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Synthesis and Reactivity of Palladium(II) Fluoride Complexes Containing Nitrogen-Donor Ligands

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Abstract

This article describes the synthesis, characterization, and reactivity of palladium(II) fluoride complexes containing sp^2 and sp^3 nitrogen-containing supporting ligands. Both *cis* and *trans* complexes of general structure $(N)(N')Pd^{II}(R)(F)$ ($R = Ar$ or CH_3) as well as *cis*- $(N)_2Pd^{II}(F)_2$ are reported. Crystallographic characterization of these molecules has allowed structural comparisons to related phosphine-ligated species. Furthermore, these studies have revealed that nitrogen-donor ligands support some of the longest and the shortest Pd–F bonds reported to date. The thermal decomposition of $(N)(N')Pd^{II}(R)(F)$ has also been examined, and no products of C–F bond-forming reductive elimination were obtained in any cases.

Introduction

Organopalladium complexes containing fluoride ligands are of significant current interest due to their potential intermediacy in both C–F activation and C–F bond-forming transformations.^{1,2} Grushin and coworkers published the first example of an isolable aryl palladium fluoride complex, *trans*-(PPh_3)₂ $Pd^{II}(Ph)(F)$, in 1997.³ Following this seminal report, a variety of related compounds bearing phosphine supporting ligands have been prepared and characterized.^{2–5} The thermal decomposition of all of these complexes has been studied in detail, with the ultimate goal of achieving C–F bond-forming reductive elimination to generate aryl fluorides. However, this transformation has proven challenging, as P–F bond-formation typically predominates over the desired C–F coupling in these Pd^{II} phosphine complexes.^{4,6}

In contrast to the extensive literature on $Pd^{II}(R)(F)$ phosphine complexes, palladium fluorides bearing nitrogen-donor ligands remain rare.⁷ Early reports suggested that phosphines might be essential to stabilize the M–F bond; however, very recent communications by our group²ⁱ and by Grushin⁸ have shown that sp^2 nitrogen-donors can also support stable $Pd^{II}(Ar)(F)$ species. Such adducts could be valuable intermediates for C–F bond-forming transformations, since competing P–F coupling is clearly not possible in these systems. Herein, we report the synthesis, characterization, and reactivity of a series of aryl and alkyl palladium fluorides containing both sp^2 and sp^3 nitrogen donor ligands. X-ray crystallographic characterization of many of these complexes has allowed structural comparisons to related phosphine-containing species. In addition, the thermal decomposition of the new compounds has been investigated.

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†Electronic Supplementary Information (ESI) available: Full details of the crystallographic data for compounds **8**, **10–13**, and **15**. See DOI: 10.1039/b000000x/

Results and Discussion

Our general synthetic approach to the palladium(II) fluoride complexes described herein involved reaction of the corresponding Pd^{II} iodides with AgF, using a procedure very similar to that developed by Grushin.^{2a} The palladium(II) iodide precursors, in turn, were prepared using three different synthetic strategies that are summarized in Scheme 1. The cyclometalated C~N complexes **2–5** were generated by reaction of the readily available cyclopalladated dimers [(phpy)Pd(I)]₂⁹ (**1a**) and [(bzq)Pd(I)]₂ (**1b**) (phpy = 2-phenylpyridine; bzq = benzo[*h*]quinoline) with 2,6-lutidine, 4-*tert*-butylpyridine (*t*Bu-py), or PPh₃, respectively. Complex **6** was accessed by reaction of the known pincer complex (NCN)Pd(Br)¹⁰ (NCN = *N,N,N',N'*-tetramethyl-1,3-xylylenediamine) with NaI. Finally, **7** was prepared by reaction of (*t*Bu-bpy)Pd(Me)₂¹¹ (*t*Bu-bpy = 4,4'-di-*tert*-butylbipyridine) with MeI.

Synthesis of (phpy)Pd(lutidine)(F), **8** and (phpy)Pd(*t*Bu-py)(F), **9**

The 2-phenylpyridine complexes **8** and **9** were prepared by sonication of **2** and **3** with AgF in benzene under an N₂ atmosphere for 5 h at 25 °C. The products were isolated by filtration through Celite and recrystallization from CH₂Cl₂/pentanes to afford **8** as a yellow solid (47%) and **9** as a white solid (45%). Analysis of **8** and **9** by ¹⁹F NMR spectroscopy revealed characteristic Pd^{II} fluoride resonances as broad singlets at –260.3 ppm and –243.4 ppm, respectively. The ¹H NMR spectrum of **8** shows signals indicative of an unsymmetrical square planar complex, with H_a and H_b of the 2-phenylpyridine ligand appearing as doublets at 8.70 and 5.77 ppm, respectively. Similar diagnostic upfield and downfield peaks were observed in the ¹H NMR spectrum of **9** at 8.96 (H_a) and 6.50 ppm (H_b). Notably, the ¹H NMR resonances for H_a in **8** and **9** appear approximately 1 ppm upfield from those in the corresponding palladium(II) iodides **2** and **3** (9.89 and 9.91 ppm, respectively). Literature precedent suggests that this large Δδ is indicative of a *cis* orientation between the fluoride ligand and the pyridine nitrogen of the phpy (Scheme 2).⁹

It is particularly notable that both **3** and **9** are stable, isolable complexes that do not undergo loss of the 4-*tert*-butylpyridine ligand (with concomitant generation of halide bridged Pd dimers) upon work up. In contrast, previous reports have suggested that alkyl/aryl substituents at the 2-and/or 6-positions of the pyridine ligand are frequently necessary to limit formation of halide bridged dimers in related systems.⁹

Recrystallization of **8** by slow diffusion of pentanes into a THF solution at –35 °C afforded colorless needles suitable for X-ray crystallographic analysis. The X-ray structure of **8** is shown in Figure 1, and it confirms the predicted *cis* configuration of the phpy nitrogen atom and the fluoride ligand. Interestingly, the Pd–F bond distance of 2.1024(17) Å in **8** is the longest reported for an isolable monomeric Pd^{II}(Ar)(F) complex. The next closest is 2.085(3) Å in *trans*-(PPh₃)₂Pd(Ph)(F).^{3, 12}

Synthesis of (bzq)Pd(lutidine)(F), **10**

Compound **10** was prepared as a yellow solid (57% yield) using an analogous procedure to the synthesis of **8** and **9** (Scheme 3). Its ¹⁹F NMR spectrum contains a broad singlet at –270.4 ppm for the Pd-bound fluoride ligand. The ¹H NMR spectrum of **10** shows signals indicating an unsymmetrical square planar complex, with H_a and H_b of the benzo[*h*]quinoline ligand appearing as doublets at 9.03 and 5.95 ppm, respectively. Similar to **8** and **9**, the chemical shift of H_a in **10** is nearly 1 ppm upfield from that of the corresponding Pd iodide (**4**), indicative of a *cis* orientation of the fluoride and bzq nitrogen ligands.

Slow diffusion of pentanes into a CH₂Cl₂ solution of **10** in CH₂Cl₂ at –35 °C provided yellow blocks of this complex. An X-ray crystal structure was obtained, and the structure of **10** is shown in Figure 2. As predicted on the basis of the NMR spectral data, this complex contains *cis* fluoride and bzq nitrogen substituents. Notably, the sole difference between complexes **8** and **10** is the nature of the cyclometalated ligand. In the 2-phenylpyridine complex **8**, this ligand is slightly twisted out of the square plane with a C11–C6–C5–N1 dihedral angle of 6.16 °. In contrast, the more rigid benzo[*h*]quinoline¹³ of **10** is essentially planar (the C11–C12–C13–N1 dihedral angle in **10** is 0.75 °). The increased rigidity of **10** may account for the significantly shorter (by 0.042 Å) Pd–F bond (2.0604(12) Å) and significantly longer (by 0.017 Å) Pd–C bond (1.9769(19) Å) in this complex relative to those in **8**.

Synthesis of (bzq)Pd(PPh₃)(F), **11**

Compound **11** was isolated as a pale yellow solid in 84% yield from the reaction of **5** with AgF (Scheme 3). In this case, the fluoride ligand appears as an apparent singlet at –247.2 ppm by ¹⁹F NMR spectroscopy. In addition, the ³¹P NMR spectrum of **11** shows a corresponding broad doublet at 40.7 ppm. The ³¹P/¹⁹F coupling constant (*J*_{PF} = 8 Hz) is similar to that observed for other *cis* fluoride and phosphine ligands at Pd^{II} centers.^{2a,3,4c}

X-ray quality crystals of **11** were obtained by slow diffusion of pentanes into a CH₂Cl₂ solution at –35 °C, and the structure of **11** is shown in Figure 3. Compound **11** is unique in that it is the first example of a Pd^{II} aryl fluoride containing both P- and N-donor ligands. Replacing the 2,6-lutidine of **10** with a PPh₃ in **11** leads to a 0.027 Å increase in the Pd–C_{bzq} bond length to 2.004(2) Å. This may be due to unfavourable steric interactions between the *cis* PPh₃ and σ-aryl_{bzq} groups. Correspondingly, the Pd–F bond of **11** was shorter (by 0.030 Å) in **11** versus **10**.

Synthesis of (NCN)Pd(F), **12**

Pincer complex **12** was synthesized in 63% yield using an analogous procedure to that for **8**–**11**. Complex **12** is the first example of an isolable palladium fluoride containing sp³ nitrogen donor ligands.¹⁴ This molecule shows a broad singlet at –243.7 ppm for the Pd–F bond by ¹⁹F NMR spectroscopy.

Colorless crystals of **12** were generated by slow diffusion of pentanes in a CH₂Cl₂ solution of this compound at –35 °C. An X-ray crystal structure was obtained and is shown in Figure 4. Intriguingly, the Pd–F bond distance in **12** of 2.0959(7) Å is comparable to that in complex **8**.¹² The other metric parameters (for example, the Pd–N and Pd–C bond lengths) are very similar to those in related (NCN)Pd–Cl species.¹⁵

Synthesis of (^{*t*}Bu-bpy)Pd(4-FC₆H₄)(F), **13**

Complex **13** was prepared by reaction of (^{*t*}Bu-bpy)Pd(*p*-FC₆H₄)(I) with AgF as previously reported in the literature (Scheme 4).²ⁱ The ¹⁹F NMR spectrum of **13** shows two resonances – a broad singlet at –340.7 ppm for the Pd–F and a multiplet at –122.9 ppm for the Ar–F.

Crystallization of **13** was achieved by diffusion of pentanes into a fluorobenzene solution of the complex at –35 °C. This afforded yellow blade-like crystals, and the structure of **13** is shown in Figure 5. This X-ray structure confirms the square planar geometry of **13** as well as the *cis* orientation of the *p*-F phenyl and fluoride ligands. Complex **13** is a rare example of a monomeric Pd–F compound with the F *trans* to an L-type ligand.^{6,16} Notably, the Pd–F bond in **13** (1.999(4) Å) is significantly (0.078 Å) shorter than that in the closely related *trans*-configured complexes *trans*-(py)₂Pd(Ph)(F) and *trans*-(^{*t*}Bu-py)₂Pd(Ph)(F) (Pd–F = 2.077(4) Å and 2.079(2) Å, respectively). Indeed, **13** contains the shortest known Pd–F bond

for a monomeric $\text{Pd}^{\text{II}}(\text{Ar})(\text{F})$ complex,¹² with the closest being in *trans*-(*i*Pr₃P)₂Pd(F)(4-C₅F₄N) (Pd–F = 2.0158(16) Å).^{1e} Interestingly, the Pd–C bond distance in **13** of 1.981(8) Å is nearly identical to that in *trans*-(py)₂Pd(Ph)(F) and *trans*-(*t*Bu-py)₂Pd(Ph)(F) (1.982(3) and 1.978(2) Å, respectively).⁸

Synthesis of (*t*Bu-bpy)Pd(CH₃)(F), **14**

Compound **14** was synthesized in 69% yield similarly to **8–13** by sonication of palladium iodide **7** with AgF in benzene (Scheme 4). ¹⁹F NMR spectroscopy shows a resonance for the fluorine bound to palladium as a broad singlet at –347.4 ppm. The ¹H NMR spectrum shows the methyl ligand as a doublet at 0.84 ppm with *J*_{HF} = 6 Hz. The ¹³C NMR signal for the Me group appears as a doublet at 0.0039 ppm with *J*_{CF} = 1.3 Hz. Notably **14** is the first example of an alkyl Pd^{II}–F containing N-donor ligands.^{2a}

Synthesis of (*t*Bu-bpy)Pd(F)₂, **15**

Compound **15** was accessed by stirring Pd^{II} diiodide **7** and AgF in CH₂Cl₂ according to a previously reported procedure (Scheme 4).²ⁱ Analysis by ¹⁹F NMR spectroscopy revealed a broad singlet at –354.06 ppm corresponding to Pd–F. The ¹H NMR spectrum shows signals indicative of a symmetrical square planar complex with the protons at the 6-position of the *t*Bu-bpy ligand appearing at 8.51 ppm.

Complex **15** was crystallized by vapor diffusion of pentanes into an acetone solution of the compound at –35 °C to afford colorless blocks for X-ray crystallographic analysis. The X-ray structure of this complex is shown in Figure 6.

Intriguingly, the observed Pd–F length in **15** (1.9708(11)) is very similar to those in *trans*-(*t*Bu-py)₂Pd(F)₂ (1.947(4) and 1.958(4) Å), which contains the shortest Pd–F bonds ever observed in a molecular Pd fluoride complex.⁸ In the case of *trans*-(*t*Bu-py)₂Pd(F)₂, Grushin and Marshall reasonably argued that the short Pd–F distances resulted from field/inductive effects associated with the two *trans* fluoride ligands. They suggested that these ligands increased the ionic character of the Pd^{II}–F interaction and thereby enhanced electrostatic contributions to the bonding.⁸ The observation of nearly identical Pd–F bond lengths in the *cis* complex **15** suggests that a *trans* orientation of the two fluoride ligands is not essential to see a similar structural effect.¹⁷ A comparison of the Pd–F bond length in **15** to that for other complexes reported herein (as well as selected examples from the literature) is shown in Figure 7 and Figure 8.

Thermolysis of aryl Pd^{II} fluorides

Palladium fluorides **8–14** are potential intermediates in C–F bond-forming reactions.² Thus, a final set of experiments was conducted to study the thermal decomposition of these complexes. Heating compounds **8–14** in nitrobenzene at 150 °C for 16 h resulted in the precipitation of palladium black, indicating that the Pd centers were reduced from Pd^{II} to Pd⁰. However, analysis of the crude reaction mixtures by gas chromatography and ¹⁹F NMR spectroscopy showed that no products of C–F bond-forming reductive elimination were formed. Instead, the major organic products were biaryls resulting from coupling between two of the σ-aryl ligands. This process likely proceeds via well-precedented Ar transfer between Pd centers, followed by C–C bond-forming reductive elimination.^{2i,8,18} Notably, these results are similar to those reported by Grushin for the thermal decomposition of *trans*-(*t*Bu-py)₂Pd(Ph)(F).⁸

Conclusions

In summary, this report described the synthesis, characterization, and reactivity a series of Pd^{II}-F complexes containing sp² and sp³ nitrogen donor ligands. We have disclosed the first examples of isolable Pd^{II} fluorides containing (a) sp³ nitrogen ligands, (b) both σ -alkyl and nitrogen ligands, and (c) both phosphorus and nitrogen ligands. Structural analysis of these compounds by X-ray crystallography has revealed both the longest (complex **8**) and shortest (complex **13**) Pd-F bonds reported to date for monomeric Pd^{II} aryl fluorides. In addition, we report the intriguing finding that *cis*-(^tBu-bpy)Pd(F)₂ has Pd-F bond distances within error of the related complex *trans*-(^tBu-py)₂Pd(F)₂. Finally, thermolysis of all of these new complexes was shown to result in C-C rather than C-F bond-forming reactions. These results further highlight the challenges associated with achieving C-F bond forming reductive elimination from Pd^{II} centers.

Experimental Section

General

NMR spectra were obtained on a Varian Inova 400 (399.96 MHz for ¹H; 376.34 MHz for ¹⁹F; 100.57 MHz for ¹³C) or MR400 (400.53 MHz for ¹H; 376.87 MHz for ¹⁹F; 100.71 MHz for ¹³C) spectrometer. ¹H, ¹⁹F and ¹³C chemical shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak used as an internal reference. ¹⁹F NMR spectra are referenced on a unified scale, where the single primary reference is the frequency of the residual solvent peak in the ¹H NMR spectrum.¹⁹ Several ¹⁹F NMR experiments were conducted using “No-D” parameters and are noted accordingly.²⁰ ¹H and ¹⁹F multiplicities are reported as follows: singlet (s), broad singlet (br s), doublet (d), doublet of doublets (dd), triplet (t), and multiplet (m). Elemental analyses were conducted by Atlantic Microlabs in Norcross, Georgia. Microanalysis for many of the Pd-F complexes described herein was consistently low in C. This is believed to result from the hygroscopic nature of these materials because of the possibility of strong H-bonding interactions between the Pd-F and H₂O.^{2a,2i} The amount of water could not be accurately quantified by ¹H NMR analysis due to broadening of the signal *via* rapid exchange. Full ¹H, ¹⁹F and ¹³C NMR spectra are provided for each of these Pd-F compounds in the electronic supporting information. Gas chromatographs were obtained on a Shimadzu 17A using a Restek Rtx®-5 (crossbond 5% diphenyl polysiloxane, 15 m, 0.25 mm ID, 0.25 mm ID, 0.25 μ m df) column. Sonication was performed using a VWR Model 75H7 ultrasound bath, with the temperature regulated by a Neslab RTE-111 recirculating chiller.

Materials and Reagents

The palladium complexes Pd(dba)₂·21 (NCN)PdBr,¹⁰ (^tBu-bpy) PdMe₂,¹¹ [(phpy)Pd(OAc)]₂,²² [(bzq)Pd(OAc)]₂,²³ (bzq)₂,²⁴ (phpy)₂,²⁴ and (4,4'-difluoro-1,1'-biphenyl)₂ were prepared according to literature procedures. Palladium fluorides (^tBu-bpy)Pd(*p*-FC₆H₄)(F) and (^tBu-bpy)PdF₂ were prepared according to previously reported procedures.^{2d} AgF and 1-fluoro-4-iodobenzene were obtained from Matrix Chemicals. MeI, ^tBu-bpy, 2,6-lutidine, and LiI were obtained from Aldrich. ^tBu-py was obtained from TCI America. PPh₃ was obtained from Strem Chemicals. All reagents were used as received. Nitrobenzene-*d*₅, CD₂Cl₂, and CDCl₃ were obtained from Cambridge Isotope Laboratories. All other solvents were obtained from Fisher Chemical. Dichloromethane and pentane were purified using an Innovative Technologies (IT) solvent purification system consisting of a copper catalyst, activated alumina, and molecular sieves. Benzene was distilled from Na⁰/benzophenone and stored over activated 4 Å molecular sieves. Acetone was distilled from CaSO₄. All syntheses were conducted using standard Schlenk techniques or in an inert atmosphere glovebox unless otherwise noted.

Preparations

[(phpy)Pd(I)]₂ (1a)—In air, [(phpy)Pd(OAc)]₂ (1.5 g, 2.2 mmol, 1 equiv) was weighed into a 250 mL Erlenmeyer flask and dissolved in acetone (100 mL). In a separate flask, LiI (1.2 g, 8.8 mmol) was dissolved in water (50 mL). The LiI solution was added slowly to the stirring solution of [(phpy)Pd(OAc)]₂, and the resulting mixture was stirred at room temperature overnight. The reaction mixture was filtered, and the solid obtained was washed with a 1:1 solution of MeOH/H₂O (3 × 10 mL) followed by a 1:1 mixture of hexanes/Et₂O (3 × 3 mL). The resulting material was dried *in vacuo*, yielding the product (**1a**) as a yellow solid (1.7 g, 95% yield). Spectroscopic data for this complex matched that reported in the literature.⁹

[(bzq)Pd(I)]₂ (1b)—Complex **1b** was synthesized via an analogous procedure to the preparation of **1a**, with [(bzq)Pd(OAc)]₂ (1.5 g, 2.2 mmol) as the starting material. The product was obtained as a dark yellow solid (1.6 g, 88% yield). ¹H NMR (95% CDCl₃, 5% C₅D₅N): δ 9.87 (br s, 2H), 8.17 (d, *J* = 8 Hz, 2H), 7.65 (d, *J* = 9 Hz, 2H), 7.52 (d, *J* = 9 Hz, 4H), 7.54 (m, 2H), 7.21 (d, *J* = 8 Hz, 2H), 6.14 (br s, 2H); ¹³C NMR (CDCl₃, 1 drop of C₅D₅N): δ 154.84, 149.34, 141.34, 136.95, 135.43, 133.42, 128.62, 128.42, 126.84, 123.50, 123.11, 121.72 (two aromatic ¹³C resonances appear to be coincidentally overlapping). (Found: C, 38.07, H, 1.93, N, 3.50. C₂₂H₁₆I₂N₂Pd₂ requires 37.94, H, 1.96, N, 3.40).

(phpy)Pd(lutidine)(I), 2—Complex **2** was prepared under ambient conditions using a modification of the literature procedure.⁹ To a stirring suspension of dimer **1a** (0.50 g, 0.65 mmol, 1 equiv) in acetone (16 mL) was added 2,6-lutidine (0.30 mL, 4 equiv) dropwise. The resulting clear solution was stirred for 15 min. The solvent was then removed under vacuum, and the resulting solid was recrystallized from CH₂Cl₂/hexanes and dried *in vacuo* yielding **2** as a yellow solid (0.53 g, 83% yield). ¹H NMR (CDCl₃): δ 9.89 (d, *J* = 5 Hz, 1H), 7.79 (t, *J* = 8 Hz, 1H), 7.66 (multiple peaks, 2H), 7.43 (d, *J* = 8 Hz, 1H), 7.22 (multiple peaks, 2H), 7.10 (multiple peaks, 2H), 6.85 (t, *J* = 8 Hz, 1H), 5.58 (d, *J* = 6 Hz, 1H), 3.12 (s, 6H). ¹³C NMR (CDCl₃): δ 165.07, 159.79, 156.94, 154.03, 145.92, 138.29, 130.25, 129.65, 124.97, 123.37, 123.02, 122.83, 118.48, 28.57 (two aromatic ¹³C resonances appear to be coincidentally overlapping). (Found: C, 43.44, H, 3.31, N, 5.88. C₁₈H₁₇IN₂Pd requires C, 43.70, H, 3.36, N, 5.63).

(phpy)Pd(^tBu-py)(I), 3—Complex **3** was prepared via an analogous procedure to the preparation of **2**, using **1a** (1.0 g, 1.3 mmol, 1 equiv) and ^tBu-py (1.5 mL, 5.1 mmol, 4 equiv) as starting materials. The product was obtained as a pale yellow solid (0.93 g, 69% yield). ¹H NMR (CDCl₃): δ 9.91 (d, *J* = 5 Hz, 1H), 8.80 (d, *J* = 6 Hz, 2H), 7.76 (m, 1H), 7.64 (d, *J* = 8 Hz, 1H), 7.43–7.39 (multiple peaks, 3H), 7.10–7.07 (multiple peaks, 2H), 6.92 (m, 1H), 5.87 (d, *J* = 8 Hz, 1H), 1.34 (s, 9H). ¹³C NMR (CDCl₃): δ 165.24, 162.67, 157.36, 155.96, 153.02, 145.88, 138.37, 131.28, 129.47, 125.05, 123.42, 122.71, 118.55, 35.22, 30.32 (two aromatic ¹³C resonances appear to be coincidentally overlapping). (Found: C, 45.65, H, 4.15, N, 5.26. C₂₂H₂₁IN₂Pd requires C, 45.95, H, 4.05, N, 5.36).

(bzq)Pd(lutidine)(I), 4—Complex **4** was prepared via an analogous procedure to the preparation of **2**, using **1b** (0.50 g, 0.61 mmol, 1 equiv) and 2,6-lutidine (0.30 mL, 4.5 equiv) as starting materials. The product was obtained as a yellow solid (0.52 g, 82% yield). ¹H NMR (CDCl₃): δ 10.1 (d, *J* = 6 Hz, 1H), 8.27 (d, *J* = 8 Hz, 1H), 7.73–7.68 (multiple peaks, 2H), 7.62–7.56 (multiple peaks, 2H), 7.47 (m, 1H), 7.28–7.19 (multiple peaks, 3H), 5.81 (d, *J* = 8 Hz, 1H), 3.12 (s, 6H). ¹³C NMR (CDCl₃): δ 160.09, 155.39, 155.19, 152.63, 141.59, 138.32, 136.92, 133.54, 128.64, 128.58, 127.33, 126.96, 123.71, 123.12, 123.03, 122.11, 28.67. (Found: C, 45.48, H, 3.16, N, 5.40. C₂₀H₁₇IN₂Pd requires C, 46.31, H, 3.30, N, 5.40).

(bzq)Pd(PPh₃)(I), 5—Complex **5** was prepared via an analogous procedure to the preparation of **4**, using **1b** (0.50 g, 0.61 mmol, 1 equiv) and PPh₃ (0.72 g, 2.7 mmol, 4.5 equiv) as starting materials. The product was obtained as a yellow solid (0.53 g, 65% yield). ¹H NMR (CDCl₃): δ 10.46 (br s, 1H), 8.27 (d, *J* = 8 Hz, 1H), 7.87-7.83 (multiple peaks, 6H), 7.70 (m, 1H), 7.60 (m, 1H), 7.50 (m, 1H), 7.45-7.40 (multiple peaks, 4H), 7.36-7.33 (multiple peaks, 6H), 6.87 (t, *J* = 8 Hz, 1H), 6.65 (t, *J* = 8 Hz, 1H). ³¹P NMR (CDCl₃): δ 44.67 (1P). ¹³C NMR (CDCl₃): δ 155.41, 155.18, 154.46, 143.06, 137.19, 135.82, 135.63 (d, *J* = 12 Hz), 133.92, 133.43 (d, *J* = 52 Hz), 130.74, 129.07, 128.01 (d, *J* = 11 Hz), 127.87, 127.17, 123.42, 123.31, 122.12 (d, *J* = 3 Hz). (Found C, 55.01, H, 3.39, N, 2.14. C₃₁H₂₃INPPd requires C, 55.26, H, 3.44, N, 2.08).

(NCN)Pd(I), 6—In air, (NCN)PdBr (2.0 g, 3.1 mmol, 1.0 equiv) was weighed into a 250 mL Erlenmeyer flask and dissolved in acetone (141 mL). In a separate 100 mL Erlenmeyer flask, LiI (1.7 g, 13 mmol, 4 equiv) was dissolved in water (71 mL). The aqueous LiI solution was added slowly to the stirring solution of (NCN)PdBr in acetone, and the resulting solution was stirred at 23 °C for an additional 12 h. The reaction mixture was then filtered through a frit, and the resulting solid washed with water (3 × 5 mL) and diethyl ether (3 × 5 mL). The solvent was removed *in vacuo*, and the product was further purified by recrystallization from CH₂Cl₂/hexanes. The product was obtained as a microcrystalline yellow solid (0.71 g, 90% yield). ¹H NMR (CDCl₃): δ 6.97 (t, *J* = 8 Hz, 1H), 6.74 (d, *J* = 8 Hz, 2H), 3.98 (s, 4H), 2.99 (s, 12H); ¹³C NMR (CDCl₃): δ 159.19, 145.15, 124.60, 119.75, 73.94, 54.84. (Found C, 33.95, H, 4.34, N, 6.59. C₁₂H₁₉IN₂Pd requires C, 33.94, H, 4.51, N, 6.60).

(^tBu-bpy)Pd(Me)(I), 7—In the glovebox, (^tBu-bpy)PdMe₂ (0.77 g, 3.1 mmol, 1.9 equiv) was weighed into a 20 mL scintillation vial and dissolved in acetone (2 mL). MeI was added dropwise to this solution. The reaction was stirred for 30 min, during which time it changed from a clear yellow solution to a cloudy suspension. Pentanes (8 mL) was added to completely precipitate the product, and the solids were collected, and washed with pentanes (3 × 2 mL). The resulting material was dried *in vacuo* to yield **7** as a yellow solid. Further purification by recrystallization from CH₂Cl₂/hexanes afforded analytically pure compound (0.86 g, 52% yield). ¹H NMR (CDCl₃): δ 9.29 (d, *J* = 6 Hz, 1H), 8.46 (d, *J* = 6 Hz, 1H), 8.08 (d, *J* = 2 Hz, 1H), 8.02 (d, *J* = 2 Hz, 1H), 7.59 (dd, *J* = 6, 2 Hz, 1H), 7.44 (dd, *J* = 6, 2 Hz, 1H), 1.45 (s, 9H), 1.42 (s, 9H), 0.738 (s, 3H). ¹³C NMR (CDCl₃): δ 163.93, 163.27, 157.29, 154.01, 152.21, 146.93, 124.39, 123.94, 120.09, 118.98, 36.01, 35.87, 30.63, 30.57, 7.63. (Found C, 44.19, H, 5.31, N, 5.61. C₁₉H₂₇IN₂Pd requires C, 44.16, H, 5.27, N, 5.42).

(phpy)Pd(lutidine)(F), 8—In the glovebox, **2** (0.66 g 1.3 mmol, 1 equiv) and AgF (0.66 g, 5.2 mmol, 3.9 equiv) were weighed into an amber glass jar. Benzene (27 mL) was added, and the reaction was sonicated for 5 h. Under N₂, the resulting mixture was then filtered through Celite and washed with CH₂Cl₂ (3 × 5 mL). This filtration was repeated, and then the solvent removed *in vacuo*. The resulting solid was recrystallized from CH₂Cl₂/pentanes, and the product was obtained as a yellow solid (0.23 g, 47% yield). ¹H NMR (CDCl₃): δ 8.70 (br d, *J* = 6 Hz 1H), 7.72 (t, *J* = 8 Hz, 1H), 7.58-7.52 (multiple peaks, 2H), 7.32 (d, *J* = 8 Hz, 1H), 7.13-7.08 (multiple peaks, 3H), 6.93 (m, 1H), 6.70 (m, 1H), 5.77 (d, *J* = 8 Hz, 1H), 3.13 (s, 6H). ¹⁹F NMR (CDCl₃): δ -260.3 (br s, 1F). ¹³C NMR (CDCl₃): δ 164.55, 160.11, 149.35, 145.72, 138.71, 138.31, 133.12, 129.19, 128.12, 124.07, 123.09, 122.76, 121.80, 117.80, 27.76. (Found C, 53.40, H, 4.66, N, 6.61. C₁₈H₁₇FN₂Pd requires C, 55.90, H, 4.43, N, 7.24%).

(phpy)Pd(^tBu-py)(F), 9—Complex **9** was prepared via an analogous procedure to the preparation of **8**, using **3** (0.60 g, 1.2 mmol, 1 equiv), AgF (0.57 g, 4.5 mmol, 3.9 equiv),

and benzene (23 mL) as starting materials and conducting the sonication for 3 h. The product was obtained as a white solid (0.22 g, 45% yield). ^1H NMR (CDCl_3): δ 8.96 (d, J = 5 Hz, 1H), 8.82 (d, J = 6 Hz, 2H), 7.82 (m, 1H), 7.62 (d, J = 8 Hz, 1H), 7.44-7.41 (multiple peaks, 3H), 7.17 (m, 1H), 7.06 (m, 1H), 6.94 (m, 1H), 6.50 (d, J = 8 Hz, 1H), 1.34 (s, 9H); ^{19}F NMR (CD_2Cl_2): δ -243.4; ^{13}C NMR (CD_2Cl_2): δ 164.71, 162.80, 152.06, 149.56, 145.98, 138.73, 133.76, 129.10, 128.21, 124.19, 123.17, 122.45, 121.69, 117.83, 35.08, 30.18. (Found : C, 57.95, H, 5.01, N, 6.67. $\text{C}_{20}\text{H}_{21}\text{FN}_2\text{Pd}$ requires C, 57.91, H, 5.10, N, 6.75).

(bzq)Pd(lutidine)(F), 10—Complex **10** was prepared via an analogous procedure to the preparation of **8**, using **4** (0.40 g, 0.77 mmol, 1 equiv) and AgF (0.38 g, 3.0 mmol, 3.9 equiv) as starting materials and conducting the sonication for 5 h. The product was obtained as a yellow solid (0.18 g, 57% yield). ^1H NMR (CDCl_3): δ 9.03 (br d, J = 5 Hz, 1H), 8.19 (d, J = 8 Hz, 1H), 7.62-7.59 (multiple peaks, 2H), 7.50 (d, J = 8 Hz, 1H), 7.46-7.40 (multiple peaks, 2H), 7.17 (d, J = 8 Hz, 2H), 7.05 (d, J = 8 Hz, 1H), 5.95 (d, J = 8 Hz, 1H), 3.20 (s, 6H). ^{19}F NMR (CDCl_3): δ -270.4. ^{13}C NMR (CDCl_3): δ 160.52, 154.66, 148.40, 141.58, 138.45, 137.04, 133.15, 130.19, 128.69, 128.38, 128.27, 126.31, 123.31, 122.88, 122.29, 121.15, 27.99. (Found : C 54.76; H, 4.53 N, 6.35. $\text{C}_{20}\text{H}_{17}\text{FN}_2\text{Pd}$ requires 58.48; H, 4.17 N, 6.82).

(bzq)Pd(PPh₃)(F), 11—Complex **11** was prepared via an analogous procedure to the preparation of **8**, using **5** (0.40 g, 0.59 mmol, 1 equiv) and AgF (0.29 g, 2.3 mmol, 3.9 equiv) as starting materials and conducting the sonication for 5 h. The product was obtained as white solid (0.28 g, 84% yield). ^1H NMR (CDCl_3): δ 9.30 (m, 1H), 8.29 (d, J = 8 Hz, 1H), 7.82-7.77 (multiple peaks, 6H), 7.70 (d, J = 9 Hz, 1H), 7.60 (d, J = 8 Hz, 1H), 7.55 (m, 1H) 7.47-7.42 (multiple peaks, 4H), 7.39-7.34 (multiple peaks, 6H), 7.33 (s, C_6H_6 , 6H), 6.79 (t, J = 8 Hz 1H), 6.54 (m, 1H). ^{19}F NMR (CDCl_3): δ -247.2 (apparents, 1F). ^{31}P NMR (CDCl_3): δ 40.7 (d, J = 8 Hz, 1P). ^{13}C NMR (CDCl_3): δ 153.34, 147.37, 147.31, 142.94, 137.52, 135.37 (d, J = 12 Hz), 133.67, 130.85, 130.82, 129.91 (d, J = 50 Hz), 129.04, 128.32 (C_6H_6), 128.23 (d, J = 8 Hz), 128.07, 126.46, 123.09, 122.64, 121.16 (J = 4 Hz). (Found : C, 68.43, H, 4.47, N, 2.38. $\text{C}_{31}\text{H}_{23}\text{FNPPd} \cdot \text{C}_6\text{H}_6$ requires C, 69.00, H, 4.54, N, 2.95).

(NCN)Pd(F), 12—In the glovebox, **6** (0.50 g, 1.2 mmol, 1 equiv) and AgF (0.59 g, 4.6 mmol, 3.9 equiv) were dissolved in benzene (23 mL) in a 50 mL amber glass jar. The jar was sealed with a Teflon-lined cap, and the reaction was sonicated in the dark at 25 °C for 3 h. The resulting suspension was filtered through a plug of Celite in the drybox. The plug was washed with benzene (1 $\times$ 5 mL) and then with CH_2Cl_2 (5 $\times$ 2 mL). The solvent was removed under reduced pressure. The solid was collected and dried *in vacuo* affording the product (**8**) as a white solid (0.24 g, 63% yield). ^1H NMR (CD_2Cl_2): δ 6.90 (t, J = 8 Hz, 1H), 6.72 (d, J = 8 Hz, 2H), 3.95 (s, 4H), 2.84 (s, 12H). ^{19}F NMR (CD_2Cl_2): δ -243.7 (br s, 1F). ^{13}C NMR (CD_2Cl_2): δ 145.76, 129.48, 124.14, 119.97, 74.57, 52.28. (Found : C, 42.55, H, 6.30, N, 8.04. $\text{C}_{12}\text{H}_{19}\text{FN}_2\text{Pd}$ requires C, 45.51, H, 6.05, N, 8.85).

(^tBu-bpy)Pd(Me)(F), 14—Complex **14** was prepared via an analogous procedure to the preparation of **8**, using **7** (0.40 g, 0.77 mmol, 1 equiv) and AgF (0.38 g, 3.0 mmol, 3.9 equiv) as starting materials and conducting the sonication for 3 h. The product was obtained as a yellow solid (0.22 g, 69% yield). ^1H NMR (CDCl_3): δ 8.69 (d, J = 6 Hz, 1H), 8.48 (d, J = 6 Hz, 1H), 7.98 (s, 1H), 7.97 (s, 1H), 7.59 (dd, J = 5 Hz, 2 Hz, 1H), 7.42 (dd, J = 6 Hz, 2 Hz, 1H), 1.43 (s, 9H), 0.84 (d, J = 6 Hz, 3H). ^{19}F NMR (CDCl_3): δ -347.4 (br s, 1F). ^{13}C NMR (CDCl_3): δ 163.96, 163.37, 157.75, 152.92, 150.75, 148.08, 124.15, 124.02, 119.77, 118.32, 36.01, 35.92, 30.72, 30.49, 0.039 (d, J = 1.3 Hz). (Found : C, 54.04, H, 6.65, N, 6.56. $\text{C}_{19}\text{H}_{27}\text{FN}_2\text{Pd}$ requires C, 55.82, H, 6.66, N, 6.85).

General procedure for the thermolysis of compounds 8–13—In the glovebox, each Pd–F (10 mg) was weighed into a 4 mL scintillation vial and dissolved in nitrobenzene-*d*₅ to generate a 0.03 M solution. The vials were sealed with Teflon-lined caps, and the reactions were stirred at 150 °C for 16 h. The reactions were cooled to room temperature, 4-fluoronitrobenzene was added as an internal standard, and the distribution of products was analyzed by ¹⁹F NMR spectroscopy and gas chromatography.

Crystallographic data—X-ray diffraction data were collected with a Bruker SMART APEX CCD-based X-ray diffractometer equipped with a low-temperature device and fine focus Mo-target X-ray tube. The structures were solved and refined with the Bruker SHELXTL (version 6.12) software package.²⁶ The crystallographic data, details of data collection and refinement, for the X-ray structures reported herein is summarized in Table 1. Structures **8** and **15** were twinned. The twin domains were related by a 4.2 degree rotation about the direct (0.900 0.100 1) axis or reciprocal (0.048 0.031 1) axis and a refined twin volume fraction of 0.281(1) for **8**. Structure **15** twin domains were refined by a 180 degree rotation about the direct (1 1 0) axis and a refined twin volume fraction of 0.886(2). Further experimental details as well as full tables of bond distances and bond angles are included for structures **8**, **10–12** and, **15** in the electronic supporting information. Full experimental details for **13** were previously reported by our group (see ref. 2i). In addition, Pd–F bond distances from all reported monomeric Pd–F complexes are shown in Figure 8.²⁷

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Abbreviations

dba	dibenzylidene acetone
NCN	<i>N,N,N',N'</i> -tetramethyl-1,3-xylylenediamine
^t Bu-bpy	4,4'-di- <i>tert</i> -butyl-2,2'-bipyridine
phpy	2-phenylpyridine
bzq	benzo[<i>h</i>]quinoline
<i>p</i> -FPh	4-fluorophenyl
^t Bu-py	4- <i>tert</i> -butylpyridine

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Notes and references

1. For reviews and examples, see: (a) Hudlicky M. J. Fluor. Chem 1989;44:345–359. (b) Doherty NM, Hoffman NW. Chem. Rev 1991;91:553–573.H. (c) Kiplinger L, Richmond TG, Osterberg CE. Chem. Rev 1994;94:373–431. (d) Murphy EF, Murugavel R, Roesky HW. Chem. Rev 1997;97:3425–3468. [PubMed: 11851496] (e) Jasim NA, Perutz RN, Whitwood AC, Braun T, Izundu J, Neumann B, Rothfeld S, Stammel HG. Organometallics 2004;23:6140–6149. (f) Braun T, Steffen A, Schorlemer V, Neumann B, Stammel HG. Dalton Trans 2005;20:3331–3336. [PubMed: 16193151] (g) Steffen A, Braun T, Neumann B, Stammel H-G. Angew. Chem., Int. Ed

- 2007;46:8674–8678. (h) Amii H, Uneyama K. Chem. Rev 2009;109:2119–2183. [PubMed: 19331346]
2. (a) Pilon MC, Grushin VV. Organometallics 1998;17:1774–1781. (b) Grushin VV. Angew. Chem., Int. Ed 1998;37:994–996. (c) Flemming JP, Pilon MC, Borbulevitch OY, Antipin MY, Grushin VV. Inorg. Chim. Acta 1998;280:87–98. (d) Hull KL, Anani WQ, Sanford MS. J. Am. Chem. Soc 2006;128:7134–7135. [PubMed: 16734446] (e) Yandulov DV, Tran NT. J. Am. Chem. Soc 2007;129:1342–1358. [PubMed: 17263419] (f) Vigalok A. Chem. Eur. J 2008;14:5102–5108. (g) Furuya T, Kaiser HM, Ritter T. Angew. Chem., Int. Ed 2008;47:5993. (h) Furuya T, Ritter T. J. Am. Chem. Soc 2008;130:10060–10061. [PubMed: 18616246] (i) Ball ND, Sanford MS. J. Am. Chem. Soc 2009;131:3796–3797. [PubMed: 19249867] (j) Watson DA, Su M, Teveroskiy G, Zhang Y, García-Furtanet J, Kinzel T, Buchwald SL. Science. 2009 August 13; (10.1126/science.1178239).
 3. Fraser SL, Antipin MY, Khroustalyov VN, Grushin VV. J. Am. Chem. Soc 1997;119:4769–4770.
 4. (a) Marshall WJ, Thorn DL, Grushin VV. Organometallics 1998;17:5427–5430. (b) Grushin VV. Organometallics 2000;19:1888–1900. (c) Grushin VV, Marshall WJ. Angew. Chem., Int. Ed 2002;41:4476–4479. (d) Grushin VV. Chem. Eur. J 2002;8:1006–1014. (e) Grushin VV, Marshall WJ. J. Am. Chem. Soc 2006;128:12644–12645. [PubMed: 17002347]
 5. There are also several examples of organopalladium fluorides of which the Pd–F bond is a part of a Lewis acid/base complex (*e.g.*, Pd–F⁺BF₃ or Pd–FHF). See: (a) Rheingold AL, Wu GZ, Heck RF. Inorg. Chim. Acta 1987;131:147–150. (b) Roe DC, Marshall WJ, Davidson F, Soper PD, Grushin VV. Organometallics 2000;19:4575–4582.
 6. P–F bond formation predominates upon thermolysis of both *trans* and *cis*-Pd^{II} aryl fluorides. Marshall WJ, Grushin VV. Organometallics 2003;22:555–562.
 7. Grushin VV, Marshall WJ. Organometallics 2008;27:4825–4828.
 8. Grushin VV, Marshall WJ. J. Am. Chem. Soc 2009;131:918–919. [PubMed: 19123791]
 9. Black DSC, Deacon GB, Edwards GL. Aust. J. Chem 1994;47:217–227.
 10. Alsters PL, Baesjou PJ, Janssen MD, Kooijman H, Sicherer-Roetman A, Spek AL, Van Koten G. Organometallics 1992;11:4124–4135.
 11. Liu G, Puddephatt RJ. Inorg. Chim. Acta 1996;251:319–323.
 12. Determined by computing the bond length ± 3 standard deviations; 95% confidence level.
 13. Racowski JM, Dick AR, Sanford MS. J. Am. Chem. Soc 2009;131:10974. [PubMed: 19459631]
 14. (NH₃)₂PdF₂ has been implicated but not fully characterized. Müller H. Liebigs Ann. Chem 1853;86:341–368.
 15. Slagt MQ, Rodríguez G, Grutters MMP, Klein Gebbink RJM, Kloppe W, Jenneskens LW, Lutz M, Spek AL, van Koten G. Chem. Eur. J 2004;10:1331–1344.
 16. This is a rare example of a monomeric Pd^{II}(Ar)(F) monomer with the fluoride *trans* to an L-type ligand. However, there are several examples of this orientation in Pd^{II}(F)₂ complexes and Pd^{II} fluoride bridged dimers. See: (a) Yahav A, Goldberg I, Vigalok A. J. Am. Chem. Soc 2003;125:13634–13635. [PubMed: 14599181] (b) Kaspi AW, Yahav-Levi A, Goldberg I, Vigalok A. Inorg. Chem 2008;47:5–7. [PubMed: 18052157] (c) Grushin VV, Marshall WJ. Angew. Chem., Int. Ed 2002;41:4476–4479. (d) Grushin VV, Marshall WJ. Organometallics 2007;26:4997–5002.
 17. The molecular orbital basis for the observed short Pd–F bonds in **15** is not fully understood and may be different from that leading to the similar structural features in *trans*-(^tBu-py)₂Pd(F)₂.
 18. For examples of related processes at Pd^{II}, see: (a) Grushin VV, Marshall WJ. J. Am. Chem. Soc 2006;128:4632–4641. [PubMed: 16594700] (b) Cardenas DJ, Martin-Matute B, Echavarren AM. J. Am. Chem. Soc 2006;128:5033–5040. [PubMed: 16608337]
 19. For further information on this method, see the following website:
www.iupac.org/publications/pac/2001/7311/7311x1795.html
 20. Hoye TR, Eklov BM, Ryba TD, Voloshin M, Yao L. Org. Lett 2004;6:953–956. [PubMed: 15012073]
 21. Takahashi Y, Ito SS, Sukai S, Ishii Y. J. Chem. Soc., D 1970;17:1065–1066.
 22. Aiello I, Crispini A, Ghedini M, La Deda M, Barigelli F. Inorg. Chim. Acta 2000;308:121–128.
 23. Hull KL, Sanford MS. J. Am. Chem. Soc 2009;131:9651–9653. [PubMed: 19569623]

24. Hull KL, Lanni EL, Sanford MS. J. Am. Chem. Soc 2006;128:14047–14049. [PubMed: 17061885]
25. Wright SW, Hageman DL, McClure LD. J. Org. Chem 1994;59:6095–6097.
26. Sheldrick, GM. SHELXTL, v/ 6.12; Brucker Analytical X-ray. Madison, WI: 2001.
27. The data presented in Figure 8 was obtained from the Cambridge Crystallographic Database (July 1, 2009). All Pd^{II}-fluorides with terminal Pd–F bonds (monomers) that were not altered by intermolecular H-bond type interactions in the crystal structure were included (see ref. 8).

Figure 1.

X-ray crystal structure of **8**. Thermal ellipsoids are drawn at 50% probability, hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Pd1-C11 1.960(3), Pd1-N1 2.017(2), Pd1-N2 2.055(2), Pd1-F1 2.1024(17). Selected bond angles (°): C11-Pd1-N1 82.13(11), C11-Pd1-N2 93.68(10), N1-Pd1-N2 175.36(9), C11-Pd1-F1 173.88(9), N1-Pd1-F1 92.32(8), N2-Pd1-F1 91.95(8).

Figure 2.

X-ray crystal structure of **10**. Thermal ellipsoids are drawn at 50% probability, hydrogen atoms and CH_2Cl_2 are omitted for clarity. Selected bond lengths ($\text{\AA}$): Pd1-C11 1.9769(19), Pd1-N1 2.0325(15), Pd(1)-N(2) 2.0519(15), Pd1-F1 2.0604(12). Selected bond angles ($^\circ$): C11-Pd1-N1 82.89(7), C11-Pd1-N2 92.46(7), N1-Pd1-N2 174.46(6), C11-Pd1-F1 174.14(6), N1-Pd1-F1 91.29(6), N2-Pd1-F1 93.32(5).

Figure 3.

X-ray crystal structure of **11**. Thermal ellipsoids are drawn at 50% probability, hydrogen atoms and CH_2Cl_2 are omitted for clarity. Two polymorphs were present (only one is shown, see Supporting Information for more information). Selected bond lengths ($\text{\AA}$): Pd1-C11 2.004(2), Pd1-F1 2.0301(15), Pd1-N1 2.0762(19), Pd1-P1 2.2458(6). Selected bond angles ($^\circ$): C11-Pd1-F1 169.77(8), C11-Pd1-N1 82.52(9), F1-Pd1-N1 87.36(7), C11-Pd1-P1 96.97(7), F1-Pd1-P1 93.23(5), N2-Pd1-P1 176.20(6).

Figure 4.

X-ray crystal structure of **12**. Thermal ellipsoids are drawn at 50% probability, hydrogen atoms and CH_2Cl_2 are omitted for clarity. Selected bond lengths Pd1-C7 1.9068(11), Pd1-N1 2.0954(9), Pd(1)-N(2) 2.1019(9), Pd1-F1 2.0959(7). Selected bond angles ($^\circ$): C7-Pd1-N1 81.69(4), C7-Pd1-N2 81.61(4), N1-Pd1-N2 163.27(4), C7-Pd1-F1 176.62(4), N1-Pd1-F1 96.89(3), N2-Pd1-F1 99.74(3).

Figure 5.

X-ray crystal structure of **13**. Thermal ellipsoids are drawn at 50% probability, hydrogen atoms and CH_2Cl_2 are omitted for clarity. The structure was solved as two identical structures in a unit cell (only one is shown, see Supporting Information for more information). Selected bond lengths ($\text{\AA}$): Pd1-C1 1.981(8), Pd1-F1 1.999(4), Pd1-N2 2.026(6), Pd1-N1 2.086(7). Selected bond angles ($^\circ$): C1-Pd1-F1 89.9(3), C1-Pd1-N2 96.6(3), F1-Pd1-N2 173.5(2), C1-Pd1-N1 174.3(3), F1-Pd1-N1 93.8(2), N2-Pd1-N1 79.7(3).

Figure 6.

X-ray crystal structure of **15**. Thermal ellipsoids are drawn at 50% probability, hydrogen atoms and CH₂Cl₂ are omitted for clarity. Selected bond lengths (Å): Pd1-F1 1.9708(11), Pd1-N1 1.9722(15). Selected bond angles (°): F1-Pd1-F1A 91.70(7), F1-Pd1-N1A 174.52(6), F1A-Pd1-N1A 93.64(6), F1-Pd1-N1 93.64(6), F1A-Pd1-N1 174.52(6), N1A-Pd1-N1 81.04(9). Symmetry transformations used to generate equivalent atoms: #1 $-x+3/2$, $-y+1/2$, z ; #2 $-x+1/2$, $-y+1/2$, z .

Figure 7.

Comparison of Pd-F bond lengths of selected literature Pd^{II}-F compounds (grey) and compounds **8**, **13**, **15**, (green). Error bars demonstrate three standard deviations (95 % confidence level) in the error of the bond lengths.

Figure 8. Comparison of Pd-F bond lengths of literature Pd^{II}-F compounds (grey) and the new complexes **8**, **10-13**, and **15** (green).

Scheme 1.
Synthesis of palladium(II) iodide complexes **2–7**.

Scheme 2.
Synthesis of complexes **8** and **9**

Scheme 3.
Synthesis of complexes **10** and **11**

Scheme 4.
Synthesis of complexes **13**–**15**.

Table 1
Crystallographic data, details of data collection and refinement for **8**, **10–13**, and **15**.

	8	10^a	11^a	12^c	13^b	15^a
Molecular Formula	C ₁₈ H ₁₇ FN ₂ Pd	C ₂₁ H ₁₉ Cl ₂ FN ₂ Pd	C ₃₂ H ₂₅ Cl ₂ FNPPd	C ₁₃ H ₂₁ Cl ₂ FN ₂ Pd	C ₅₇ H ₆₅ F ₄ N ₄ Pd ₂	C ₁₀ H ₂ Cl ₂ F ₂ N ₂ Pd
<i>M</i>	386.74	495.68	650.80	401.62	1094.93	497.72
Crystal System	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Orthorhombic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1	<i>P</i> -1	<i>I</i> a	<i>P</i> ccn
(standard setting)						
<i>a</i> /Å	9.6607(11)	13.904(4)	8.7399(5)	8.4407(6)	17.9592(12)	11.1616(9)
<i>b</i> /Å	9.2742(10)	11.409(3)	17.2959(9)	9.5451(6)	17.5332(12)	11.9919(9)
<i>c</i> /Å	17.810(2)	14.366(4)	20.3468(11)	11.5693(8)	20.2950(14)	15.6096(10)
<i>α</i> /°			96.861(1)	105.314(1)		
<i>β</i> /°	96.023(2)	117.158(3)	98.293(1)	95.629(1)	95.135(1)	90
<i>γ</i> /°			104.123(1)	116.010(1)		
<i>V</i> /Å ³	1586.9(3)	2027.8(9)	2913.0(3)	782.97(9)	6364.9(8)	2089.3(3)
Z, calculated density	4, 1.619	4, 1.624	4, 1.484	2, 1.704	4, 1.143	4, 1.582
(Mg/m ³)						
Absorption	1.177	1.195	0.904	1.525	0.610	1.166
coefficient/mm ⁻¹						
Crystal size/mm	0.33 × 0.14 × 0.07	0.34 × 0.20 × 0.16	0.25 × 0.24 × 0.05	0.32 × 0.30 × 0.22	0.25 × 0.10 × 0.09	0.10 × 0.10 × 0.10
<i>T</i> /K	85	108	85	85	85	85
Reflection collected	39833	44848	128348	38567	70232	92957
Independent	4339 (0.0578)	5037 (0.0379)	14487 (0.0328)	4384 (0.0282)	11189 (0.0652)	6735 (0.0631)
reflections (<i>R</i> _{int})						
Data/parameters	4339/211	5037/246	14487/79	4084/176	11189/682	6735/128
<i>wR</i> ₂ (obs. and all data)	0.0797 and 0.0842	0.0508 and 0.0551	0.0934 and 0.0961	0.0386 and 0.0387	0.1553 and 0.1651	0.1032 and 0.1102
<i>R</i> ₁ (obs. and all data)	0.0323 and 0.0383	0.0214 and 0.0307	0.0367 and 0.0403	0.0147 and 0.0150	0.0552 and 0.0700	0.0386 and 0.0507

^aCrystal structure contains an equivalent of CH₂Cl₂.

^bThere are two independent palladium complexes in the asymmetric unit, ref 1e.

c, There are two independent palladium complexes and two equivalents of CH_2Cl_2 in the asymmetric unit.