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Synthesis and reactivity of palladium(II) fluoride complexes containing nitrogen-donor ligands†

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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 case.

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*-$(PPh_3)_2Pd^{II}(Ph)(F)$, 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 group[2i] and by Grushin[8] 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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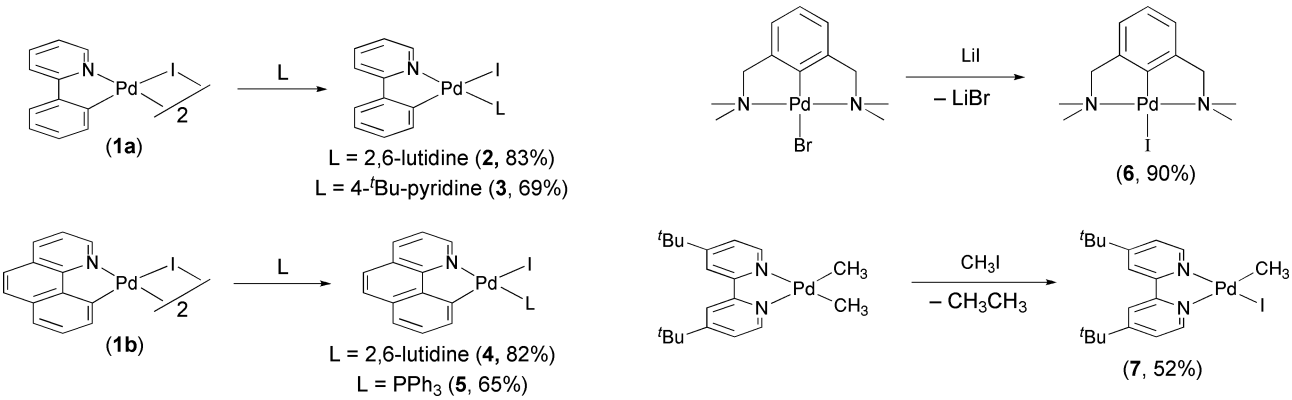
† Electronic supplementary information (ESI) available: Full details of the crystallographic data for compounds **8**, **10–13**, and **15**. CCDC reference numbers 733308–733309 & 741019–741022. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b914426a

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 $[(phpy)Pd(I)]_2$[9] (**1a**) and $[(bzq)Pd(I)]_2$

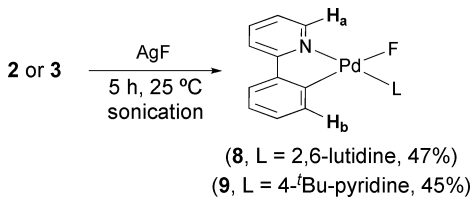


Scheme 1 Synthesis of palladium(II) iodide complexes **2–7**.

(**1b**) (phpy = 2-phenylpyridine; bzq = benzo[*h*]quinoline) with 2,6-lutidine, 4-*tert*-butylpyridine (^{t}Bu-py), or PPh_3, 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($Me)_2$[11] (^{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 N_2 atmosphere for 5 h at 25 °C. The products were isolated by filtration through Celite® and recrystallization from CH_2Cl_2/pentanes to afford **8** as a yellow solid (47%) and **9** as a white solid (45%). Analysis of **8** and **9** by ^{19}F NMR spectroscopy revealed characteristic Pd^{II} fluoride resonances as broad singlets at –260.3 ppm and –243.4 ppm, respectively. The ^{1}H 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 ^{1}H NMR spectrum of **9** at 8.96 (H_a) and 6.50 ppm (H_b). Notably, the ^{1}H 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 $\Delta\delta$ is indicative of a *cis* orientation between the fluoride ligand and the pyridine nitrogen of the phpy (Scheme 2).[9]



Scheme 2 Synthesis of complexes **8** and **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 Fig. 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*-$(PPh_3)_2$Pd(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 ^{19}F NMR spectrum contains a broad singlet at –270.4 ppm for the Pd-bound fluoride ligand. The ^{1}H NMR spectrum of **10** shows signals

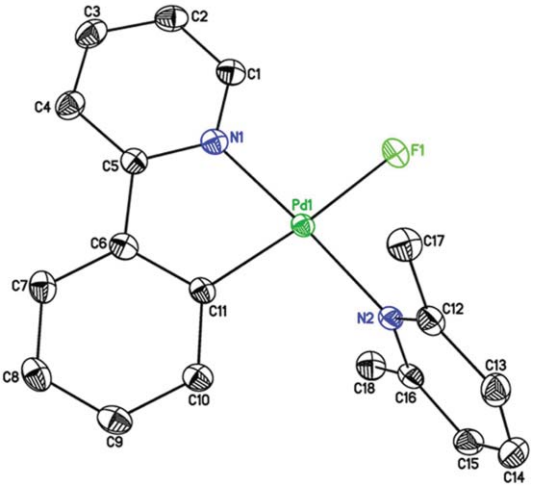
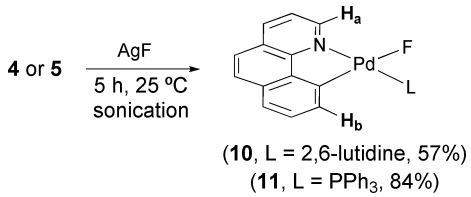


Fig. 1 X-ray crystal structure of **8**. Thermal ellipsoids are drawn at 50% probability, hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Pd1-C11 1.960(3), Pd1-N1 2.017(2), Pd1-N2 2.055(2), Pd1-F1 2.1024(17). Selected bond angles (°): C11-Pd1-N1 82.13(11), C11-Pd1-N2 93.68(10), N1-Pd1-N2 175.36(9), C11-Pd1-F1 173.88(9), N1-Pd1-F1 92.32(8), N2-Pd1-F1 91.95(8).



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

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 CH_2Cl_2 solution of **10** in CH_2Cl_2 at –35 °C provided yellow blocks of this complex. An X-ray crystal structure was obtained, and the structure of **10** is shown in Fig. 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*]quinoline[13] 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(PPh_3)(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 ^{19}F NMR

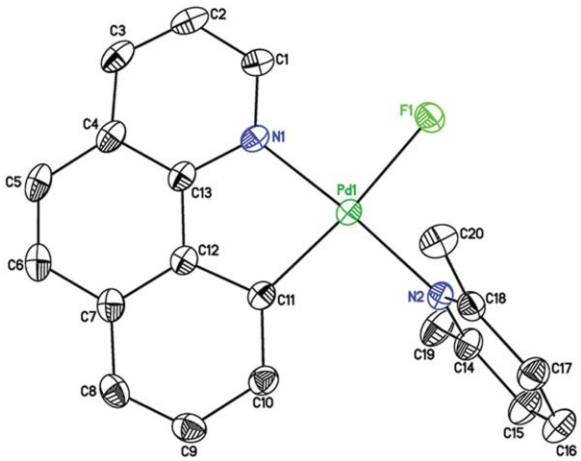


Fig. 2 X-ray crystal structure of **10**. Thermal ellipsoids are drawn at 50% probability, hydrogen atoms and CH_2Cl_2 are omitted for clarity. Selected bond lengths (Å): Pd1-C11 1.9769(19), Pd1-N1 2.0325(15), Pd(1)-N(2) 2.0519(15), Pd1-F1 2.0604(12). Selected bond angles (°): C11-Pd1-N1 82.89(7), C11-Pd1-N2 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).

spectroscopy. In addition, the ^{31}P NMR spectrum of **11** shows a corresponding broad doublet at 40.7 ppm. The $^{31}P/^{19}F$ coupling constant (J_{PF} = 8 Hz) is similar to that observed for other *cis* fluoride and phosphine ligands at Pd^{II} centers.[2a,3,16]

X-ray quality crystals of **11** were obtained by slow diffusion of pentanes into a CH_2Cl_2 solution at −35 °C, and the structure of **11** is shown in Fig. 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 PPh_3 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

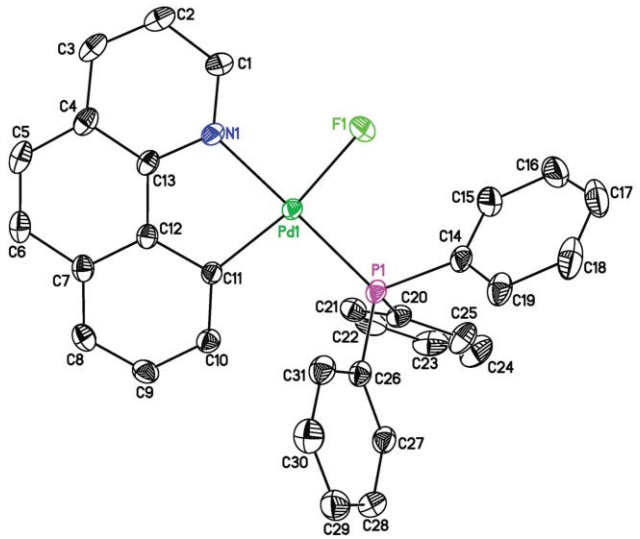


Fig. 3 X-ray crystal structure of **11**. Thermal ellipsoids are drawn at 50% probability, hydrogen atoms and CH_2Cl_2 are omitted for clarity. Two polymorphs were present (only one is shown, see ESI† for more information). Selected bond lengths (Å): Pd1-C11 2.004(2), Pd1-F1 2.0301(15), Pd1-N1 2.0762(19), Pd1-P1 2.2458(6). Selected bond angles (°): 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).

cis PPh_3 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 sp^3 nitrogen donor ligands.[14] This molecule shows a broad singlet at −243.7 ppm for the Pd–F bond by ^{19}F NMR spectroscopy.

Colorless crystals of **12** were generated by slow diffusion of pentanes in a CH_2Cl_2 solution of this compound at −35 °C. An X-ray crystal structure was obtained and is shown in Fig. 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]

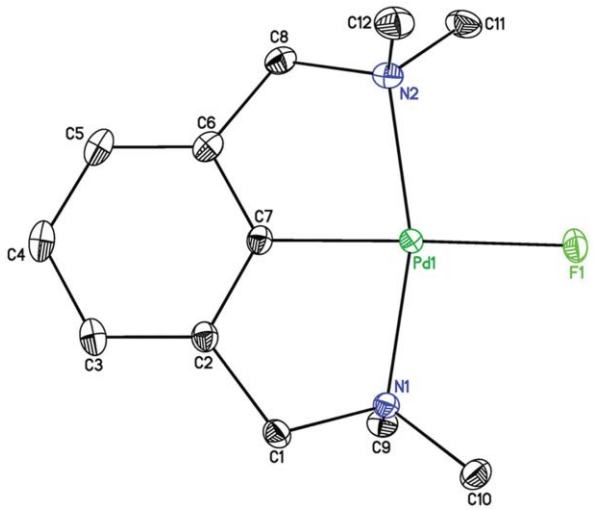
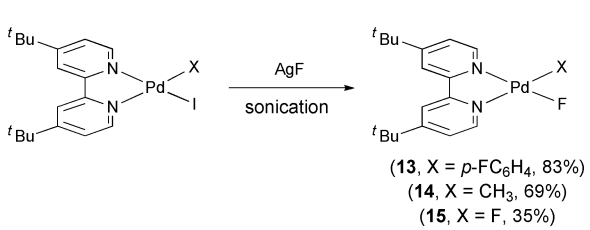


Fig. 4 X-ray crystal structure of **12**. Thermal ellipsoids are drawn at 50% probability, hydrogen atoms and CH_2Cl_2 are omitted for clarity. Selected bond lengths Pd1-C7 1.9068(11), Pd1-N1 2.0954(9), Pd(1)-N(2) 2.1019(9), Pd1-F1 2.0959(7). Selected bond angles (°): C7-Pd1-N1 81.69(4), C7-Pd1-N2 81.61(4),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

Synthesis of (^{t}Bu-bpy)Pd(4-FC_6H_4)(F), 13

Complex **13** was prepared by reaction of (^{t}Bu-bpy)Pd(*p*-FC_6H_4)(I) with AgF as previously reported in the literature (Scheme 4).[2i] The ^{19}F 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.



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

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 Fig. 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 $Pd^{II}(Ar)(F)$ complex,[12] with the closest being in *trans*-$(^iPr_3P)_2Pd(F)(4\text{-}C_5F_4N)$ (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]

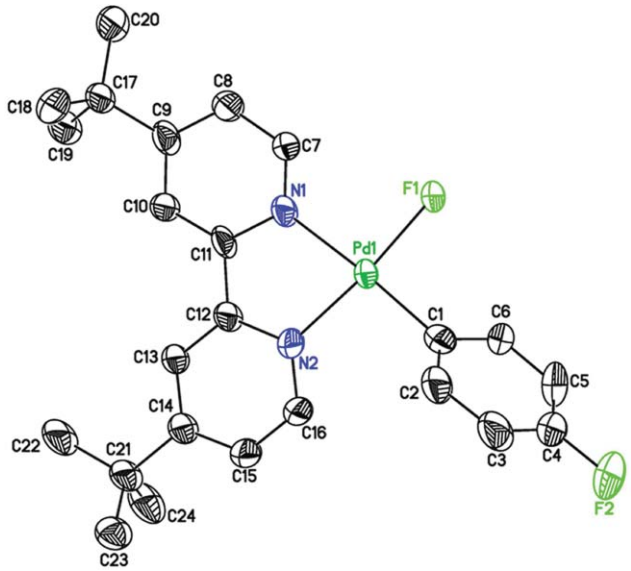


Fig. 5 X-ray crystal structure of **13**. Thermal ellipsoids are drawn at 50% probability, hydrogen atoms and CH_2Cl_2 are omitted for clarity. The structure was solved as two identical structures in a unit cell (only one is shown, see ESI† for more information). Selected bond lengths (Å): Pd1-C1 1.981(8), Pd1-F1 1.999(4), Pd1-N2 2.026(6), Pd1-N1 2.086(7). Selected bond angles (°): 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).

Synthesis of $(^t$Bu-bpy)Pd$(CH_3)(F)$, 14

Compound **14** was synthesized in 69% yield similarly to **8–13** by sonication of palladium iodide **7** with AgF in benzene (Scheme 4). ^{19}F NMR spectroscopy shows a resonance for the fluorine bound to palladium as a broad singlet at −347.4 ppm. The ^{1}H NMR spectrum shows the methyl ligand as a doublet at 0.84 ppm with $J_{HF} = 6$ Hz. The ^{13}C 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 CH_2Cl_2 according to a previously reported procedure (Scheme 4).[2i] Analysis by ^{19}F NMR spectroscopy revealed a broad singlet at −354.06 ppm corresponding to Pd–F. The ^{1}H 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 Fig. 6.

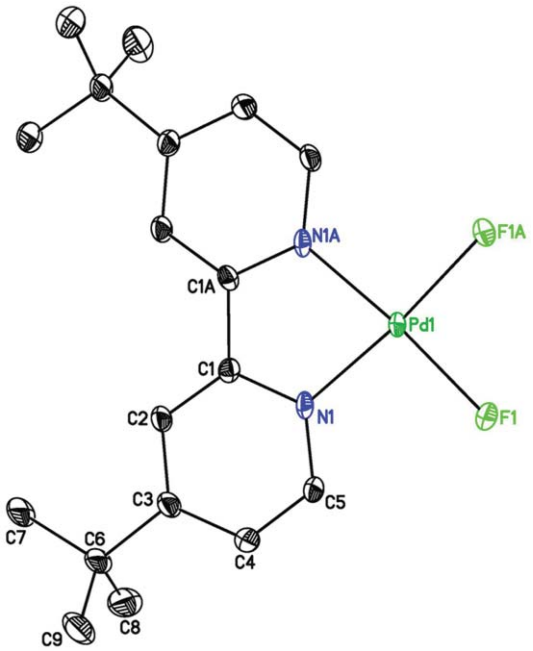


Fig. 6 X-ray crystal structure of **15**. Thermal ellipsoids are drawn at 50% probability, hydrogen atoms and CH_2Cl_2 are omitted for clarity. Selected bond lengths (Å): Pd1-F1 1.9708(11), Pd1-N1 1.9722(15). Selected bond angles (°): F1-Pd1-F1A 91.70(7), F1-Pd1-N1A 174.52(6), F1A-Pd1-N1A 93.64(6), F1-Pd1-N1 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.

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 Fig. 7 and 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

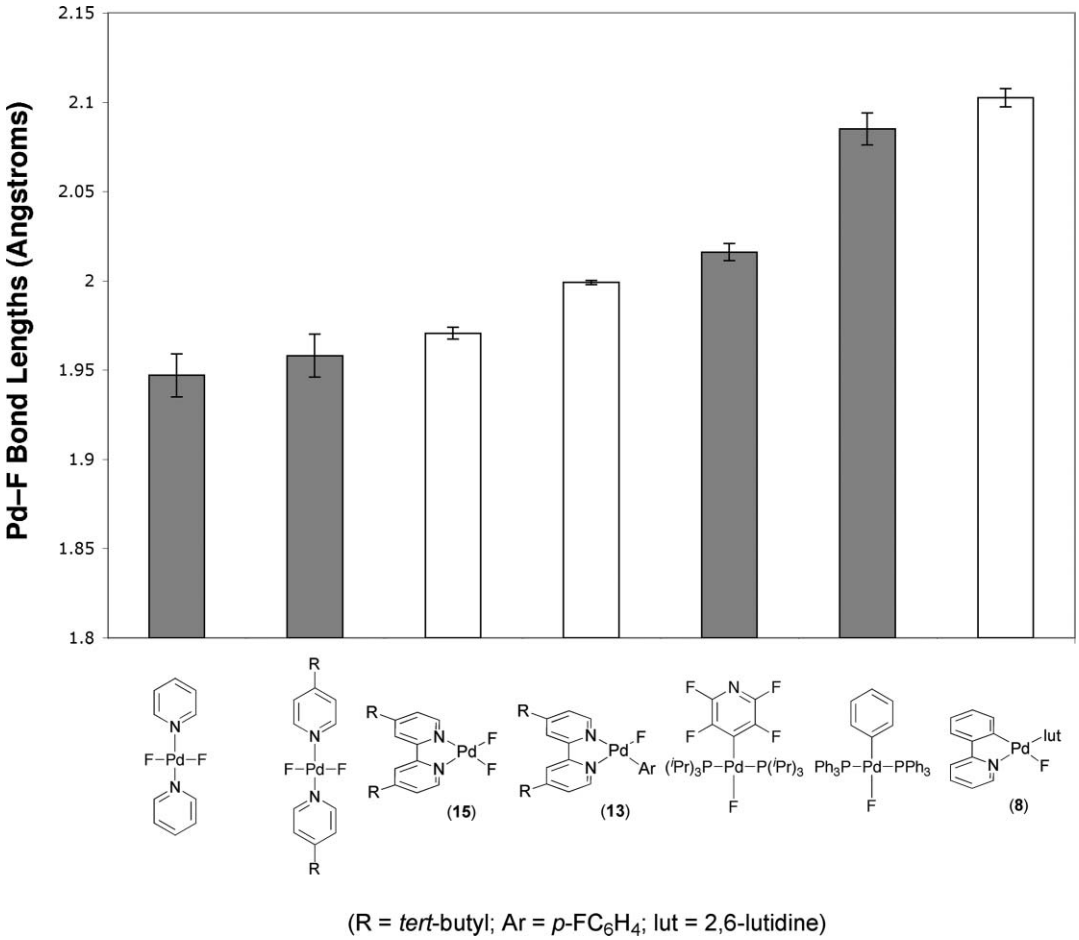


Fig. 7 Comparison of Pd–F bond lengths of selected literature Pd^{II}–F compounds (grey) and compounds (**8**, **13**, **15**, white). Error bars demonstrate three standard deviations (95% confidence level) in the error of the bond lengths.

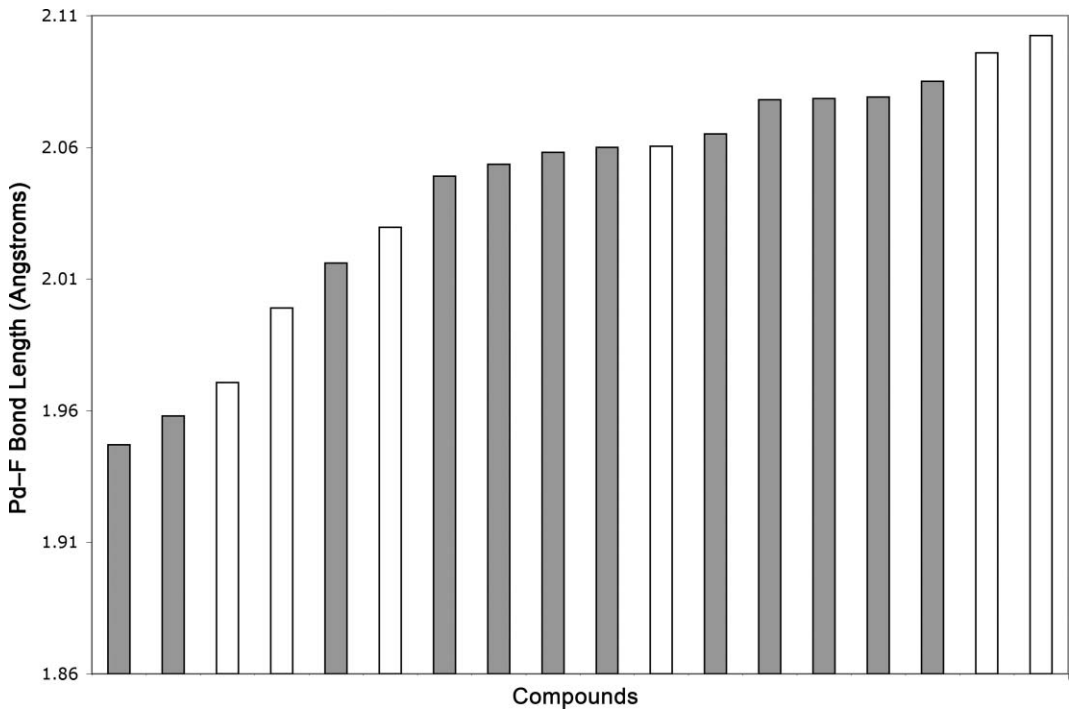


Fig. 8 Comparison of Pd–F bond lengths of literature Pd^{II}–F compounds (grey) and the new complexes **8**, **10–13**, and **15** (white).

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 Pd^0. However, analysis of the crude reaction mixtures by gas chromatography and ^{19}F 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)$_2$Pd(Ph)(F).[8]

Conclusions

In summary, this report described the synthesis, characterization, and reactivity a series of Pd^{II}–F complexes containing sp^2 and sp^3 nitrogen donor ligands. We have disclosed the first examples of isolable Pd^{II} fluorides containing (a) sp^3 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*-(^{t}Bu-bpy)Pd(F)$_2$ has Pd–F bond distances within the error of the related complex *trans*-(^{t}Bu-py)$_2$Pd(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 ^{19}F; 100.57 MHz for ^{13}C) or a MR400 (400.53 MHz for ^1H: 376.87 MHz for ^{19}F; 100.71 MHz for ^{13}C) spectrometer. ^1H, ^{19}F and ^{13}C chemical shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak used as an internal reference. ^{19}F 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 ^{19}F NMR experiments were conducted using "No-D" parameters and are noted accordingly.[20] ^1H and ^{19}F 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 H_2O.[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,^{19}F and ^{13}C NMR spectra are provided for each of these Pd–F compounds in the ESI.† 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 μm 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] (^{t}Bu-bpy)PdMe$_2$,[11] [(phpy)Pd(OAc)]$_2$,[22] [(bzq)Pd(OAc)]$_2$,[23] (bzq)$_2$,[24] (phpy)$_2$,[24] and (4,4′-difluoro-1,1′-biphenyl)[25] were prepared according to literature procedures. Palladium fluorides (^{t}Bu-bpy)Pd(*p*-FC$_6$H$_4$)(F) and (^{t}Bu-bpy)PdF$_2$ were prepared according to previously reported procedures.[2i] AgF and 1-fluoro-4-iodobenzene were obtained from Matrix Chemicals. MeI, ^{t}Bu-bpy, 2,6-lutidine, and LiI were obtained from Aldrich. ^{t}Bu-py was obtained from TCI America. PPh_3 was obtained from Strem Chemicals. All reagents were used as received. Nitrobenzene-d_5, CD_2Cl_2, and $CDCl_3$ 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 Na^0/benzophenone and stored over activated 4 Å molecular sieves. Acetone was distilled from $CaSO_4$. 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–H_2O (3 × 10 mL) followed by a 1 : 1 mixture of hexanes–Et_2O (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% $CDCl_3$, 5% C_5D_5N): 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); ^{13}C NMR ($CDCl_3$, 1 drop of C_5D_5N): 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 ^{13}C resonances appear to be coincidentally overlapping). (Found: C, 38.07, H, 1.93, N, 3.50. $C_{22}H_{16}I_2N_2Pd_2$ 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 CH_2Cl_2–hexanes and dried *in vacuo*

yielding **2** as a yellow solid (0.53 g, 83% yield). ^{1}H NMR ($CDCl_3$): 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). ^{13}C NMR ($CDCl_3$): 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 ^{13}C resonances appear to be coincidentally overlapping). (Found: C, 43.44, H, 3.31, N, 5.88. $C_{18}H_{17}IN_2Pd$ requires C, 43.70, H, 3.36, N, 5.63).

(phpy)Pd('Bu-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 'Bu-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). ^{1}H NMR ($CDCl_3$): 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). ^{13}C NMR ($CDCl_3$): 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 ^{13}C resonances appear to be coincidentally overlapping). (Found: C, 45.65, H, 4.15, N, 5.26. $C_{22}H_{21}IN_2Pd$ 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). ^{1}H NMR ($CDCl_3$): 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). ^{13}C NMR ($CDCl_3$): 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. $C_{20}H_{17}IN_2Pd$ requires C, 46.31, H, 3.30, N, 5.40).

(bzq)Pd(PPh_3)(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 PPh_3 (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). ^{1}H NMR ($CDCl_3$): 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). ^{31}P NMR ($CDCl_3$): δ 44.67 (1P). ^{13}C NMR ($CDCl_3$): 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. $C_{31}H_{23}INPPd$ 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 CH_2Cl_2–hexanes. The product was obtained as a microcrystalline yellow solid (0.71 g, 90% yield). ^{1}H NMR ($CDCl_3$): δ 6.97 (t, J = 8 Hz, 1H), 6.74 (d, J = 8 Hz, 2H), 3.98 (s, 4H), 2.99 (s, 12H); ^{13}C NMR ($CDCl_3$): δ 159.19, 145.15, 124.60, 119.75, 73.94, 54.84. (Found C, 33.95, H, 4.34, N, 6.59. $C_{12}H_{19}IN_2Pd$ requires C, 33.94, H, 4.51, N, 6.60).

('Bu-bpy)Pd(Me)(I), 7. In the glovebox, (*t*-Bu-bpy)$PdMe_2$ (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 CH_2Cl_2/hexanes afforded analytically pure compound (0.86 g, 52% yield). ^{1}H NMR ($CDCl_3$): 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). ^{13}C NMR ($CDCl_3$): 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. $C_{19}H_{27}IN_2Pd$ 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 N_2, the resulting mixture was then filtered through Celite® and washed with CH_2Cl_2 (3 × 5 mL). This filtration was repeated, and then the solvent removed *in vacuo*. The resulting solid was recrystallized from CH_2Cl_2–pentanes, and the product was obtained as a yellow solid (0.23 g, 47% yield). ^{1}H NMR ($CDCl_3$): 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). ^{19}F NMR ($CDCl_3$): δ –260.3 (br s, 1F). ^{13}C NMR ($CDCl_3$): 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. $C_{18}H_{17}FN_2Pd$ requires C, 55.90, H, 4.43, N, 7.24%).

(phpy)Pd('Bu-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). ^{1}H 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. $C_{20}H_{21}FN_2Pd$ 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). ^{1}H 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. $C_{20}H_{17}FN_2Pd$ requires 58.48; H, 4.17 N, 6.82).

(bzq)Pd(PPh$_3$)(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 a white solid (0.28 g, 84% yield). ^{1}H 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 (apparent s, 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. $C_{31}H_{23}FNPPd\cdot C_6H_6$ 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 × 5 mL) and then with CH_2Cl_2 (5 × 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). ^{1}H 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. $C_{12}H_{19}FN_2Pd$ requires C, 45.51, H, 6.05, N, 8.85).

('Bu-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). ^{1}H 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. $C_{19}H_{27}FN_2Pd$ 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 ^{19}F 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,

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	$C_{18}H_{17}FN_2Pd$	$C_{21}H_{19}Cl_2FN_2Pd$	$C_{32}H_{25}Cl_2FNPPd$	$C_{13}H_{21}Cl_2FN_2Pd$	$C_{57}H_{65}F_4N_4Pd_2$	$C_{19}H_{26}Cl_2F_2N_2Pd$
M	386.74	495.68	650.80	401.62	1094.93	497.72
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Orthorhombic
Space group (standard setting)	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	Ia	$Pccn$
a/Å	9.6607(11)	13.904(4)	8.7399(5)	8.4407(6)	17.9592(12)	11.1616(9)
b/Å	9.2742(10)	11.409(3)	17.2959(9)	9.5451(6)	17.5332(12)	11.9919(9)
c/Å	17.810(2)	14.366(4)	20.3468 (11)	11.5693(8)	20.2950(14)	15.6096(10)
α/°			96.861(1)	105.314(1)		
β/°	96.023(2)	117.158(3)	98.293(1)	95.629(1)	95.135(1)	90
γ/°			104.123(1)	116.010(1)		
V/Å^3	1586.9(3)	2027.8(9)	2913.0(3)	782.97(9)	6364.9(8)	2089.3(3)
Z, calculated density/Mg m^{-3}	4, 1.619	4, 1.624	4, 1.484	2, 1.704	4, 1.143	4, 1.582
Absorption coefficient/mm^{-1}	1.177	1.195	0.904	1.525	0.610	1.166
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
T/K	85	108	85	85	85	85
Reflections collected	39833	44848	128348	38567	70232	92957
Independent reflections (R_{int})	4339 (0.0578)	5037 (0.0379)	14487 (0.0328)	4384 (0.0282)	11189 (0.0652)	6735 (0.0631)
Data/parameters	4339/211	5037/246	14487/79	4084/176	11189/682	6735/128
wR_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
R_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

[a] Crystal structure contains an equivalent of CH_2Cl_2. [b] There 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.

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° 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° 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 ESI.† 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 Fig. 8.[27]

Abbreviations

dba	= dibenzylidene acetone
NCN	= *N*,*N*,*N*′,*N*′-tetramethyl-1,3-xylylenediamine
^{t}Bu-bpy	= 4,4′-di-*tert*-butyl-2,2′-bipyridine
phpy	= 2-phenylpyridine
bzq	= benzo[*h*]quinoline
p-FPh	= 4-fluorophenyl
^{t}Bu-py	= 4-*tert*-butylpyridine

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Notes and references

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