also conceivable that the intramolecular C−H···F−Pd interactions (see above) mediate proton abstraction at elevated temperatures.[19,20] This reaction path is worth taking into consideration when using (alkyl)$_3$P late transition metal fluorides in synthesis and catalysis.

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[20] Thermal decomposition of **1**, **2**, **5**, and **6** under similar conditions did not produce observable free FHF^- but rather led to the formation of PdFHF species, as can be judged by the appearance of ^{19}F resonance signals at about $\delta = -280$ and -180 ppm from the proximal and distal F, respectively.[12]

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