Supporting Information for:

Synthesis and Reactivity of a Mono-σ-Aryl Palladium(IV) Fluoride Complex

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General Procedures:

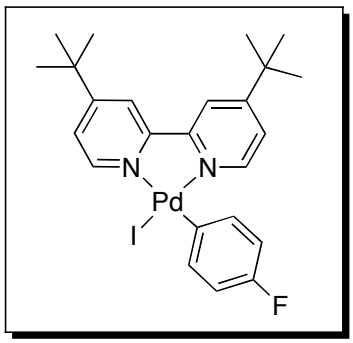
NMR spectra were obtained on a Varian Inova 400 (399.96 MHz for ^{1}H; 376.34 MHz for ^{19}F; 100.57 MHz for ^{13}C) or a MR400 (400.53 MHz for ^{1}H: 376.87 MHz for ^{19}F; 100.71 MHz for ^{13}C) spectrometer. ^{1}H, ^{19}F and ^{13}C chemical shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak used as an internal reference. ^{19}F NMR spetra are referenced on a unified scale, where the single primary reference is the frequency of the residual solvent peak in the ^{1}H NMR spectrum.[1] Several ^{19}F NMR experiments were conducted using "No-D" parameters and are noted accordingly.[2] ^{1}H and ^{19}F multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), quartet (q), and multiplet (m). Elemental analyses were conducted by Atlantic Microlabs in Norcross, Georgia. Sonication was performed using a VWR Model 75H7 ultrasound bath, with the temperature regulated by a Neslab RTE-111 recirculating chiller. IR spectra were obtained on a Perkin-Elmer Spectrum BX FT-IR spectrometer.

Materials and Methods:

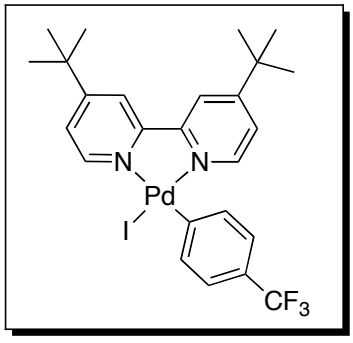
The palladium complexes $Pd(dba)_2$[3] and (*t*-Bu-bpy)$PdCl_2$[4] were prepared according to literature procedures. Authentic samples of biaryl products **4a–c** were prepared as described in the literature by McClure and coworkers.[5] AgF, XeF_2, 1-fluoro-4-iodobenzene, 1-iodobenzotrifluoride, 1,4-difluorobenzene (**3a**), and 4-fluorobenzotrifluoride (**3b**) were obtained from Matrix Chemicals. 4,4′-Di-*tert*-butyl-2,2′-bipyridine, 4-iodoanisole, 1-chloro-4-fluorobenzene, 1-fluoro-2,4,6-trimethylpyridium tetrafluoroborate, and *N*-fluorosulfanimide were obtained from Aldrich. 4-Fluoroanisole (**3c**) was obtained from Acros. All reagents were used as received. Nitrobenzene-d_5, CD_2Cl_2, and $CDCl_3$ were obtained from Cambridge Isotope Laboratories, and nitrobenzene was obtained from Acros. All other solvents were obtained from Fisher Chemical. Tetrahydrofuran, dichloromethane, and pentane were purified using an Innovative Technologies (IT) solvent purification system consisting of a copper catalyst, activated alumina, and molecular sieves. CD_2Cl_2 was distilled from CaH_2. Acetone was distilled from $CaSO_4$. Nitrobenzene and nitrobenzene-d_5 were distilled from P_2O_5 and placed over 4Å molecular sieves. Benzene and hexanes were distilled from Na^0/benzophenone. All syntheses were conducted using standard Schlenk techniques or in an inert atmosphere glovebox unless otherwise stated.

Experimental Details

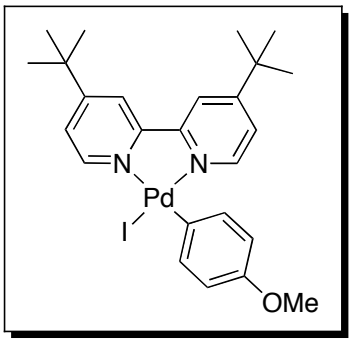
General procedure for the synthesis of complexes **1a-1c**: Under nitrogen, $Pd(dba)_2$ (2.9 g, 5.1 mmol, 1.0 equiv) was weighed into a 250 mL round bottom flask and dissolved in THF (72 mL). 4, 4′-Di-*tert*-butylbipyridine (1.9 g, 6.6 mmol, 1.3 equiv) was added, and the resulting mixture was stirred at 25 ºC for 15 min. The aryl iodide (7.1 mmol, 1.4 equiv) was added, and the reaction was warmed to 60 °C for 3 h. The reaction mixture was filtered through a plug of Celite, and the solvent was removed under reduced pressure. The resulting solid was washed with hexanes (3 x 50 mL) and then with a 50:50 mixture of ether and hexanes (~400 mL) until residual dibenzylidene acetone (dba) was completely removed. The product was then redissolved in CH_2Cl_2 (20 mL) and stirred with activated charcoal for 30 min. This suspension was filtered through a plug of Celite, and the solvent was removed *in vacuo* to yield the products as orange solids.



Complex **1a** (1.6 g, 31% yield). ^{1}H NMR ($CDCl_3$): δ 9.47 (d, J = 6 Hz, 1H), 7.95 (multiple peaks, 2H), 7.53 (d, J = 6 Hz, 1H), 7.48 (d, J = 6 Hz, 1H), 7.30 (multiple peaks, 3H), 6.81 (multiple peaks, 2H), 1.40 (s, 9H), 1.37 (s, 9H); ^{19}F NMR ($CDCl_3$): δ –123.2 (m, 1F); ^{13}C NMR ($CDCl_3$): δ 163.33, 163.27, 160.93 (d, J = 239.8 Hz), 155.91, 153.86, 152.52, 149.55, 138.52, 136.67 (d, J = 5 Hz), 123.86 (br s), 123.54, 118.43, 118.01, 113.98 (d, J = 19 Hz), 35.53, 35.48, 30.38, 30.26. Anal. Calc. for $C_{24}H_{28}FIN_2Pd$: C, 48.30, H, 4.73, N, 4.69; Found: C, 48.09, H, 4.75, N, 4.72. Notably, small amounts (~7%) of [(*t*-Bu-bpy)Pd(I)$_2$] were observed in the ^{1}H, and ^{13}C NMR spectra of most isolated samples of **1a**.

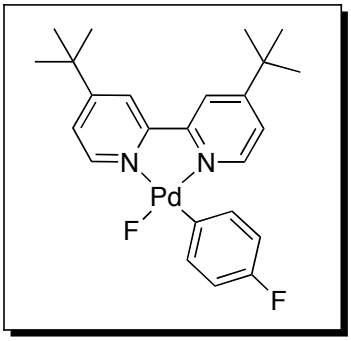


Complex **1b** (1.1 g, 33% yield). ^{1}H NMR ($CDCl_3$): δ 9.49 (d, J = 6 Hz, 1H), 7.95 (multiple peaks, 2H), 7.55 (d, J = 8 Hz, 2H), 7.48 (multiple peaks, 2H), 7.34 (m, 1H), 7.25 (d, J = 8 Hz, 2H), 1.41 (s, 9H), 1.38 (s, 9H); ^{19}F NMR ($CDCl_3$): δ –61.8 (s, 3F); ^{13}C NMR ($CDCl_3$): 163.54, 163.43, 155.94, 153.84, 153.60, 152.65, 149.52, 136.82, 125.48 (q, J = 32 Hz), 124.99 (q, J = 272 Hz), 123.97, 123.73, 123.02 (q, J = 4 Hz), 118.49, 118.05, 35.54, 35.48, 30.56, 30.23. Anal. Calc. for $C_{25}H_{28}F_3IN_2Pd$: C, 46.42, H, 4.36, N, 4.33; Found: C, 46.36, H, 4.33, N, 4.35. Notably, small amounts (~8%) of [(*t*-Bu-bpy)Pd(I)$_2$] were observed in the ^{1}H and ^{13}C NMR spectra of most isolated samples of **1b**.

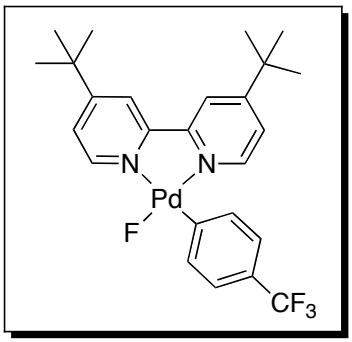


Complex **1c** (1.0 g, 33% yield). ^{1}H NMR ($CDCl_3$): δ 9.49 (d, *J* = 6 Hz, 1H), 7.94 (multiple peaks, 2H), 7.61 (dd, *J* = 6, 2 Hz, 1H), 7.48 (dd, *J* = 6, 2 Hz, 1H), 7.31 (dd, *J* = 5, 2 Hz, 1H), 7.25 (d, *J* = 8 Hz, 2H), 6.73 (d, *J* = 8 Hz, 2H), 3.76 (s, 3H), 1.41 (s, 9H), 1.37 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 163.09, 163.05, 156.64, 155.87, 153.87, 153.77, 152.58, 149.86, 136.36, 134.06, 123.81, 123.46, 117.84, 113.58, 55.16, 35.48, 35.43, 30.38, 30.26. Anal. Calc. for $C_{25}H_{31}IN_2OPd$: C, 49.32, H, 5.13, N, 4.60; Found: C, 49.12, H, 5.19, N, 4.60. Notably, small amounts (~8%) of [(*t*-Bu-bpy)Pd$(I)_2$] were observed in the ^{1}H, and ^{13}C NMR spectra of most isolated samples of **1c**.

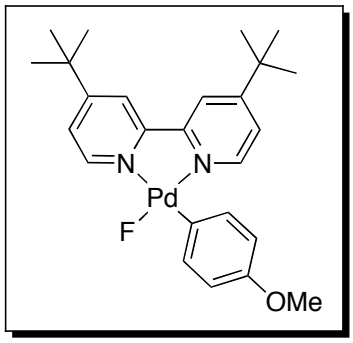
General procedure for the synthesis of complexes **2a-2c**. [(*t*-Bu-bpy)Pd(Ar)(I)] (3.6-3.8 mmol, 1 equiv) and AgF (3.9 equiv) were dissolved in benzene (20 mL) in a 50 mL amber glass jar. The jar was sealed with a Teflon-lined cap, and the reaction was sonicated in the dark at 25 °C for 1.5-4 h. The resulting mixture was filtered through a plug of Celite in the drybox. The plug was washed with benzene (1 x 5 mL) and then with CH_2Cl_2 (5 x 2 mL). This filtration was repeated to remove residual silver salts. The solvent was then removed under reduced pressure, and pentane was added to precipitate a yellow solid. The solid was collected and dried *in vacuo* to afford the product as a yellow solid. It should be noted that without the second filtration, the filtrate changes color from yellow to gold over several minutes, which is indicative of impurities in the product (as confirmed by ^{1}H and ^{19}F NMR spectroscopy).



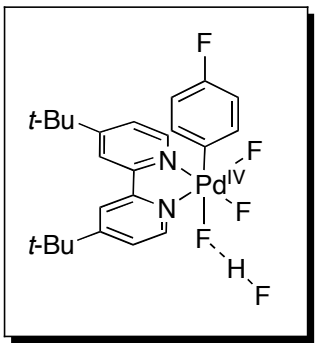
Complex **2a** (0.42 g, 83% yield). ^{1}H NMR (CD_2Cl_2): δ 8.74 (d, *J* = 6 Hz, 1H), 8.08 (d, *J* = 6 Hz, 1H), 8.00 (d, *J* = 2 Hz, 1H), 7.98 (d, *J* = 2 Hz, 1H), 7.62 (dd, *J* = 4, 2 Hz, 1H), 7.40 (multiple peaks, 2H), 7.29 (dd, *J* = 4, 2 Hz, 1H), 6.85 (dd, *J* = 11, 9 Hz, 2H), 1.44 (s, 9H), 1.38 (s, 9H); ^{19}F NMR (CD_2Cl_2): δ –122.9 (m, 1F), –340.67 (br s, 1F); ^{13}C NMR (CD_2Cl_2): δ 164.71, 163.88, 161.75 (d, *J* = 238 Hz), 157.34, 153.44, 153.05, 148.49 (d, *J* = 3 Hz), 146.60, 135.80 (d, *J* = 5 Hz), 124.27, 124.11, 119.66, 118.59, 113.54 (d, *J* = 19 Hz), 36.13, 35.98, 30.72, 30.47. Complex **2a** is extremely hygroscopic, and even after extensive drying under vacuum, ^{1}H NMR spectroscopic analysis in dry CD_2Cl_2 showed the presence of 0.60 equiv of H_2O/complex (observed as a broad resonance at 1.42 ppm). The microanalysis results are consistent with this stoichiometry. Anal. Calc. for $C_{24}H_{28}F_2N_2Pd$•0.60 H_2O: C, 57.68, H, 5.77, N, 5.61; Found: C, 57.89, H, 5.87, N, 5.31. Notably, traces (~3%) of [(*t*-Bu-bpy)Pd$(F)_2$] were observed in the ^{1}H, ^{19}F, and ^{13}C NMR spectra of most isolated samples of **2a**.



Complex **2b** (0.39 g, 77% yield). ^{1}H NMR (CD_2Cl_2): δ 8.74 (d, J = 6 Hz, 1H), 8.01 (multiple peaks, 3H), 7.64 (multiple peaks, 3H), 7.30 (multiple peaks, 3H), 1.45 (s, 9H), 1.39 (s, 9H); ^{19}F NMR (CD_2Cl_2): –62.10 (s, 3F), –341.6(s, 1F); ^{13}C NMR (CD_2Cl_2): δ 164.94, 164.17, 157.31, 153.45, 152.96, 148.44 (q, J = 4 Hz), 136.84, 135.87 (q, J = 3 Hz), 126.10 (q, J = 31 Hz), 125.80 (q, J = 271 Hz), 124.37, 124.11, 122.84 (q, J = 4 Hz), 119.87, 118.77, 36.17, 36.02, 30.71, 30.46. Complex **2b** is extremely hygroscopic, and even after extensive drying under vacuum, ^{1}H NMR spectroscopic analysis in dry CD_2Cl_2 showed the presence of 0.67 equiv of H_2O/complex (observed as a broad resonance at 1.41 ppm). The microanalysis results are consistent with this stoichiometry. Anal. Calc. for $C_{25}H_{28}F_4N_2Pd$•0.67 H_2O: C, 54.42, H, 5.23, N, 5.07; Found: C, 54.28, H, 5.43, N, 5.05. Notably, trace amounts (~4%) of [(*t*-Bu-bpy)Pd$(F)_2$] were observed in the ^{1}H, ^{19}F, and ^{13}C NMR spectra of most isolated samples of **2b**.

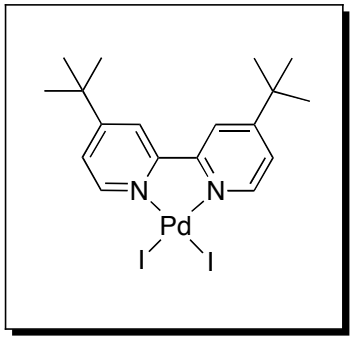


Complex **2c** (0.21 g, 45% yield). Notably, trace amounts (~6%) of [(*t*-Bu-bpy)Pd$(F)_2$] were observed in the ^{1}H, ^{19}F, and ^{13}C NMR spectra of most isolated samples of **2c**. ^{1}H NMR (CD_2Cl_2): δ 8.77 (d, J = 6 Hz, 1H), 8.17 (d, J = 6 Hz, 1H), 8.02 (d, J = 2 Hz, 1H), 7.99 (d, J = 2 Hz, 1H), 7.61 (dd, J = 4, 2 Hz, 1H), 7.31 (d, J = 8 Hz, 2H), 7.28 (d, J = 8, 2 Hz, 1H), 6.72 (d, J = 8 Hz, 2H), 3.77 (s, 3H), 1.44 (s, 9H), 1.38 (s, 9H); ^{19}F NMR (CD_2Cl_2): δ –338.7 (s, 1F); ^{13}C NMR (CD_2Cl_2): δ 164.53, 163.65, 157.64, 157.30, 153.41, 153.18, 148.48, 135.86, 135.31, 124.17, 124.05, 119.57, 118.52, 113.06, 55.63, 36.10, 35.94, 30.72, 30.47. Complex **2c** is extremely hygroscopic, and even after extensive drying under vacuum, ^{1}H NMR spectroscopic analysis in dry CD_2Cl_2 showed the presence of 0.86 equiv of H_2O/complex (observed as a broad resonance at 1.41 ppm). The microanalysis results are consistent with this stoichiometry. Anal. Calc. for $C_{25}H_{31}FN_2OPd$•0.86 H_2O: C, 58.26, H, 6.23, N, 5.44; Found: C, 58.02, H, 6.18, N, 5.29. Notably, trace amounts (~4%) of [(*t*-Bu-bpy)Pd$(F)_2$] were observed in the ^{1}H, ^{19}F, and ^{13}C NMR spectra of most isolated samples of **2b**.

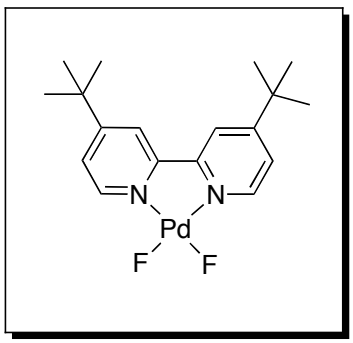


Complex **5a**. In a glovebox, **2a** (10 mg, 0.02 mmol, 1 equiv) was dissolved in nitrobenzene (1 mL) and added to a 4 mL scintillation vial containing XeF_2 (10 mg, 0.06 mmol, 3 equiv). The vial was sealed with a Teflon-lined cap and stirred for 25 ºC for 10 s to yield an orange solution. The reaction mixture was then stirred at 80 °C for 2 min to afford a yellow solution. Hexanes (10 mL) was added to precipitate the crude inorganic product. The resulting yellow solid was collected, washed with hexanes (3 x 2 mL), and dried *in vacuo* to yield the crude product. This material was further purified by recrystallization from THF/hexanes and was obtained as a pale yellow solid (4.1 mg,

38% yield). The microanalysis results were consistently slightly low in carbon, which is likely due to traces of H_2O (see above for a discussion of the hygroscopicity of **2-c**). Anal. Calc. for $C_{24}H_{29}F_5N_2Pd$: C, 52.71, H, 5.34, N, 5.12; Found: C, 51.99, H, 5.56, N, 5.30. Characterization by NMR spectroscopy is reported in d_5-nitrobenzene and CD_2Cl_2, and low temperature NMR experiments were carried out in CD_2Cl_2 (due to the high freezing point of nitrobenzene). However, it is to be noted that **5a** shows significant reactivity with CD_2Cl_2 at room temperature; therefore, some impurities were observed in the spectra in CD_2Cl_2, and these grew in as the samples were allowed to stand for longer times.[8] ^{1}H NMR (d_5-nitrobenzene): δ 9.48 (d, J = 6 Hz, 2H), 8.76 (s, 2H), 8.03 (d, 6Hz, 2H), 7.58 (m, 2H), 6.88 (m, 2H), 1.42 (s, 18H); ^{19}F NMR (d_5-nitrobenzene): δ –116.7 (m, 1F), –204.8 (br. s, 1F, Pd–F *trans* from C), –253.2 (br s, 2F, Pd–F *trans* to N). A minor impurity with ^{19}F NMR resonances at δ –116.6 and –247 ppm proved extremely challenging to remove completely from samples of **5a**. ^{1}H NMR (CD_2Cl_2, 22 °C): δ 12.86 (br s, 1H), 8.96 (d, J = 6 Hz, 2H), 8.19 (s, 2H), 7.83 (d, J = 6 Hz, 2H), 6.89 (m, 2H), 6.82 (m, 2H), 1.48 (s, 18H); ^{19}F NMR (CD_2Cl_2, 22 °C): δ –117.2 (br s, 1F), –206.3 (m, 1F, Pd–F *trans* to Ar), –257.4 (br s, 2F, Pd–F *trans* to N); ^{1}H NMR (CD_2Cl_2, –70 °C): δ 12.71 (dd, J = 370, 31 Hz, 1H, Pd–F*H*F), 8.96 (br s, 2H), 8.10 (br s, 2H), 7.84 (br s, 2H), 6.83 (m, 4H), 1.41 (s, 18H); ^{19}F NMR (CD_2Cl_2, –70 °C): δ –116.7 (m, 1F), –177.6 (dd, J = 364, 116 Hz, 1F, Pd–FH*F*), –204.5 (m, 1F, Pd–*F*HF), –256.9 (d, J = 60 Hz, 2F, *trans* to N).



(*t*-Bu-bpy)Pd(I)$_2$.[6] Using standard air-free techniques, (*t*-Bu-bpy)$PdCl_2$ (500 mg, 1.1 mmol, 1 equiv) was dissolved in acetone (15 mL). NaI (0.49 g, 3.0 mmol, 2.7 equiv) was added, and the reaction mixture was stirred for 2 h. The resulting purple precipitate was collected on a frit and washed with copious amounts of acetone (~50 mL).[7] The crude product was then dissolved in CH_2Cl_2 (20 mL) and stirred with charcoal for 30 min. This suspension was filtered through a plug of Celite and washed with CH_2Cl_2 (20 mL). The solvent was removed *in vacuo* to afford the product as a purple solid (0.64 g, 91% yield). ^{1}H NMR ($CDCl_3$): δ 9.89 (d, J = 6 Hz, 2H), 7.93 (d, J = 2 Hz, 2H), 7.53 (dd, J = 6, 2 Hz, 2H), 1.45 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 164.00, 156.28, 153.77, 124.39, 119.00, 35.68, 30.28. Anal. Calc. for $C_{18}H_{24}I_2N_2Pd$: C, 34.39, H, 3.85, N, 4.46; Found: C, 34.49, H, 3.77, N, 4.49.



(*t*-Bu-bpy)Pd(F)$_2$. Using a modification of Vigalok's procedure,[7] (*t*-Bu-bpy)Pd(I)$_2$ (90 mg, 0.14 mmol, 1.0 equiv) and AgF (50 mg, 0.42 mmol, 3.0 equiv) were weighed into a 20 mL scintillation vial and dissolved in CH_2Cl_2 (4 mL). The vial was covered in aluminum foil, and the mixture was stirred for 3 h at room temperature. The resulting suspension was filtered through a plug of Celite, concentrated, and the product was precipitated with pentane. This solid was collected and washed with pentane (3 x 2 mL). It was then redissolved in CH_2Cl_2 (2 mL), and

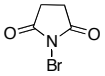
the suspension was filtered through a plug of Celite. The solvent was removed *in vacuo*, to yield the product as a pale yellow solid (20 mg, 35% yield). ^{1}H NMR (CD_2Cl_2): δ 8.51 (d, J = 6 Hz, 2H), 7.88 (s, 2H), 7.54 (d, J = 6 Hz, 2H), 1.42 (s, 18H); ^{19}F NMR (CD_2Cl_2): δ –354.06 (s, 2F); ^{13}C NMR (CD_2Cl_2): δ 165.95, 156.05, 149.49, 124.19, 119.46, 36.37, 30.59. Complex **6** is extremely hygroscopic, and even after extensive drying under vacuum, ^{1}H NMR spectroscopic analysis in dry CD_2Cl_2 showed the presence of 0.86 equiv of H_2O/complex (observed as a broad resonance at 1.45 ppm). The microanalysis results are consistent with this stoichiometry. Anal. Calc. for $C_{18}H_{24}F_2N_2Pd$•0.86 H_2O: C, 50.47, H, 5.85, N, 6.54; Found: C, 50.70, H, 5.92, N, 6.41.

General procedure for oxidative fluorination of **2a-2c**. In a glovebox, the Pd^{II} fluoride (**2a-2c**) (10 mg, 1 equiv) was dissolved in nitrobenzene (1 mL). This solution was added to a 4 mL scintillation vial containing XeF_2 (3 equiv). The vial was sealed with a Teflon-lined cap, vigorously shaken, and then heated at 90 °C for 1 h. The resulting mixture was cooled to room temperature, hexafluorobenzene was added as an internal standard, and the reactions were analyzed by ^{19}F NMR spectroscopy. The identities of the organic products were confirmed by the synthesis of authentic samples of these materials.

It is important to note that the optimal conditions for ^{19}F NMR spectroscopic analysis of these reactions were as follows: spectral width = –80 to –180 ppm, relaxation delay = 5 s, and acquisition time = 6.4 s. These conditions were required due to the faster relaxation time of the standard relative to the fluoroarene products.

Studies of the reactivity of **5a**. In a glovebox, **5a** (1 equiv) was dissolved in nitrobenzene (0.012 M solution). Hexafluorobenzene was added as an internal standard, the NMR tube was sealed with a Teflon-lined cap, and the reaction mixture was shaken vigorously. This reaction was then analyzed by ^{19}F NMR spectroscopy to determine the ratio of starting material to standard. The NMR tube was the returned to the glovebox, and the oxidant (3 equiv) was added as a solid. The tube was shaken vigorously, removed from the glovebox, and heated in an oil bath at 80 °C for 1 h. After cooling, the reaction was again analyzed by ^{19}F NMR to determine the percent conversion of the starting material to the product.

Table S1: Reactivity of **5a** with Electrophilic Oxidants

Entry	Oxidant	Yield 3a
1	XeF_2	92%
2	$(PhSO_2)_2NF$	83%
3		50%
4		≥95%
5	$PhICl_2$	65%[a]
6	$PhI(OAc)_2$	9%[b]

[a]18% of 1-chloro-4-fluorobenzene was also formed.
[b]87% of 1-acetoxy-4-fluorobenzene was formed.

Figure S1: ^{19}F NMR spectrum of **5a** in d^5-nitrobenzene.

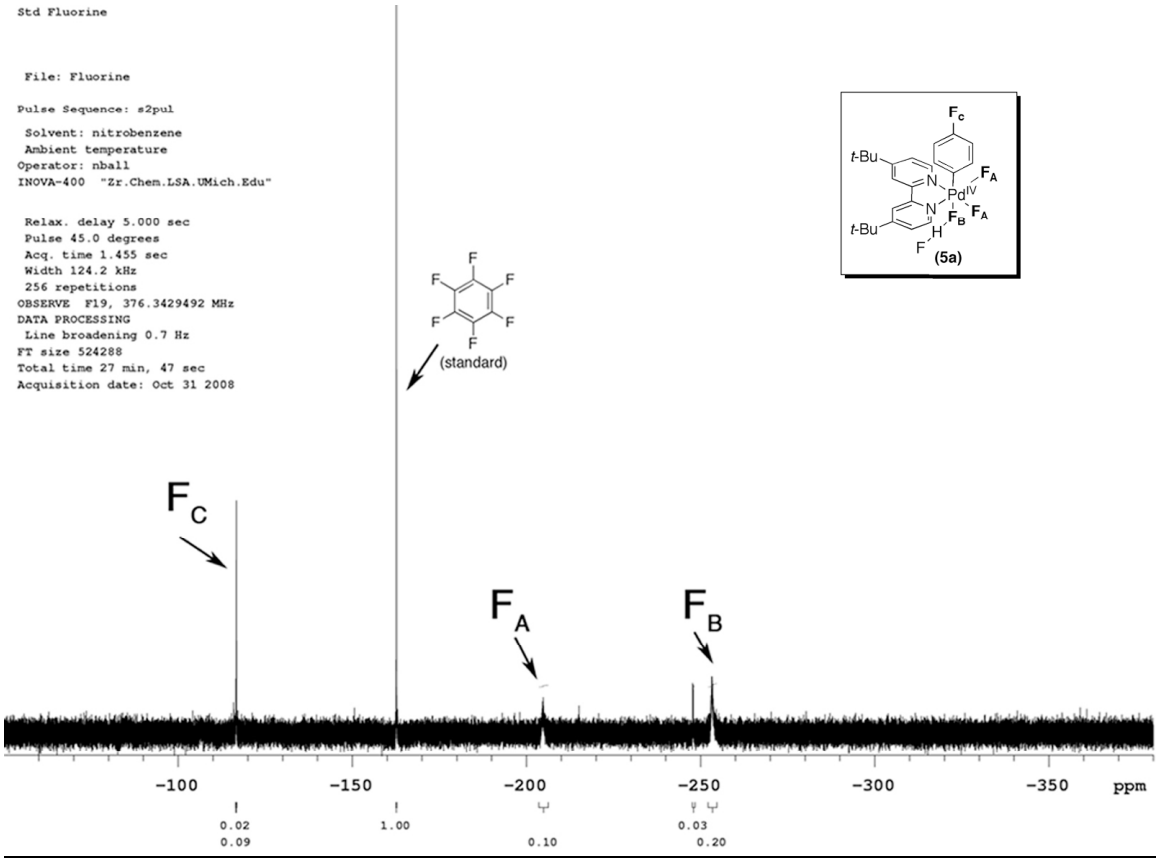


Figure S2: ^{1}H NMR spectrum of **5a** in d^{5}-nitrobenzene.

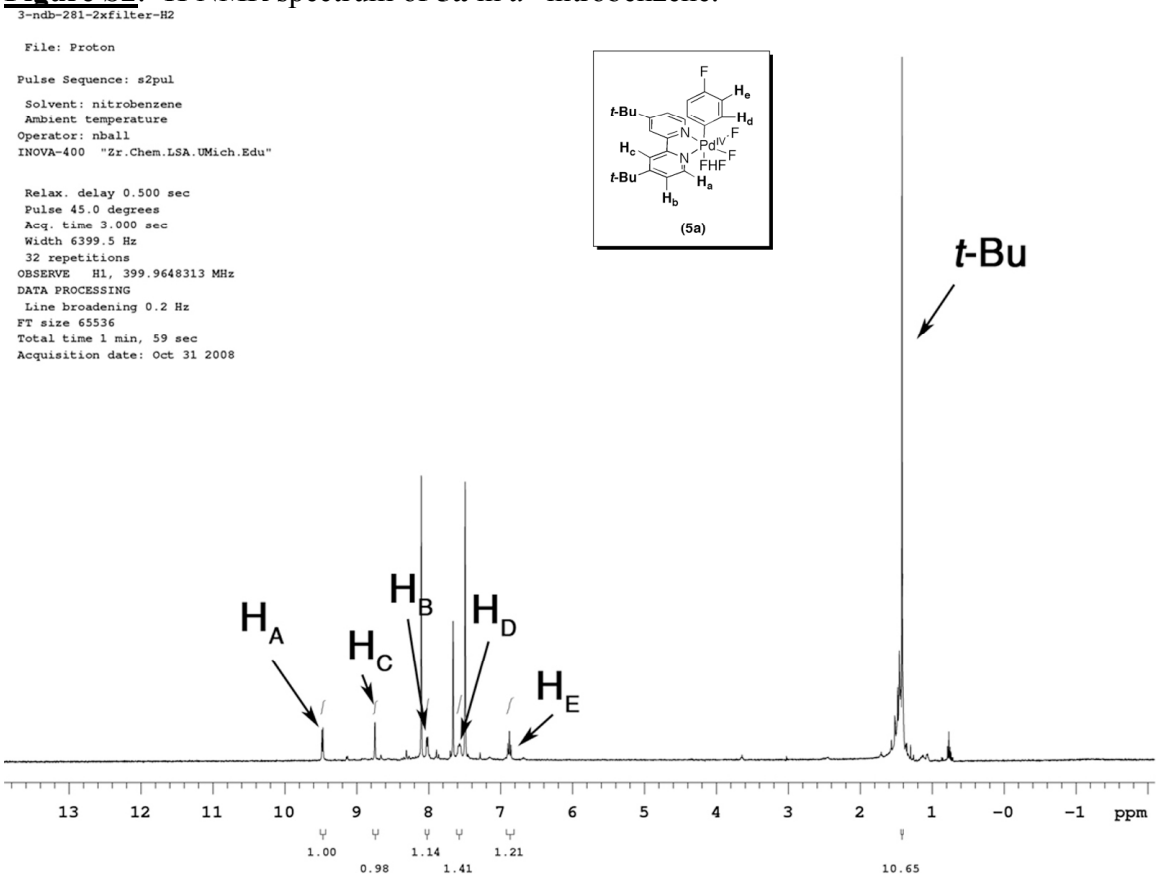


Figure S3: ORTEP drawing of **2a**.

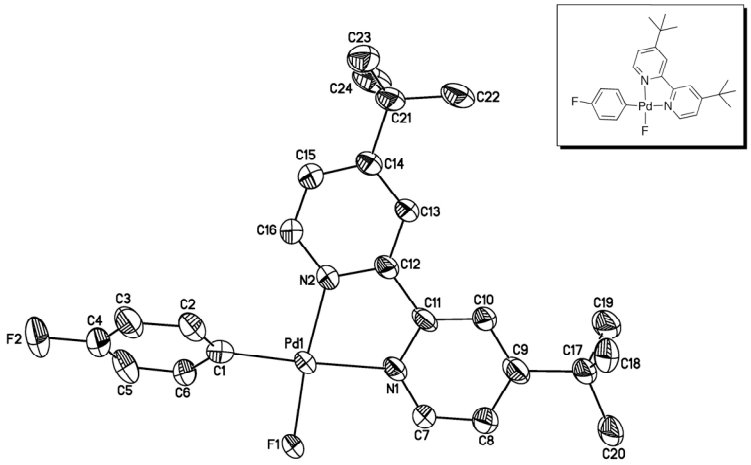
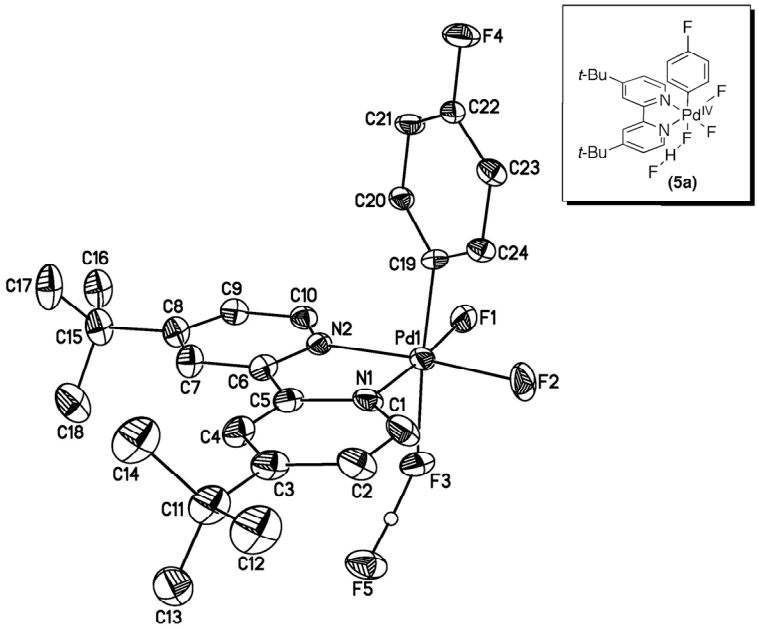


Figure S4: ORTEP drawing of **5a**.



References

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Structure Determination of Complex 2a

Yellow, blade-like crystals of **2a** were grown from a fluorobenzene/pentane solution at -30 deg. C. A crystal of dimensions 0.25 x 0.10 x 0.09 mm was mounted on a Bruker SMART APEX CCD-based X-ray diffractometer equipped with a low temperature device and fine focus Mo-target X-ray tube (λ = 0.71073 A) operated at 1500 W power (50 kV, 30 mA). The X-ray intensities were measured at 85(1) K; the detector was placed at a distance 5.055 cm from the crystal. A total of 3365 frames were collected with a scan width of 0.5° in ω and 0.45° in phi with an exposure time of 60 s/frame. The integration of the data yielded a total of 70232 reflections to a maximum 2θ value of 50.10° of which 11189 were independent and 9308 were greater than $2\sigma(I)$. The final cell constants (Table 1) were based on the xyz centroids of 9918 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection; the data were processed with SADABS and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 6.12) software package, using the space group Ia with Z = 4 for the formula $2(C_{24}H_{28}N_2F_2Pd)$, $3(C_6H_6)_{0.5}$. There are two crystallographically independent molecules in the asymmetric unit. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0552 and wR2 = 0.1553 [based on I > 2sigma(I)], R1 = 0.0700 and wR2 = 0.1651 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file.

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Table S2. Crystal data and structure refinement for **2a**.

Identification code	**2a**	
Empirical formula	C57 H65 F4 N4 Pd2	
Formula weight	1094.93	
Temperature	85(2) K	
Wavelength	0.71073 A	
Crystal system, space group	Monoclinic, Ia	
Unit cell dimensions	a = 17.9592(12) A	alpha = 90 deg.
	b = 17.5332(12) A	beta = 95.135(1) deg.

	c = 20.2950(14) A gamma = 90 deg.
Volume	6364.9(8) A^3
Z, Calculated density	4, 1.143 Mg/m^3
Absorption coefficient	0.610 mm^-1
F(000)	2252
Crystal size	0.25 x 0.10 x 0.09 mm
Theta range for data collection	2.28 to 25.05 deg.
Limiting indices	-21<=h<=21, -20<=k<=20, -24<=l<=24
Reflections collected / unique	70232 / 11189 [R(int) = 0.0652]
Completeness to theta = 25.05	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9472 and 0.8625
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11189 / 218 / 682
Goodness-of-fit on F^2	1.135
Final R indices [I>2sigma(I)]	R1 = 0.0552, wR2 = 0.1553
R indices (all data)	R1 = 0.0700, wR2 = 0.1651
Absolute structure parameter	-0.01(4)
Largest diff. peak and hole	0.805 and -0.469 e.A^-3

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for nb96.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Pd(1)	6312(1)	8562(1)	4325(1)	38(1)
Pd(2)	4128(1)	1052(1)	1788(1)	37(1)
F(1)	7409(2)	8351(3)	4456(2)	45(1)
F(2)	6265(4)	8562(6)	7326(3)	113(3)
F(3)	4192(3)	-77(2)	1803(2)	44(1)
F(4)	4956(3)	948(3)	4782(2)	64(2)
N(1)	6304(4)	8661(4)	3300(3)	39(2)
N(2)	5211(4)	8765(4)	4081(3)	44(2)
N(3)	3975(3)	2169(4)	1633(3)	40(1)
N(4)	3754(4)	1053(4)	792(3)	38(2)
C(1)	6264(5)	8563(5)	5297(4)	44(2)
C(2)	5997(5)	9189(7)	5634(4)	65(3)
C(3)	6004(6)	9156(9)	6316(5)	91(5)
C(4)	6269(6)	8578(8)	6656(4)	76(4)
C(5)	6546(6)	7960(7)	6360(4)	74(3)

C(6)	6565(5)	7956(6)	5679(4)	50(2)
C(7)	6885(5)	8627(5)	2962(4)	43(2)
C(8)	6873(5)	8855(6)	2294(4)	49(2)
C(9)	6204(5)	9114(5)	1983(4)	45(2)
C(10)	5584(4)	9137(5)	2344(3)	42(2)
C(11)	5649(4)	8901(5)	2989(4)	40(2)
C(12)	5021(4)	8905(5)	3422(3)	39(2)
C(13)	4281(4)	9019(4)	3199(3)	39(2)
C(14)	3709(4)	8975(5)	3620(4)	43(2)
C(15)	3930(5)	8839(5)	4275(4)	47(2)
C(16)	4661(5)	8735(6)	4489(4)	51(2)
C(17)	6149(4)	9416(6)	1271(4)	51(2)
C(18)	5954(5)	10279(6)	1282(4)	60(2)
C(19)	5511(5)	8970(7)	861(4)	64(3)
C(20)	6875(5)	9311(7)	952(4)	64(3)
C(21)	2879(4)	9089(5)	3382(4)	47(2)
C(22)	2792(5)	9346(7)	2653(5)	64(3)
C(23)	2546(5)	9718(5)	3781(4)	49(2)
C(24)	2489(5)	8354(7)	3479(6)	70(3)
C(25)	4448(5)	1101(4)	2748(4)	37(2)
C(26)	3955(5)	1347(5)	3205(4)	48(2)
C(27)	4102(5)	1302(6)	3882(4)	50(2)
C(28)	4797(5)	1026(5)	4116(4)	48(2)
C(29)	5317(5)	813(6)	3700(4)	53(2)
C(30)	5153(4)	848(5)	3004(4)	46(2)
C(31)	4150(4)	2724(5)	2083(3)	42(2)
C(32)	4010(5)	3488(5)	1932(4)	45(2)
C(33)	3680(4)	3712(5)	1314(4)	41(2)
C(34)	3498(4)	3127(5)	867(3)	39(2)
C(35)	3648(4)	2377(5)	1023(3)	36(2)
C(36)	3507(4)	1720(5)	559(4)	41(2)
C(37)	3133(4)	1810(5)	-70(3)	39(2)
C(38)	3032(4)	1161(5)	-471(4)	44(2)
C(39)	3304(4)	468(5)	-224(4)	46(2)
C(40)	3661(5)	429(5)	421(4)	45(2)
C(41)	3534(5)	4551(5)	1172(4)	47(2)
C(42)	4297(6)	4959(6)	1197(5)	63(2)
C(43)	3048(6)	4886(6)	1681(4)	68(3)
C(44)	3151(6)	4682(6)	459(4)	68(3)
C(45)	2570(5)	1226(5)	-1156(4)	46(2)
C(46)	1775(5)	1467(6)	-1026(4)	55(2)
C(47)	2935(6)	1824(6)	-1562(4)	60(2)
C(48)	2515(6)	472(6)	-1525(4)	65(3)
C(49)	4728(11)	8164(12)	9045(10)	84(4)
C(50)	4771(12)	8142(13)	8376(11)	88(4)
C(51)	4162(13)	8327(13)	7960(11)	93(4)

C(52)	3527(12)	8531(11)	8185(11)	85(4)
C(53)	3475(11)	8502(11)	8838(11)	81(4)
C(54)	4057(10)	8316(9)	9299(8)	81(4)
C(55)	1433(10)	6288(9)	1932(8)	108(5)
C(56)	1371(15)	6965(12)	2264(12)	108(5)
C(57)	1085(13)	7600(12)	1926(12)	99(5)
C(58)	782(10)	7625(11)	1324(11)	85(4)
C(59)	785(11)	6955(11)	1013(10)	89(4)
C(60)	1129(14)	6302(12)	1277(10)	98(5)
C(61)	69(18)	6250(20)	4123(18)	174(9)
C(62)	381(17)	6820(17)	3781(19)	169(9)
C(63)	726(18)	6610(19)	3236(18)	166(9)
C(64)	863(16)	5910(20)	3070(17)	167(9)
C(65)	455(17)	5356(17)	3328(19)	168(9)
C(66)	161(18)	5499(19)	3928(19)	173(9)

Table S4. Bond lengths [A] and angles [deg] for **2a**.

Pd(1)-C(1)	1.981(8)
Pd(1)-F(1)	1.999(4)
Pd(1)-N(2)	2.026(6)
Pd(1)-N(1)	2.086(7)
Pd(2)-C(25)	1.983(9)
Pd(2)-F(3)	1.983(4)
Pd(2)-N(3)	1.998(7)
Pd(2)-N(4)	2.073(7)
F(2)-C(4)	1.360(11)
F(4)-C(28)	1.363(9)
N(1)-C(7)	1.300(11)
N(1)-C(11)	1.351(10)
N(2)-C(16)	1.347(10)
N(2)-C(12)	1.372(9)
N(3)-C(31)	1.353(10)
N(3)-C(35)	1.370(9)
N(4)-C(36)	1.323(11)
N(4)-C(40)	1.331(11)
C(1)-C(6)	1.397(11)
C(1)-C(2)	1.400(13)
C(2)-C(3)	1.384(12)
C(3)-C(4)	1.294(15)
C(4)-C(5)	1.354(14)
C(5)-C(6)	1.386(11)
C(7)-C(8)	1.412(11)
C(8)-C(9)	1.382(12)
C(9)-C(10)	1.388(11)
C(9)-C(17)	1.534(11)
C(10)-C(11)	1.367(11)
C(11)-C(12)	1.492(11)
C(12)-C(13)	1.380(10)
C(13)-C(14)	1.396(11)
C(14)-C(15)	1.372(11)
C(14)-C(21)	1.540(10)
C(15)-C(16)	1.358(12)
C(17)-C(20)	1.519(12)
C(17)-C(18)	1.553(14)
C(17)-C(19)	1.563(13)
C(21)-C(24)	1.487(14)
C(21)-C(23)	1.521(12)
C(21)-C(22)	1.541(12)
C(25)-C(30)	1.397(12)

C(25)-C(26)	1.407(12)
C(26)-C(27)	1.377(12)
C(27)-C(28)	1.381(12)
C(28)-C(29)	1.367(12)
C(29)-C(30)	1.418(11)
C(31)-C(32)	1.392(12)
C(32)-C(33)	1.395(11)
C(33)-C(34)	1.389(11)
C(33)-C(41)	1.518(12)
C(34)-C(35)	1.374(11)
C(35)-C(36)	1.497(11)
C(36)-C(37)	1.397(10)
C(37)-C(38)	1.401(12)
C(38)-C(39)	1.388(12)
C(38)-C(45)	1.558(11)
C(39)-C(40)	1.407(11)
C(41)-C(43)	1.528(13)
C(41)-C(42)	1.542(12)
C(41)-C(44)	1.562(11)
C(45)-C(47)	1.518(13)
C(45)-C(48)	1.519(13)
C(45)-C(46)	1.534(13)
C(49)-C(50)	1.366(18)
C(49)-C(54)	1.379(18)
C(50)-C(51)	1.360(19)
C(51)-C(52)	1.32(2)
C(52)-C(53)	1.338(19)
C(53)-C(54)	1.378(18)
C(55)-C(56)	1.375(18)
C(55)-C(60)	1.392(18)
C(56)-C(57)	1.382(19)
C(57)-C(58)	1.293(19)
C(58)-C(59)	1.334(18)
C(59)-C(60)	1.387(18)
C(61)-C(62)	1.37(2)
C(61)-C(66)	1.384(19)
C(62)-C(63)	1.37(2)
C(63)-C(64)	1.31(2)
C(64)-C(65)	1.35(2)
C(65)-C(66)	1.393(19)

C(1)-Pd(1)-F(1)	89.9(3)
C(1)-Pd(1)-N(2)	96.6(3)
F(1)-Pd(1)-N(2)	173.5(2)
C(1)-Pd(1)-N(1)	174.3(3)
F(1)-Pd(1)-N(1)	93.8(2)

N(2)-Pd(1)-N(1)	79.7(3)
C(25)-Pd(2)-F(3)	90.9(3)
C(25)-Pd(2)-N(3)	97.9(3)
F(3)-Pd(2)-N(3)	171.0(2)
C(25)-Pd(2)-N(4)	176.8(3)
F(3)-Pd(2)-N(4)	91.6(2)
N(3)-Pd(2)-N(4)	79.5(2)
C(7)-N(1)-C(11)	118.2(7)
C(7)-N(1)-Pd(1)	126.0(6)
C(11)-N(1)-Pd(1)	114.8(5)
C(16)-N(2)-C(12)	118.3(6)
C(16)-N(2)-Pd(1)	126.6(5)
C(12)-N(2)-Pd(1)	115.0(5)
C(31)-N(3)-C(35)	118.2(7)
C(31)-N(3)-Pd(2)	125.3(5)
C(35)-N(3)-Pd(2)	116.4(5)
C(36)-N(4)-C(40)	120.2(7)
C(36)-N(4)-Pd(2)	114.7(5)
C(40)-N(4)-Pd(2)	124.4(6)
C(6)-C(1)-C(2)	117.3(8)
C(6)-C(1)-Pd(1)	120.2(6)
C(2)-C(1)-Pd(1)	122.3(7)
C(3)-C(2)-C(1)	118.9(10)
C(4)-C(3)-C(2)	122.4(10)
C(3)-C(4)-C(5)	121.4(9)
C(3)-C(4)-F(2)	121.0(10)
C(5)-C(4)-F(2)	117.6(10)
C(4)-C(5)-C(6)	119.3(9)
C(5)-C(6)-C(1)	120.5(9)
N(1)-C(7)-C(8)	123.4(8)
C(9)-C(8)-C(7)	118.0(8)
C(8)-C(9)-C(10)	118.3(7)
C(8)-C(9)-C(17)	121.6(8)
C(10)-C(9)-C(17)	120.0(7)
C(11)-C(10)-C(9)	119.5(7)
N(1)-C(11)-C(10)	122.5(7)
N(1)-C(11)-C(12)	113.5(7)
C(10)-C(11)-C(12)	123.9(7)
N(2)-C(12)-C(13)	119.7(6)
N(2)-C(12)-C(11)	115.9(6)
C(13)-C(12)-C(11)	124.4(6)
C(12)-C(13)-C(14)	122.0(7)
C(15)-C(14)-C(13)	116.0(7)
C(15)-C(14)-C(21)	121.0(7)
C(13)-C(14)-C(21)	123.0(7)
C(16)-C(15)-C(14)	121.4(7)

N(2)-C(16)-C(15)	122.6(7)
C(20)-C(17)-C(9)	112.0(7)
C(20)-C(17)-C(18)	109.1(8)
C(9)-C(17)-C(18)	108.6(6)
C(20)-C(17)-C(19)	109.2(7)
C(9)-C(17)-C(19)	108.1(8)
C(18)-C(17)-C(19)	109.9(7)
C(24)-C(21)-C(23)	110.2(8)
C(24)-C(21)-C(14)	107.4(7)
C(23)-C(21)-C(14)	110.0(6)
C(24)-C(21)-C(22)	111.8(8)
C(23)-C(21)-C(22)	106.8(8)
C(14)-C(21)-C(22)	110.6(7)
C(30)-C(25)-C(26)	117.1(8)
C(30)-C(25)-Pd(2)	121.7(6)
C(26)-C(25)-Pd(2)	121.1(6)
C(27)-C(26)-C(25)	124.4(8)
C(26)-C(27)-C(28)	116.7(8)
F(4)-C(28)-C(29)	119.4(8)
F(4)-C(28)-C(27)	118.6(7)
C(29)-C(28)-C(27)	122.0(7)
C(28)-C(29)-C(30)	120.7(7)
C(25)-C(30)-C(29)	119.0(7)
N(3)-C(31)-C(32)	121.1(7)
C(31)-C(32)-C(33)	121.5(8)
C(34)-C(33)-C(32)	115.9(7)
C(34)-C(33)-C(41)	124.4(7)
C(32)-C(33)-C(41)	119.7(7)
C(35)-C(34)-C(33)	121.7(7)
N(3)-C(35)-C(34)	121.6(7)
N(3)-C(35)-C(36)	113.5(7)
C(34)-C(35)-C(36)	124.9(6)
N(4)-C(36)-C(37)	123.0(8)
N(4)-C(36)-C(35)	115.0(6)
C(37)-C(36)-C(35)	122.0(8)
C(36)-C(37)-C(38)	117.8(8)
C(39)-C(38)-C(37)	118.6(7)
C(39)-C(38)-C(45)	121.9(7)
C(37)-C(38)-C(45)	119.3(8)
C(38)-C(39)-C(40)	119.7(8)
N(4)-C(40)-C(39)	120.7(8)
C(33)-C(41)-C(43)	110.1(7)
C(33)-C(41)-C(42)	107.8(7)
C(43)-C(41)-C(42)	111.1(8)
C(33)-C(41)-C(44)	111.8(7)

C(43)-C(41)-C(44)	109.8(8)
C(42)-C(41)-C(44)	106.2(7)
C(47)-C(45)-C(48)	110.2(7)
C(47)-C(45)-C(46)	111.0(8)
C(48)-C(45)-C(46)	107.8(8)
C(47)-C(45)-C(38)	108.2(7)
C(48)-C(45)-C(38)	112.4(7)
C(46)-C(45)-C(38)	107.3(6)
C(50)-C(49)-C(54)	120.4(17)
C(51)-C(50)-C(49)	119.8(19)
C(52)-C(51)-C(50)	121.5(19)
C(51)-C(52)-C(53)	118.2(19)
C(52)-C(53)-C(54)	124.5(18)
C(53)-C(54)-C(49)	115.2(16)
C(56)-C(55)-C(60)	114.2(15)
C(55)-C(56)-C(57)	119.7(18)
C(58)-C(57)-C(56)	127.1(19)
C(57)-C(58)-C(59)	113.4(18)
C(58)-C(59)-C(60)	124.5(19)
C(59)-C(60)-C(55)	120.5(17)
C(62)-C(61)-C(66)	119(2)
C(63)-C(62)-C(61)	117(2)
C(64)-C(63)-C(62)	125(2)
C(63)-C(64)-C(65)	117(2)
C(64)-C(65)-C(66)	118(2)
C(61)-C(66)-C(65)	119(2)

Symmetry transformations used to generate equivalent atoms:

Table S5. Anisotropic displacement parameters (A^2 x 10^3) for **2a**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Pd(1)	27(1)	60(1)	25(1)	3(1)	-5(1)	2(1)
Pd(2)	27(1)	56(1)	26(1)	0(1)	-4(1)	5(1)
F(1)	31(2)	76(3)	28(2)	7(2)	-6(2)	5(2)
F(2)	84(5)	222(10)	30(3)	-9(4)	-14(3)	31(5)
F(3)	42(2)	58(3)	31(2)	3(2)	-7(2)	7(2)
F(4)	66(3)	97(4)	26(2)	-2(2)	-11(2)	6(3)

N(1)	30(4)	58(4)	28(3)	-5(3)	-7(3)	2(3)
N(2)	31(3)	73(5)	29(3)	8(3)	-2(3)	-1(3)
N(3)	33(3)	59(4)	25(3)	5(3)	-4(2)	2(3)
N(4)	30(4)	53(4)	29(3)	0(3)	0(3)	1(3)
C(1)	27(4)	65(5)	41(4)	-1(4)	3(4)	-1(4)
C(2)	40(5)	116(9)	36(4)	-5(5)	-9(4)	14(5)
C(3)	48(6)	180(14)	41(5)	-33(7)	-12(4)	39(7)
C(4)	45(5)	153(11)	30(4)	-2(6)	-1(4)	23(6)
C(5)	60(6)	118(9)	40(5)	11(5)	-18(4)	8(6)
C(6)	38(4)	80(6)	32(4)	15(4)	1(3)	7(4)
C(7)	30(4)	68(5)	31(4)	7(4)	1(3)	2(4)
C(8)	38(5)	77(6)	32(4)	-4(4)	4(3)	7(4)
C(9)	36(4)	63(5)	33(4)	-7(4)	-9(3)	10(4)
C(10)	29(4)	71(6)	25(4)	-6(3)	-1(3)	1(3)
C(11)	28(4)	59(5)	32(4)	-6(3)	-10(3)	10(3)
C(12)	27(4)	62(5)	27(3)	-10(3)	-6(3)	0(3)
C(13)	28(4)	57(5)	30(4)	-1(3)	-4(3)	1(3)
C(14)	27(4)	65(5)	35(4)	-4(4)	-5(3)	-4(4)
C(15)	33(4)	73(6)	36(4)	6(4)	5(3)	-1(4)
C(16)	33(4)	90(7)	29(4)	6(4)	3(3)	4(4)
C(17)	33(4)	95(7)	24(3)	1(4)	-1(3)	11(4)
C(18)	55(5)	95(7)	28(4)	10(4)	5(4)	7(5)
C(19)	44(5)	114(9)	32(4)	-7(5)	-5(4)	12(5)
C(20)	52(5)	117(8)	23(4)	0(4)	0(3)	15(5)
C(21)	25(4)	72(6)	44(4)	-7(4)	-5(3)	-2(4)
C(22)	29(5)	104(9)	54(6)	-8(5)	-12(4)	7(5)
C(23)	35(4)	61(5)	52(5)	-3(4)	4(3)	-4(4)
C(24)	33(5)	83(7)	91(8)	2(6)	-12(5)	-3(5)
C(25)	32(5)	43(5)	35(4)	0(3)	1(4)	-3(3)
C(26)	27(4)	76(6)	40(4)	7(4)	-1(3)	10(4)
C(27)	33(4)	79(6)	37(4)	-2(4)	6(4)	-5(4)
C(28)	50(5)	69(6)	25(4)	-2(4)	-3(3)	3(4)
C(29)	32(4)	88(7)	38(4)	-4(4)	-10(3)	6(4)
C(30)	27(4)	76(6)	33(4)	-11(4)	-1(3)	4(4)
C(31)	38(4)	60(5)	26(3)	-2(3)	-4(3)	-6(4)
C(32)	36(4)	67(6)	31(4)	-4(3)	5(3)	1(4)
C(33)	31(4)	59(5)	31(4)	2(3)	-2(3)	1(3)
C(34)	30(4)	60(5)	24(3)	0(3)	-5(3)	-2(3)
C(35)	24(3)	60(5)	25(3)	3(3)	1(3)	1(3)
C(36)	32(4)	59(5)	32(4)	-4(4)	0(3)	-10(4)
C(37)	33(4)	56(5)	27(3)	3(3)	-1(3)	-7(3)
C(38)	33(4)	73(6)	25(4)	-4(3)	3(3)	-8(4)
C(39)	41(4)	64(5)	31(4)	-5(4)	-6(3)	-3(4)
C(40)	44(5)	60(5)	31(4)	-2(4)	2(3)	5(4)
C(41)	43(4)	63(5)	33(4)	7(4)	-5(3)	-2(4)
C(42)	66(6)	65(6)	58(5)	-3(4)	-3(4)	-20(5)

C(43)	77(7)	76(7)	49(5)	5(5)	-1(5)	2(6)
C(44)	74(7)	79(7)	47(5)	9(5)	-15(5)	-10(5)
C(45)	47(5)	64(5)	27(4)	2(3)	5(3)	-3(4)
C(46)	44(5)	84(7)	33(4)	3(4)	-15(4)	-6(4)
C(47)	73(7)	79(6)	28(4)	3(4)	-1(4)	1(5)
C(48)	72(6)	91(7)	29(4)	-6(4)	-13(4)	-4(5)
C(49)	82(8)	53(7)	113(10)	4(8)	-5(8)	-9(7)
C(50)	86(8)	60(8)	116(10)	8(8)	-1(8)	-13(7)
C(51)	98(9)	59(8)	119(10)	11(8)	-11(8)	-16(8)
C(52)	88(9)	40(7)	122(10)	12(8)	-20(9)	-15(7)
C(53)	82(8)	32(7)	125(10)	10(8)	-9(8)	-18(7)
C(54)	85(9)	41(7)	116(10)	9(8)	-4(8)	-4(7)
C(55)	76(9)	103(9)	145(12)	-40(9)	7(9)	-25(8)
C(56)	77(9)	107(10)	139(11)	-45(9)	7(9)	-25(9)
C(57)	67(9)	98(9)	133(11)	-45(9)	26(8)	-25(8)
C(58)	42(7)	95(8)	125(11)	-33(9)	40(7)	-36(7)
C(59)	56(8)	100(9)	117(11)	-32(8)	34(8)	-36(7)
C(60)	73(9)	97(9)	128(11)	-42(9)	30(8)	-28(8)
C(61)	66(11)	194(19)	260(20)	89(18)	-3(12)	34(12)
C(62)	58(11)	189(18)	250(20)	88(18)	-20(12)	31(11)
C(63)	63(12)	188(18)	240(20)	93(18)	-23(11)	27(12)
C(64)	66(11)	189(19)	240(20)	98(18)	-19(11)	30(11)
C(65)	71(12)	186(18)	240(20)	104(18)	-9(12)	37(11)
C(66)	73(12)	189(18)	260(20)	94(19)	3(12)	35(12)

Table S6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **2a**.

	x	y	z	U(eq)
H(2A)	5813	9628	5398	78
H(3A)	5807	9574	6542	109
H(5A)	6725	7534	6616	89
H(6A)	6785	7538	5470	60
H(7A)	7341	8439	3175	52
H(8A)	7311	8832	2065	59
H(10A)	5118	9315	2145	50
H(13A)	4156	9131	2744	46
H(15A)	3564	8818	4584	57
H(16A)	4789	8638	4946	61
H(18A)	6353	10554	1543	89
H(18B)	5481	10349	1480	89
H(18C)	5905	10477	829	89
H(19A)	5465	9157	404	96
H(19B)	5038	9049	1057	96
H(19C)	5632	8425	865	96
H(20A)	7276	9593	1205	96
H(20B)	6815	9505	497	96
H(20C)	7003	8768	946	96
H(22A)	3050	9834	2610	95
H(22B)	2260	9408	2507	95
H(22C)	3011	8961	2378	95
H(23A)	2806	10199	3712	74
H(23B)	2605	9584	4252	74
H(23C)	2014	9775	3637	74
H(24A)	2560	8208	3947	105
H(24B)	2697	7958	3209	105
H(24C)	1954	8413	3346	105
H(26A)	3489	1557	3036	57
H(27A)	3744	1454	4173	60
H(29A)	5795	640	3879	64
H(30A)	5517	701	2716	55
H(31A)	4372	2590	2510	50
H(32A)	4143	3865	2257	54
H(34A)	3263	3249	441	46
H(37A)	2952	2294	-220	46
H(39A)	3249	21	-489	55

H(40A)	3837	-49	593	54
H(42A)	4562	4895	1638	95
H(42B)	4219	5504	1107	95
H(42C)	4596	4738	864	95
H(43A)	3294	4809	2127	101
H(43B)	2561	4630	1644	101
H(43C)	2978	5433	1599	101
H(44A)	3064	5229	387	102
H(44B)	2672	4411	410	102
H(44C)	3476	4489	134	102
H(46A)	1554	1078	-757	82
H(46B)	1470	1522	-1448	82
H(46C)	1793	1955	-790	82
H(47A)	3442	1660	-1636	90
H(47B)	2958	2311	-1324	90
H(47C)	2641	1888	-1989	90
H(48A)	3017	302	-1611	98
H(48B)	2209	538	-1946	98
H(48C)	2285	89	-1256	98
H(49A)	5164	8074	9336	101
H(50A)	5225	7998	8203	105
H(51A)	4196	8308	7495	112
H(52A)	3116	8695	7892	102
H(53A)	3005	8616	8994	97
H(54A)	4000	8295	9760	98
H(55A)	1664	5848	2133	129
H(56A)	1523	6997	2724	130
H(57A)	1115	8069	2161	118
H(58A)	577	8077	1123	102
H(59A)	534	6923	582	107
H(60A)	1158	5860	1009	117
H(61A)	-207	6361	4489	209
H(62A)	358	7338	3916	203
H(63A)	879	7005	2956	200
H(64A)	1234	5789	2780	200
H(65A)	370	4882	3106	202
H(66A)	26	5089	4200	208

Structure Determination of Complex 5a.

Colorless blocks of **5a** were grown from an acetone/pentane solution at 25 deg. C. A crystal of dimensions 0.28 x 0.16 x 0.16 mm mounted on a Bruker SMART APEX CCD-based X-ray diffractometer equipped with a low temperature device and fine focus Mo-target X-ray tube (l = 0.71073 A) operated at 1500 W power (50 kV, 30 mA). The X-ray intensities were measured at 85(2) K; the detector was placed at a distance 5.055 cm from the crystal. A total of 3336 frames were collected with a scan width of 0.5° in w and 0.45° in phi with an exposure time of 20 s/frame. The integration of the data yielded a total of 44156 reflections to a maximum 2q value of 56.74° of which 7631 were independent and 6810 were greater than 2s(I). The final cell constants (Table 1) were based on the xyz centroids of 9998 reflections above 10s(I). Analysis of the data showed negligible decay during data collection; the data were processed with SADABS and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL software package, using the space group P1bar with Z = 4 for the formula $C_{24}H_{29}F_5N_2Pd$, $2(C_3H_6O)$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. The para-fluorophenyl ligand is disordered over two positions modeled by placement of partial occupancy atoms. Restraints (SADI/SIMU/DELU) were employed to maintain chemically sensible geometries. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0448 and wR2 = 0.1019 [based on I > 2sigma(I)], R1 = 0.0524 and wR2 = 0.1088 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file.

Sheldrick, G.M. SHELXTL, v. 2008/3; Bruker Analytical X-ray, Madison, WI, 2008.
Sheldrick, G.M. SADABS, v. 2008/1. Program for Empirical Absorption Correction of Area Detector Data, University of Gottingen: Gottingen, Germany, 2008.
Saint Plus, v. 7.53, Bruker Analytical X-ray, Madison, WI, 2008.

Table S7. Crystal data and structure refinement for **5a**.

Identification code	**5a**
Empirical formula	C30 H41 F5 N2 O2 Pd
Formula weight	663.05
Temperature	85(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 9.6894(7) A alpha = 73.672(1) deg. b = 12.7681(9) A beta = 77.180(1) deg. c = 13.8914(10) A gamma = 69.587(1) deg.
Volume	1530.97(19) A^3
Z, Calculated density	2, 1.438 Mg/m^3
Absorption coefficient	0.665 mm^-1
F(000)	684
Crystal size	0.28 x 0.16 x 0.16 mm
Theta range for data collection	1.75 to 28.36 deg.
Limiting indices	-12<=h<=12, -17<=k<=17, -18<=l<=18
Reflections collected / unique	44156 / 7631 [R(int) = 0.0399]
Completeness to theta =	28.36 99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9010 and 0.8356
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7631 / 96 / 438
Goodness-of-fit on F^2	1.105
Final R indices [I>2sigma(I)]	R1 = 0.0448, wR2 = 0.1019
R indices (all data)	R1 = 0.0526, wR2 = 0.1088
Largest diff. peak and hole	1.715 and -2.979 e.A^-3

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **5a**.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Pd(1)	1752(1)	-293(1)	2261(1)	29(1)
F(1)	2605(2)	-1369(2)	1392(1)	37(1)
F(2)	2559(2)	-1419(2)	3408(1)	58(1)
F(3)	-224(2)	-757(2)	2656(2)	48(1)
F(4)	7524(5)	727(4)	1311(4)	32(1)
F(4A)	7365(5)	1311(5)	1100(4)	37(1)
F(5)	-2057(2)	223(2)	3785(2)	46(1)
N(1)	841(2)	904(2)	3045(2)	27(1)
N(2)	775(2)	954(2)	1183(2)	20(1)
C(1)	957(3)	775(3)	4015(2)	38(1)
C(2)	252(3)	1652(3)	4511(2)	38(1)
C(3)	-610(3)	2705(3)	4016(2)	30(1)
C(4)	-733(3)	2814(3)	3001(2)	27(1)
C(5)	3(3)	1918(3)	2532(2)	23(1)
C(6)	-29(3)	1941(2)	1475(2)	22(1)
C(7)	-787(3)	2874(2)	798(2)	26(1)
C(8)	-743(3)	2802(3)	-197(2)	26(1)
C(9)	63(3)	1760(2)	-460(2)	23(1)
C(10)	814(3)	852(2)	246(2)	22(1)
C(11)	-1435(4)	3702(3)	4521(2)	36(1)
C(12)	-965(5)	3490(4)	5561(2)	49(1)
C(13)	-3106(4)	3856(3)	4659(2)	42(1)
C(14)	-1110(5)	4788(3)	3851(2)	47(1)
C(15)	-1607(4)	3840(3)	-927(2)	32(1)
C(16)	-1273(4)	3637(3)	-2001(2)	36(1)
C(17)	-1191(5)	4899(3)	-946(2)	41(1)
C(18)	-3266(4)	4013(4)	-550(3)	49(1)
C(19)	3603(12)	-12(7)	1894(8)	14(2)
C(19A)	3620(11)	345(8)	1886(9)	20(2)
C(20)	4177(6)	367(5)	916(4)	22(1)
C(20A)	3518(7)	1459(6)	1299(5)	37(1)
C(21)	5520(6)	611(5)	707(4)	26(1)
C(21A)	4820(7)	1784(6)	1024(5)	39(2)
C(22)	6224(7)	475(7)	1511(6)	21(1)
C(22A)	6120(8)	991(8)	1341(6)	28(2)

C(23)	5716(6)	65(5)	2501(4)	21(1)
C(23A)	6189(7)	-63(7)	1903(7)	29(1)
C(24)	4371(6)	-167(5)	2710(4)	19(1)
C(24A)	4895(7)	-398(5)	2187(5)	29(1)
O(1)	6766(5)	6214(4)	5917(4)	100(1)
C(25)	5937(6)	7151(5)	6021(7)	94(2)
C(26)	4888(8)	7228(6)	7029(6)	117(3)
C(27)	5807(8)	8136(6)	5221(9)	163(5)
C(28)	6234(3)	6081(3)	1874(2)	32(1)
C(29)	4947(4)	6251(3)	2679(2)	36(1)
C(30)	6694(5)	7107(4)	1331(4)	77(2)
O(2)	6892(3)	5152(2)	1671(2)	49(1)

Table S9. Bond lengths [A] and angles [deg] for **5a**.

Pd(1)-C(19)	1.883(10)
Pd(1)-F(2)	1.9226(18)
Pd(1)-F(1)	1.9307(19)
Pd(1)-N(1)	1.968(3)
Pd(1)-N(2)	1.977(2)
Pd(1)-F(3)	2.113(2)
Pd(1)-C(19A)	2.140(9)
F(4)-C(22)	1.358(8)
F(4A)-C(22A)	1.349(8)
N(1)-C(1)	1.336(4)
N(1)-C(5)	1.360(4)
N(2)-C(10)	1.335(3)
N(2)-C(6)	1.350(4)
C(1)-C(2)	1.373(5)
C(2)-C(3)	1.389(4)
C(3)-C(4)	1.404(4)
C(3)-C(11)	1.516(5)
C(4)-C(5)	1.372(4)
C(5)-C(6)	1.468(4)
C(6)-C(7)	1.381(4)
C(7)-C(8)	1.402(4)
C(8)-C(9)	1.392(4)
C(8)-C(15)	1.527(4)
C(9)-C(10)	1.388(4)
C(11)-C(14)	1.529(5)
C(11)-C(12)	1.534(4)
C(11)-C(13)	1.536(5)
C(15)-C(16)	1.531(4)
C(15)-C(17)	1.532(5)
C(15)-C(18)	1.533(5)

C(19)-C(20)	1.368(11)
C(19)-C(24)	1.422(11)
C(19A)-C(24A)	1.338(12)
C(19A)-C(20A)	1.408(11)
C(20)-C(21)	1.392(7)
C(20A)-C(21A)	1.405(8)
C(21)-C(22)	1.375(9)
C(21A)-C(22A)	1.383(11)
C(22)-C(23)	1.372(9)
C(22A)-C(23A)	1.340(11)
C(23)-C(24)	1.387(7)
C(23A)-C(24A)	1.403(9)
O(1)-C(25)	1.213(6)
C(25)-C(27)	1.413(10)
C(25)-C(26)	1.544(10)
C(28)-O(2)	1.214(4)
C(28)-C(29)	1.477(4)
C(28)-C(30)	1.478(5)

C(19)-Pd(1)-F(2)	87.1(3)
C(19)-Pd(1)-F(1)	84.5(3)
F(2)-Pd(1)-F(1)	92.11(9)
C(19)-Pd(1)-N(1)	95.0(3)
F(2)-Pd(1)-N(1)	92.61(10)
F(1)-Pd(1)-N(1)	175.21(8)
C(19)-Pd(1)-N(2)	95.5(3)
F(2)-Pd(1)-N(2)	174.08(9)
F(1)-Pd(1)-N(2)	93.47(9)
N(1)-Pd(1)-N(2)	81.84(9)
C(19)-Pd(1)-F(3)	174.9(3)
F(2)-Pd(1)-F(3)	90.59(10)
F(1)-Pd(1)-F(3)	91.14(9)
N(1)-Pd(1)-F(3)	89.59(9)
N(2)-Pd(1)-F(3)	87.31(9)
C(19)-Pd(1)-C(19A)	10.9(4)
F(2)-Pd(1)-C(19A)	92.0(3)
F(1)-Pd(1)-C(19A)	93.9(3)
N(1)-Pd(1)-C(19A)	85.1(3)
N(2)-Pd(1)-C(19A)	89.6(3)
F(3)-Pd(1)-C(19A)	174.2(3)
C(1)-N(1)-C(5)	119.9(3)
C(1)-N(1)-Pd(1)	125.3(2)
C(5)-N(1)-Pd(1)	114.78(18)
C(10)-N(2)-C(6)	120.5(2)
C(10)-N(2)-Pd(1)	124.70(19)
C(6)-N(2)-Pd(1)	114.67(17)

N(1)-C(1)-C(2)	121.4(3)
C(1)-C(2)-C(3)	120.7(3)
C(2)-C(3)-C(4)	116.8(3)
C(2)-C(3)-C(11)	123.5(3)
C(4)-C(3)-C(11)	119.7(3)
C(5)-C(4)-C(3)	120.5(3)
N(1)-C(5)-C(4)	120.7(2)
N(1)-C(5)-C(6)	114.2(3)
C(4)-C(5)-C(6)	125.2(3)
N(2)-C(6)-C(7)	120.5(2)
N(2)-C(6)-C(5)	114.5(2)
C(7)-C(6)-C(5)	125.0(3)
C(6)-C(7)-C(8)	120.3(3)
C(9)-C(8)-C(7)	117.5(3)
C(9)-C(8)-C(15)	123.1(2)
C(7)-C(8)-C(15)	119.4(3)
C(10)-C(9)-C(8)	119.9(2)
N(2)-C(10)-C(9)	121.2(3)
C(3)-C(11)-C(14)	109.3(3)
C(3)-C(11)-C(12)	111.7(3)
C(14)-C(11)-C(12)	108.5(3)
C(3)-C(11)-C(13)	108.2(3)
C(14)-C(11)-C(13)	110.1(3)
C(12)-C(11)-C(13)	108.9(3)
C(8)-C(15)-C(16)	111.3(2)
C(8)-C(15)-C(17)	109.8(2)
C(16)-C(15)-C(17)	109.0(3)
C(8)-C(15)-C(18)	107.3(3)
C(16)-C(15)-C(18)	108.7(3)
C(17)-C(15)-C(18)	110.8(3)
C(20)-C(19)-C(24)	120.5(7)
C(20)-C(19)-Pd(1)	123.6(7)
C(24)-C(19)-Pd(1)	115.8(6)
C(24A)-C(19A)-C(20A)	122.6(7)
C(24A)-C(19A)-Pd(1)	116.0(6)
C(20A)-C(19A)-Pd(1)	121.2(7)
C(19)-C(20)-C(21)	120.4(6)
C(21A)-C(20A)-C(19A)	117.8(7)
C(22)-C(21)-C(20)	117.9(5)
C(22A)-C(21A)-C(20A)	118.1(6)
F(4)-C(22)-C(23)	118.0(6)
F(4)-C(22)-C(21)	118.1(7)
C(23)-C(22)-C(21)	123.9(6)
C(23A)-C(22A)-F(4A)	118.7(8)
C(23A)-C(22A)-C(21A)	123.1(7)

F(4A)-C(22A)-C(21A)	118.2(8)
C(22)-C(23)-C(24)	118.1(5)
C(22A)-C(23A)-C(24A)	119.5(7)
C(23)-C(24)-C(19)	119.2(6)
C(19A)-C(24A)-C(23A)	119.0(7)
O(1)-C(25)-C(27)	122.1(8)
O(1)-C(25)-C(26)	117.9(7)
C(27)-C(25)-C(26)	119.6(6)
O(2)-C(28)-C(29)	122.2(3)
O(2)-C(28)-C(30)	121.5(3)
C(29)-C(28)-C(30)	116.3(3)

Symmetry transformations used to generate equivalent atoms:

Table S10. Anisotropic displacement parameters (A^2 x 10^3) for **5a**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Pd(1)	17(1)	36(1)	19(1)	5(1)	1(1)	-1(1)
F(1)	33(1)	29(1)	32(1)	2(1)	6(1)	-2(1)
F(2)	43(1)	60(1)	22(1)	12(1)	3(1)	20(1)
F(3)	35(1)	38(1)	56(1)	3(1)	15(1)	-16(1)
F(4)	20(2)	45(3)	33(2)	-6(2)	0(2)	-17(2)
F(4A)	24(2)	55(3)	44(3)	-21(3)	5(2)	-25(3)
F(5)	25(1)	79(2)	26(1)	-5(1)	-4(1)	-13(1)
N(1)	14(1)	43(1)	15(1)	2(1)	-1(1)	-5(1)
N(2)	16(1)	26(1)	19(1)	0(1)	-5(1)	-9(1)
C(1)	20(1)	60(2)	15(1)	1(1)	-3(1)	5(1)
C(2)	24(1)	65(2)	13(1)	-3(1)	-5(1)	-4(1)
C(3)	27(1)	48(2)	15(1)	-4(1)	-4(1)	-14(1)
C(4)	31(1)	35(2)	16(1)	0(1)	-7(1)	-12(1)
C(5)	19(1)	35(2)	16(1)	1(1)	-6(1)	-12(1)
C(6)	23(1)	28(1)	18(1)	-3(1)	-6(1)	-12(1)
C(7)	34(2)	27(1)	18(1)	-5(1)	-10(1)	-6(1)
C(8)	29(1)	30(1)	19(1)	-4(1)	-10(1)	-6(1)
C(9)	24(1)	31(1)	20(1)	-8(1)	-6(1)	-10(1)
C(10)	18(1)	28(1)	23(1)	-6(1)	-4(1)	-10(1)
C(11)	46(2)	49(2)	14(1)	-6(1)	-6(1)	-14(2)

C(12)	65(2)	68(3)	16(1)	-11(2)	-10(2)	-20(2)
C(13)	44(2)	49(2)	22(1)	-9(1)	-2(1)	-2(2)
C(14)	71(3)	54(2)	20(1)	-10(1)	-5(2)	-23(2)
C(15)	42(2)	35(2)	16(1)	-7(1)	-13(1)	0(1)
C(16)	50(2)	37(2)	19(1)	-7(1)	-15(1)	-2(1)
C(17)	66(2)	28(2)	21(1)	-7(1)	-17(1)	3(2)
C(18)	41(2)	66(2)	24(2)	-6(2)	-16(1)	7(2)
C(19)	17(3)	16(4)	17(3)	-8(3)	0(2)	-12(3)
C(19A)	12(2)	29(5)	28(3)	-16(4)	2(2)	-14(4)
C(20)	15(2)	30(3)	17(2)	2(2)	-4(2)	-7(2)
C(20A)	24(3)	42(3)	39(3)	5(3)	-6(2)	-14(3)
C(21)	16(2)	38(3)	19(2)	2(2)	1(2)	-10(2)
C(21A)	33(3)	42(4)	41(4)	2(3)	-1(3)	-22(3)
C(22)	14(3)	18(4)	30(4)	-1(3)	-2(2)	-7(3)
C(22A)	21(3)	42(4)	28(4)	-15(4)	5(2)	-17(3)
C(23)	17(2)	29(3)	18(2)	-9(2)	-2(2)	-5(2)
C(23A)	16(3)	31(4)	43(4)	-17(3)	-6(3)	-4(3)
C(24)	18(2)	26(3)	13(2)	-8(2)	1(2)	-6(2)
C(24A)	25(3)	27(3)	37(3)	-6(3)	-5(3)	-8(2)
O(1)	96(3)	65(2)	116(4)	-33(2)	-6(3)	10(2)
C(25)	57(3)	50(3)	188(7)	-53(4)	-50(4)	8(2)
C(26)	118(6)	96(5)	145(7)	-88(5)	-48(5)	26(4)
C(27)	69(4)	68(4)	322(14)	36(6)	-61(6)	-26(3)
C(28)	31(2)	36(2)	22(1)	-2(1)	-8(1)	-2(1)
C(29)	37(2)	34(2)	32(2)	-7(1)	-2(1)	-8(1)
C(30)	42(2)	54(3)	92(4)	29(2)	8(2)	-9(2)
O(2)	53(2)	50(2)	31(1)	-19(1)	-9(1)	10(1)

Table S11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **5a**.

	x	y	z	U(eq)
H(5F)	-1210(80)	-220(60)	3300(50)	70(20)
H(1A)	1540	62	4369	46
H(2A)	354	1537	5201	45
H(4A)	-1329	3512	2637	33
H(7A)	-1340	3568	1009	32
H(9A)	100	1670	-1122	28
H(10A)	1367	144	60	27

H(12A)	-1231	2827	6014	74
H(12B)	-1477	4168	5847	74
H(12C)	112	3340	5485	74
H(13A)	-3416	3993	3997	63
H(13B)	-3663	4512	4967	63
H(13C)	-3306	3162	5099	63
H(14A)	-41	4679	3763	70
H(14B)	-1655	5436	4172	70
H(14C)	-1426	4945	3188	70
H(16A)	-206	3488	-2239	55
H(16B)	-1833	4318	-2454	55
H(16C)	-1566	2975	-1999	55
H(17A)	-1480	5072	-273	61
H(17B)	-1712	5554	-1439	61
H(17C)	-116	4748	-1139	61
H(18A)	-3502	3319	-527	73
H(18B)	-3855	4664	-1011	73
H(18C)	-3500	4166	130	73
H(20A)	3656	466	377	26
H(20B)	2600	1973	1095	44
H(21A)	5936	862	30	31
H(21B)	4808	2527	631	47
H(23A)	6269	-56	3029	25
H(23B)	7105	-579	2107	35
H(24A)	3968	-426	3388	22
H(24B)	4925	-1142	2588	35
H(26A)	4681	6496	7327	176
H(26B)	3954	7841	6903	176
H(26C)	5362	7396	7498	176
H(27A)	6403	7915	4600	245
H(27B)	6165	8681	5394	245
H(27C)	4762	8495	5116	245
H(29A)	4656	5549	2925	53
H(29B)	4113	6886	2406	53
H(29C)	5218	6430	3239	53
H(30A)	7098	7344	1793	115
H(30B)	5832	7731	1083	115
H(30C)	7457	6925	756	115

Table S12. Hydrogen bonds for **5a** [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
F(5)-H(5F)...F(3)	1.05(7)	1.29(7)	2.344(3)	176(7)

Symmetry transformations used to generate equivalent atoms: