Effect of Ligand Steric Properties and Halide Identity on the Mechanisms for Oxidative Addition of Haloarenes to Trialkylphosphine Pd(0) Complexes

Fabiola Barrios-Landeros, Brad P. Carrow, and John F. Hartwig

Department of Chemistry, University of Illinois, 600 South Mathews Av, Urbana, IL 61801 and Department of Chemistry, Yale University, P.O. Box 208107, New Haven, Connecticut 06520-8107

Supporting Information

Experimental Section

General Methods. All manipulations were conducted in an inert atmosphere dry box or using standard Schlenk techniques unless otherwise specified. ^{1}H spectra were recorded on a 400 or 500 MHz spectrometer; ^{13}C spectra were recorded at 125 MHz with solvent resonances as reference; $^{31}P\{^{1}H\}$ NMR spectra were recorded at 160 or 200 MHz with external H_3PO_4 as a reference. CH_2Cl_2, THF, diethyl ether, toluene, and pentane were dried with a solvent purification system containing a 1 m column with activated alumina. All reagents were obtained from commercial sources and used without further purification. The solvents and haloarenes were added to the kinetic experiment samples with a micropipette. For volumes lower than 10 μL, a microsyringe was used.

Synthesis of $[(P^tBu_3)Pd(Ph)(Cl)]_2$ (9). In a Schlenk flask was placed 100 mg (0.26 mmol) of $(Py)_2Pd(Ph)(Cl)$ (**20**) and 107.3 mg (0.52 mmol) of P^tBu_3. The solids were suspended in 10 mL of toluene. The reaction mixture was stirred at room temperature for 30 min. The solvent was evaporated under vacuum to leave a yellow and white residue.

The flask was brought into the glove box, and the solid was treated with toluene. The yellow product dissolved in the toluene, and the white starting material remained. The yellow solution was then filtered, and the solvent was evaporated under vacuum. The resulting solid was washed with pentane and dried under vacuum to yield 47.5 mg (42% yield) of yellow product. ^{1}H NMR (C_6D_6, 400 MHz) δ 7.48 (ddd, *J* = 8.0, 3.0, 1.0 Hz, 2H), 6.86 (t, *J* = 7.5 Hz, 2H), 6.78 (tt, *J* = 6.7, 1.5 Hz, 1H), 1.30 (d, *J* = 12.0 Hz, 27H) ; ^{13}C NMR (C_6D_6, 125 MHz) δ 143.22, 138.31 (d, *J* = 2.3 Hz), 127.18 (d, *J* = 1.8 Hz), 123.72, 41.27 (d, *J* = 7.9 Hz), 33.51 (d, *J* = 3.9 Hz); ^{31}P{^{1}H} NMR (C_6D_6) δ 72.8. Anal. calcd. for $C_{18}H_{32}ClPPd$: C, 51.32; H, 7.66. Found: C, 51.60; H, 7.80.

Synthesis of [(P^tBu_3)Pd(2-CF_3-C_6H_4)(Cl)]$_2$ (10). Into a Schlenk flask was placed 200 mg (0.39 mmol) of Pd(P^tBu_3)$_2$. The solid was dissolved in 15 mL of 2-CF_3-C_6H_4Cl, and the resulting solution was heated under nitrogen at 80 °C for 1 h. The solvent was evaporated under vacuum at 50 °C, and the resulting orange residue was redissolved in toluene. The resulting solution was filtered, concentrated, layered with pentane. Cooling at −35 °C generated 114 mg of orange product (0.23 mmol, 59% yield). Recrystallization of the product in toluene layered with pentane yielded crystals suitable for X-ray diffraction. ^{1}H NMR (C_6D_6, 400 MHz) δ 1.26 (d, *J* = 12.4 Hz, 27H), 6.67 (br, 1H), 6.74 (br, 1H), 7.35 (br, 1H), 7.84 (br, 1H); ^{13}C NMR (CD_2Cl_2, 125 MHz) 139.95, 138.49, 136.09 (q, *J* = 28.7 Hz), 128.21, 127.48, 124.86 (q, *J* = 273 Hz), 123.69, 41.36 (d, *J* = 8.9 Hz), 32.89 (d, *J* = 2.7 Hz); ^{31}P{^{1}H} NMR (C_6D_6) δ 70.8; ^{19}F{^{1}H} NMR (C_6D_6, 375 MHz) δ −55.0. Anal. calcd. for $C_{19}H_{31}Cl_1F_3PPd$: C, 46.64; H, 6.39. Found: C, 46.90; H, 6.56.

Determination of Molecular Weight in Solution[1] of [(P^tBu_3)Pd(2-CF_3-C_6H_4)(Cl)]$_2$ (10). Into a 1.0 mL volumetric flask was placed 29.3 mg (0.0599 mol) of [(P^tBu_3)Pd(2-CF_3-C_6H_4)(Cl)]$_2$ (10), and the flask was filled with THF to the mark. The reference solution was prepared in a similar manner with 8.4 mg (0.045 mmol) of ferrocene. A Signer apparatus was loaded with 0.8 mL of the solution of the complex in one arm and 0.8 mL of the solution of ferrocene in the other arm. The solutions were frozen in liquid N_2, and the apparatus was evacuated to about 20 mtorr. The apparatus was then allowed to stand at room temperature. The volume in each arm was measured periodically until the volumes were constant. From the final concentrations, the molecular weight was calculated to be 530 g/mol. The molecular weight of the monomeric complex would be 489.29 g/mol, and the molecular weight of the dimeric complex would be 978.58 g/mol. The molecular weight calculated by the same method in C_6H_6 solvent is 505 g/mol.

Independent synthesis of [(1-AdP^tBu_2)Pd(Ph)(Cl)]$_2$ (11). The complex was obtained following a procedure previously reported by reaction of tetraoctylammoniun chloride with (1-AdP^tBu_2)Pd(Ph)(CF_3SO_3).[2] In a small vial, 30 mg (0.049 mmol) of (1-AdP^tBu_2)Pd(Ph)(CF_3SO_3) was dissolved in 1 mL of toluene. In a separate vial, N(octyl)$_4$Cl (26mg, 0.052 mmol) was dissolved in 1 mL of toluene. The chloride solution was added dropwise to the stirring vial containing the Pd solution. The reaction was stirred for 2 min. At this time, the reaction was filtered through a plug of Celite and concentrated to approximately 1 mL. The resulting bright yellow solution was layered with pentane and cooled to −35 °C. After 16 h, bright yellow crystals and colorless

crystals formed in the vial. The crystals were washed repeatedly with ether until only the yellow crystals remained. These crystals were dried under vacuum to yield 21 mg of product (86% yield). Crystals suitable for X-ray diffraction were obtained by recrystallization from toluene solution layered with pentane at −35 °C. ^{1}H NMR (C_6D_6, 400 MHz) δ 7.54 – 7.57 (m, 2H), 6.89 (t, *J* = 7.2 Hz, 2H), 6.80 (t, *J* = 7.2 Hz, 1H), 2.38 (br s, 6H), 1.81 (br, 3H), 1.50 – 1.63 (br m, 6H), 1.23 (d, *J* = 12.0 Hz, 18H); ^{13}C NMR (C_6D_6, 100 MHz) δ 141.8, 138.2 (d, *J* = 3.0 Hz), 127.3 (br), 123.8, 47.8 (d, *J* = 6.0 Hz), 42.0, 41.5 (d, *J* = 7.8 Hz), 36.9, 33.6 (d, *J* = 2.2 Hz), 29.9 (d, *J* = 8.1 Hz); ^{31}P{^{1}H} NMR (C_6D_6) δ 69.2. Anal. calcd. for $C_{24}H_{38}ClPPd$: C, 57.72; H, 7.67. Found: C, 57.73; H, 7.92.

Independent synthesis of [(1-AdP^{t}Bu$_2$)Pd(2-CF$_3$-C$_6$H$_4$)(Cl)]$_2$ (12). In a small vial, 150 mg (0.225 mmol) Pd(1-AdP^{t}Bu$_2$)$_2$ (**2**) was suspended in 6.74 mL (50.6 mmol) *o*-chlorobenzotrifluoride. The mixture was heated in an oil bath at 100 ^{o}C with stirring for 20 min. The resulting orange solution was concentrated to dryness under vacuum. The residue was next triturated with 3 mL acetonitrile for 1.5 hrs. The resulting yellow precipitate was collected and washed with 4x1 mL pentane. The process was repeated a second time, and the resulting solid was dried under vacuum to give 50 mg (39%, 0.089 mmol) **12**. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a THF solution at room temperature. ^{1}H NMR (C_6D_6, 500 MHz) δ 1.28 (br, 18H), 1.50 (br, 3H), 1.58 (br, 3H), 1.80 (br, 3H), 2.42 (br, 6H), 6.64 (br, 1H), 6.75 (br, 1H), 7.31 (br, 1H), 7.92 (br, 1H); ^{13}C NMR (C_6D_6, 125 MHz) 139.94, 139.01, 136.57 (q, *J* = 27.3 Hz), 128.53, 127.63, 125.48 (q, *J* = 274 Hz), 123.61, 47.69 (d, *J* = 5.8 Hz), 41.53 (d, *J* = 6.9 Hz), 41.30, 36.58, 33.25 (br), 29.50; ^{31}P{^{1}H} NMR (C_6D_6, 200 MHz) δ 70.6; ^{19}F{^{1}H}

NMR (C_6D_6, 470 MHz) δ −54.9. Anal. calcd. for $C_{25}H_{37}ClF_3PPd$: C, 52.92; H, 6.57. Found: C, 53.10; H, 6.84.

Independent synthesis of $[(CyP^tBu_2)_2Pd(3,5\text{-}(CF_3)_2C_6H_3)(I)]_2$ (13). Inside the glove box, 100 mg (0.18 mmol) of $Pd(CyP^tBu_2)_2$ (**3**) was weighed into a small vial, and 300 μL of 3,5-$(CF_3)_2C_6H_3I$ and 3 mL of toluene were added. The reaction mixture was stirred at room temperature for 2 h, after which time the solvent and excess iodoarene was evaporated under vacuum. The yellow product was redissolved in toluene, and the solution was filtered, concentrated, layered with pentane and cooled at −35 °C. After a second recrystallization under the same conditions, 60.7 mg (51%, 0.090 mmol) of yellow solid was obtained. ^{1}H NMR (C_6D_6, 400 MHz) δ 8.08 (s, 2H), 6.86 (s, 1H), 1.68 (br, 3H), 1.09 (br, 4H), 0.85 (br, 18H), 0.52 (br, 2H), 0.40 (br, 2H); ^{13}C NMR (CD_2Cl_2, 125 MHz) δ 155.64, 138.53, 128.90 (q, J = 31.9 Hz), 124.48 (q, J = 272.7 Hz), 116.79 (m), 41.06, 39.74 (d, J = 11.1 Hz), 32.49, 31.73, 28.28 (d, J = 9.7 Hz), 26.74; ^{19}F{^{1}H} NMR (C_6D_6, 375 MHz) δ −65.0; ^{31}P{^{1}H} NMR (C_6D_6) δ 63.3 (br). Anal. calcd for $C_{22}H_{32}F_6IPPd$: C, 39.16; H, 4.78. Found: C, 39.28; H, 4.72.

Independent synthesis of $[(CyP^tBu_2)Pd(Ph)(I)]_2$ (14). Inside the glove box, 100 mg (0.18 mmol) of $Pd(CyP^tBu_2)_2$ (**3**) was weighed into a small vial and mixed with 1.5 mL of PhI. The reaction was stirred at 60 °C for 40 min, after which time the excess PhI was evaporated under vacuum. The yellow product was dissolved in toluene, and the resulting solution was filtered, concentrated, and layered with pentane. Cooling at −35 °C and recrystallization of the resulting yellow solid by layering a toluene solution with pentane

yielded 42.2 mg (44%, 0.078 mmol) of yellow powder. ^{1}H NMR (C_6D_6, 500 MHz) δ 7.46 (d, *J* = 7.3 Hz, 2H), 6.88 (t, *J* = 7.3, 2H), 6.74 (t, *J* = 6.7 Hz, 1H), 2.27 (br, 2H), 2.09 (br, 1H), 1.61 (br, 4H), 1.48 (d, *J* = 10.4 Hz, 18H), 1.15 (br m, 2H), 0.87 (br, 2H); ^{13}C NMR (CD_2Cl_2, 125 MHz) δ 152.39, 138.48, 127.25, 122.64, 40.04 (br), 39.09 (d, *J* = 10.3 Hz), 32.33, 31.67, 28.06 (d, *J* = 9.8 Hz), 26.70; ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 59.8. Anal. calcd for $C_{20}H_{34}IPPd$: C,44.58, H, 6.36. Found: C, 44.86; H, 6.26.

Independent synthesis of [(CyP^{t}Bu$_2$)Pd(Ph)(Br)]$_2$ (15). Inside the glove box, 100 mg (0.18 mmol) of Pd(CyP^{t}Bu$_2$)$_2$ (**3**) was weighed into a small vial, and mixed with 3.0 mL of PhBr. The reaction mixture was stirred at 70 °C for 1 h, after which time the excess bromobenzene was evaporated under vacuum. The yellow product was redissolved in toluene, and the solution was filtered, concentrated, layered with pentane and cooled at −35 °C. After a second recrystallization, 61.1 mg (70%, 0.12 mmol) of yellow solid was obtained. Crystals suitable for X-ray diffraction were obtained upon further recrystallization of the product under the same conditions. ^{1}H NMR (C_6D_6, 500 MHz) δ 7.64 (d, *J* = 6.5 Hz, 2H), 6.94 (t, *J* = 7.3 Hz, 2H), 6.82 (t, *J* = 7.0 Hz, 1H), 2.16 (br, 3H), 1.5 – 1.2 (br, 5H), 1.37 (d, *J* = 11.5 Hz, 18H), 0.91 (br m, 1H), 0.77 (br, 2H); ^{13}C NMR (C_6D_6, 125 MHz) δ 150.51, 137.84, 127.37, 123.47, 39.65 (d, *J* = 10.6 Hz), 39.00 (d, *J* = 11.6 Hz), 32.39, 31.93, 28.32 (d, *J* = 8.5 Hz), 27.04; ^{31}P{^{1}H} NMR (C_6D_6) δ 62.58. Anal. calcd. For $C_{20}H_{34}BrPPd$: C, 48.85; H, 6.97. Found: C, 50.08; H, 6.9.

Determination of Molecular Weight in Solution[1] of [(CyP^{t}Bu$_2$)Pd(Ph)(Br)]$_2$ (15). Into a 1.0 mL volumetric flask was placed 11 mg (0.011 mmol) of [(CyP^{t}Bu$_2$)Pd(Ph)(Br)]$_2$

(**15**), and the flask was filled with THF to the mark. The reference solution was prepared in a similar manner with 3.3 mg (0.018 mmol) of ferrocene. A Signer apparatus was loaded with 1.0 mL of the solution of the complex in one arm and 1.0 mL of the solution of ferrocene in the other arm. The solutions were frozen in liquid N_2, and the apparatus was evacuated to about 50 mTorr. The apparatus was then allowed to stand at room temperature. The volume in each arm was measured periodically until the volumes were constant. From the final concentrations, the molecular weight was calculated to be 523 g/mol. The molecular weight of the monomeric complex would be 491.78 g/mol, and the molecular weight of the dimeric complex would be 983.56 g/mol.

Independent synthesis of [(CyP^{t}Bu$_2$)Pd(Ph)(Cl)]$_2$ (16). Inside the glove box, 100 mg (0.18 mmol) of Pd(CyP^{t}Bu$_2$)$_2$ (**3**) was weighed into a small vial, and mixed with 3.0 mL of PhCl. The reaction mixture was stirred at 70 °C for 2 h, after which time the excess chlorobenzene was evaporated under vacuum. The yellow product was redissolved in toluene, and the solution was filtered, concentrated, layered with pentane and cooled at −35 °C. After a second recrystallization under the same conditions, 50.5 mg (64%, 0.11 mmol) of yellow solid was obtained. ^{1}H NMR (C_6D_6, 500 MHz) δ 7.62 (br, 2H), 6.94 (br, 2H), 6.84 (br m, 1H), 2.14 (br, 2H), 2.07 (br, 1H), 1.2–1.7 (br, 5H), 1.39 (d, J = 10.9 Hz, 18H), 0.89 (br m, 1H), 0.71 (br, 2H). ^{13}C NMR (C_6D_6, 125 MHz) δ 148.69, 137.04, 126.76, 123.14, 39.00 (d, J = 13.5), 38.40 (d, J = 13.0), 31.80, 31.42, 27.92 (d, J = 9.9), 26.63; ^{31}P{^{1}H} NMR (C_6D_6) δ 64.06. Anal calcd For $C_{20}H_{34}ClPPd$: C, 53.70; H, 7.66. Found: C, 53.58; H, 7.52

Synthesis of *trans*-$(Py)_2Pd(Ph)(Cl)$ (20). In a Schlenk flask, was placed 800 mg of $Pd_2(dba)_3$ (0.87 mmol) and 80 mg of P^tBu_3 (0.40 mmol). To these solids was added a mixture of 0.7 mL of pyridine (8.6 mmol) and 5 mL of PhCl. The reaction was stirred under N_2 at 45 °C for 1.5 h. $(Py)_2Pd(Ph)(Cl)$ precipitated from the reaction mixture as a white solid. This solid was rinsed with ether and redissolved in CH_2Cl_2. The solution was filtered through plug of Celite and layered with pentane at −35 °C. The resulting white crystalline solid was isolated by filtration and dried under vacuum to obtain 361 mg (55 % yield) of product. ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 8.81 (dt, *J* = 5.2, 1.5 Hz, 4H), 7.73 (tt, *J* = 7.6, 1.6 Hz, 2H), 7.25 (ddd, *J* = 7.5, 5.3, 1.6 Hz, 4H), 7.19 (dd, *J* = 7.4, 0.9 Hz, 2H) 6.86 (m, 3H) ; ^{13}C NMR (CD_2Cl_2, 125 MHz) δ 153.42, 153.21, 138.07, 134.31, 127.46, 125.00, 123.91. Anal. calcd. for $C_{16}H_{15}ClN_2Pd$: C, 50.95; H, 4.01. Found: C, 50.72; H, 3.83.

General procedure for kinetic experiments. The amounts and reagents used to prepare each sample are described below. The solvents and haloarenes were added to the samples with a micropipette. The sample solutions were transferred to a screw top NMR tube and capped with a Teflon septum. A sealed capillary tube with a THF or DMF solution of H_3PO_4 (0.35 M) was placed inside the NMR tube to be used as an external standard. Before inserting the sample into the NMR probe, the temperature was adjusted. The temperature was measured with a type K thermocouple; the thermocouple probe was inserted into an NMR sample tube, which was lowered inside the spectrometer probe. Once the temperature was stable, the tube with the sample was inserted into the NMR

probe and ^{31}P NMR spectra were acquired at fixed time intervals throughout the length of experiment with the aid of an automated data collection program.

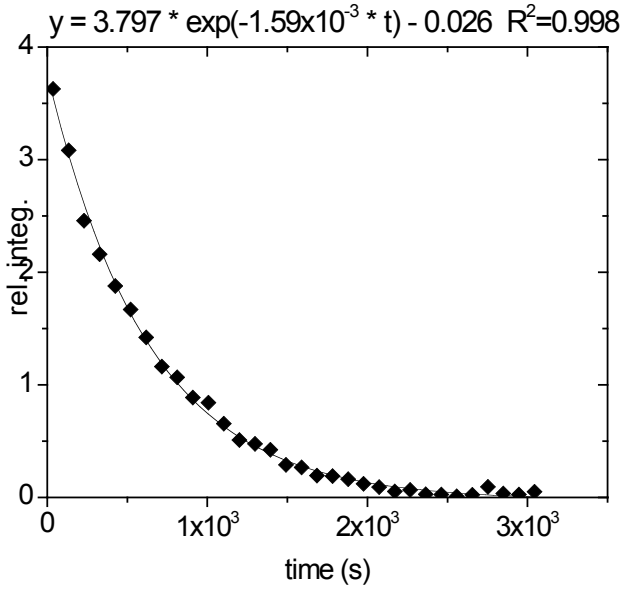


Figure S1. Representative decay of Pd(P^tBu_3)$_2$ (**1**) (0.040 M) in the presence of PhI (0.90 M) and P^tBu_3 (0.10 M) in chlorobenzene at 70 °C.

Representative procedure for the oxidative addition of PhBr to Pd(P^tBu_3)$_2$ (1). The palladium complex Pd(P^tBu_3)$_2$ (**1**) was weighed in a small vial (10.2 mg, 0.02 mmol). Into this vial was placed 40 μL of a 2.5 M (0.1 mmol) solution of P^tBu_3. Toluene (354 μL), PhBr (100 μL, 0.95 mmol) and phosphazene base were added (6 μL, 0.02 mmol) to the sample. The solution was transferred to a screw capped NMR tube, and the sample tube was placed into a preheated NMR spectrometer probe at 90°C. The disappearance of the Pd complex peak was monitored by ^{31}P NMR spectroscopy with the aid of an automated acquisition program.

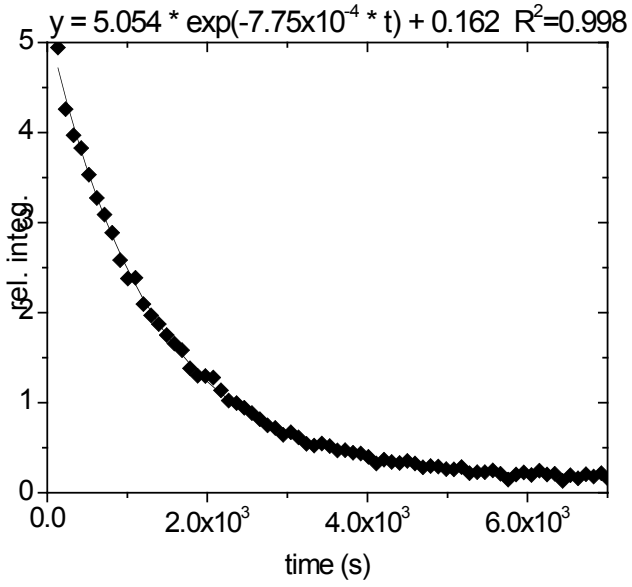


Figure S2. Representative decay of Pd(1-Ad$P^tBu_2)_2$ (**2**) (0.025 M) in the presence of PhBr (8.5 M), 1-AdP^tBu_2 (0.10 M), and *tert*-butylimino-trispyrrolidino phosphorane (0.015 M) in toluene at 90 °C.

Representative procedure for the oxidative addition of ArX (X= I, Br, Cl) to Pd(1-Ad$P^tBu_2)_2$ (2). Into a small vial was placed the palladium complex Pd(1-Ad$P^tBu_2)_2$ (6.7 mg, 0.010 mmol) and ligand 1-AdP^tBu_2 (28.0 mg, 0.10 mmol). The complex was suspended in 100 μL of toluene. The suspension was transferred to an NMR sample tube with a total of three portions of 100 μL of toluene and 100 μL ArX to ensure that all of the solid was transferred to the tube. Total sample volume equal 400 μL. Into the sample tube was added 2 μL (0.006 mmol) of phosphazene base. The sample was placed into the preheated probe at 80 – 100 °C. At this high temperature, the complex Pd(1-Ad$P^tBu_2)_2$ solubilized and the sample became homogeneous. The decay of the Pd complex was monitored by ^{31}P NMR spectroscopy with the aid of an automated acquisition program.

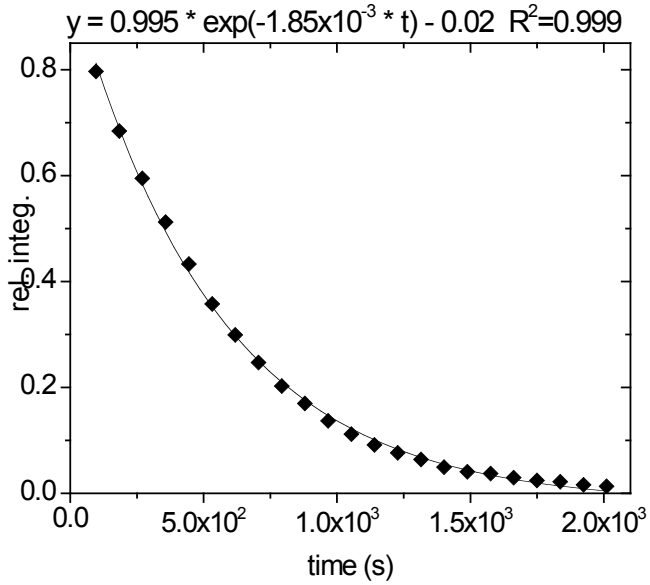


Figure S3. Representative decay of $Pd(CyP^tBu_2)_2$ (**3**) (0.036 M) in the presence of PhI (0.45 M) in toluene at 50 °C.

Representative procedure for the oxidative addition of PhX (X=I, Br, Cl) to $Pd(CyP^tBu_2)_2$ (3). Into a small vial, weighed the palladium complex $Pd(CyP^tBu_2)_2$ (**3**) (10.2 mg, 0.018 mmol) and the ligand CyP^tBu_2 (22.8 mg, 0.10 mmol). The necessary amounts of toluene and PhX were added to the vial to adjust to the desired haloarene concentration and make the final volume 500 μL. The solution was transferred to a screw capped NMR tube, and the sample was placed into a preheated NMR spectrometer probe at 50 – 80°C. The decay of the Pd complex was measured by ^{31}P NMR spectroscopy with the aid of an automated acquisition program.

Representative procedure for the oxidative addition of PhI to $Pd(PCy_3)_2$ (4). Into a small vial was weighed 141 mg of PCy_3 (0.503 mmol). This material was dissolved in

500 μL of toluene to prepare a 1.00 M stock solution. Into a separate vial was weighed 6.3 mg (0.0094 mmol) of the palladium complex $Pd(PCy_3)_2$ (**4**). To this vial, 30 μL of the phosphine stock solution (0.030 mmol) and 270 μL of toluene were added. The solution was transferred to a screw capped NMR tube and cooled to −78 °C. Then, a solution of 20 μL of PhI and 180 μL of toluene was added by syringe. The sample was introduced into the NMR spectrometer probe that was pre-cooled to −80 °C, and the decay of the Pd complex was measured by ^{31}P NMR spectroscopy with the aid of an automated acquisition program.

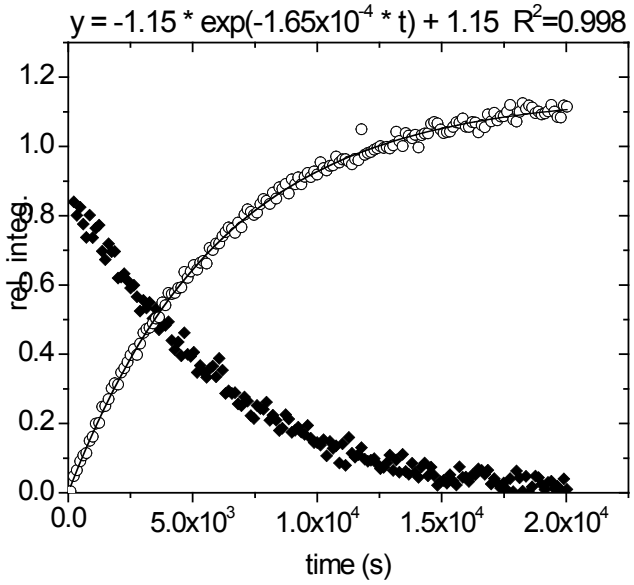


Figure S4. Representative decay of $Pd(PCy_3)_2$ (**4**) (0.019 M) in the presence of PCy_3 (0.009 M) and PhCl (2.0 M) in toluene at 70 °C.

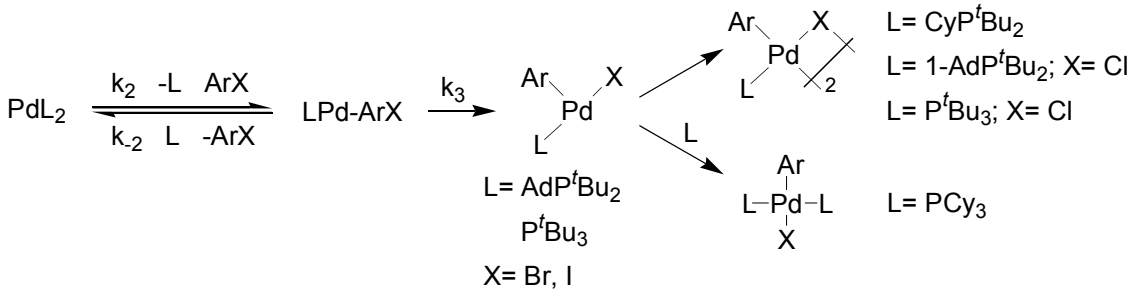
Representative procedure for the oxidative addition of PhCl to $Pd(PCy_3)_2$ (4). Into a small vial was weighed 14.1 mg of PCy_3 (0.0503 mmol). This material was dissolved in 500 μL of toluene to prepare a 0.100 M stock solution. Into a separate vial, 6.3 mg (0.0094 mmol) of the palladium complex $Pd(PCy_3)_2$ (**4**) were weighed. To this vial 50 μL

of the phosphine stock solution (0.0050 mmol), 40 μL of PhCl and 410 μL of toluene were added to make the final volume 500 μL. The solution was transferred to a screw capped NMR tube, and the sample was placed into a preheated NMR spectrometer probe at 70°C. The decay of the Pd complex was measured by ^{31}P NMR spectroscopy with the aid of an automated acquisition program.

Representative procedure for the oxidative addition of PhBr to $Pd(PCy_3)_2$ (4). The phosphine PCy_3 (25.0 mg, 0.089 mmol) and the palladium complex $Pd(PCy_3)_2$ (**4**) (6.3 mg, 0.0094 mmol) were weighed into a small vial. To this vial was added 400 μL of toluene, and the resulting solution was transferred to a screw-capped NMR tube. The sample was cooled in ice bath, and 100 μL of PhBr were added to the tube with a syringe. The sample was introduced into the NMR spectrometer probe pre-cooled at 10 °C. The decay of the Pd complex was measured by ^{31}P NMR spectroscopy with the aid of an automated acquisition program.

DERIVATION OF RATE EXPRESSIONS

Derivation of the rate expressions. Scheme 4.



$$rate = [\mathrm{PdL_2}]k_{obs} \qquad 1/k_{obs} = \frac{1}{k_2[\mathrm{ArX}]} + \frac{[\mathrm{L}]}{K_2k_3[\mathrm{ArX}]} \qquad \text{If } k_3 >> k_{-2}[\mathrm{L}]$$

$$k_{obs} = \frac{k_2k_3[\mathrm{ArX}]}{k_3 + k_{-2}[\mathrm{L}]} \qquad 1/k_{obs} = \left(\frac{1}{k_2} + \frac{[\mathrm{L}]}{K_2k_3}\right)\frac{1}{[\mathrm{ArX}]} \qquad k_{obs} = k_2[\mathrm{ArX}]$$

Under the steady state approximation,

$$\frac{\mathrm{d}[\mathrm{LPd(ArX)}]}{\mathrm{d}t} = 0 = k_2[\mathrm{PdL_2}][\mathrm{ArX}] - k_{-2}[\mathrm{LPd(ArX)}][\mathrm{L}] - k_3[\mathrm{LPd(ArX)}]$$

Solving for [LPd(ArX)],

$$[\mathrm{LPd(ArX)}] = \frac{k_2[\mathrm{ArX}][\mathrm{PdL_2}]}{k_3 + k_{-2}[\mathrm{L}]}$$

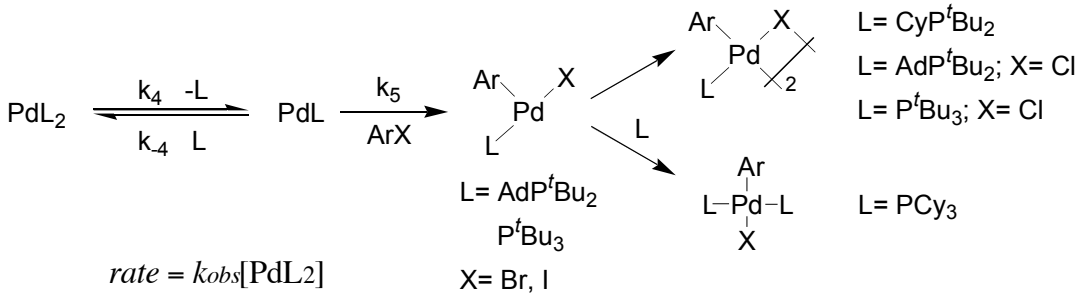
$$rate = k_3[\mathrm{LPd(ArX)}] = \frac{k_2k_3[\mathrm{ArX}][\mathrm{PdL_2}]}{k_3 + k_{-2}[\mathrm{L}]}$$

$rate = k_{obs}[\mathrm{PdL_2}]$; therefore,

$$k_{obs} = \frac{k_2k_3[\mathrm{ArX}]}{k_3 + k_{-2}[\mathrm{L}]}$$

If $k_3 >> k_{-2}[L]$; the term $k_{-2}[L]$ in k_{obs} denominator can be ignored and the expression for k_{obs} gets reduced to $k_{obs} = k_2[ArX]$.

Derivation of the rate expressions. Scheme 5.



$rate = k_{obs}[PdL_2]$

$$k_{obs} = \frac{k_4 k_5[ArX]}{k_5[ArX] + k_{-4}[L]} \qquad 1/k_{obs} = \frac{1}{k_4} + \frac{[L]}{K_4 k_5[ArX]}$$

If $k_5[ArX] >> k_{-4}[L]$ $k_{obs} = k_4$

Under the steady state approximation,

$$\frac{d[PdL]}{dt} = 0 = k_4[PdL_2] - k_{-4}[PdL][L] - k_5[PdL][ArX]$$

Solving for [PdL],

$$[PdL] = \frac{k_2[PdL_2]}{k_{-4}[L] + k_5[ArX]}$$

$$rate = k_5[PdL][ArX] = \frac{k_4 k_5[PdL_2][ArX]}{k_{-4}[L] + k_5[ArX]}$$

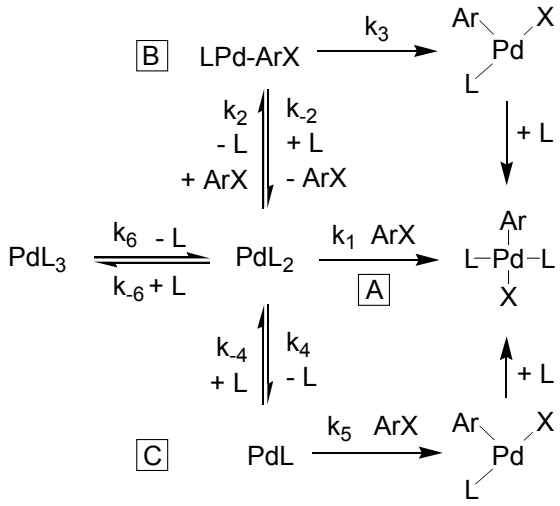
$rate = k_{obs}[PdL_2]$; therefore,

$$k_{obs} = \frac{k_4 k_5[ArX]}{k_{-4}[L] + k_5[ArX]}$$

If $k_5[ArX] >> k_{-4}[L]$

The term k_{-4}[L] in k_{obs} denominator can be ignored and the expression for k_{obs} gets reduced to $k_{obs} = k_4$.

Derivation of the rate expressions. Scheme 7.



$rate = [PdL_3]k_{obs}$

A. Direct reaction to L_2Pd

$$k_{obs} = \frac{k_6 k_1[ArX]}{k_1[ArX] + k_{-6}[L]}$$

$$1/k_{obs} = \frac{1}{k_6} + \frac{[L]}{K_6 k_1[ArX]}$$

B. Associative displacement of the ligand in L_2Pd

$$k_{obs} = \frac{k_6 k_2 k_3[ArX]}{k_2 k_3[ArX] + k_3 k_{-6}[L] + k_{-6} k_{-2}[L]^2}$$

$$1/k_{obs} = \frac{1}{k_6} + \frac{[L]}{K_6 k_2[ArX]} + \frac{[L]^2}{K_6 K_2 k_3[ArX]}$$

C. Dissociation of ligand from L_2Pd

$$k_{obs} = \frac{k_6 k_4 k_5[ArX]}{k_4 k_5[ArX] + k_5 k_{-6}[ArX][L] + k_{-6} k_{-4}[L]^2}$$

$$1/k_{obs} = \frac{1}{k_6} + \frac{[L]}{K_6 k_4} + \frac{[L]^2}{K_6 K_4 k_5[ArX]}$$

Path A

Under the steady state approximation,

$$\frac{\mathrm{d}[\mathrm{PdL_2}]}{\mathrm{d}t} = 0 = k_6[\mathrm{PdL_3}] - k_{-6}[\mathrm{PdL_2}][\mathrm{L}] - k_1[\mathrm{PdL_2}][\mathrm{ArX}]$$

Solving for [PdL_2],

$$[\mathrm{PdL_2}] = \frac{k_6[\mathrm{PdL_3}]}{k_{-6}[\mathrm{L}] + k_1[\mathrm{ArX}]}$$

$$rate = k_1[\mathrm{PdL_2}][\mathrm{ArX}] = \frac{k_6 k_1[\mathrm{PdL_3}][\mathrm{ArX}]}{k_{-6}[\mathrm{L}] + k_1[\mathrm{ArX}]}$$

rate = k_{obs}[PdL_3]; therefore,

$$k_{obs} = \frac{k_6 k_1[\mathrm{ArX}]}{k_{-6}[\mathrm{L}] + k_1[\mathrm{ArX}]}$$

Path B

Under the steady state approximation,

$$\frac{\mathrm{d}[\mathrm{LPd(ArX)}]}{\mathrm{d}t} = 0 = k_2[\mathrm{PdL_2}][\mathrm{ArX}] - k_{-2}[\mathrm{LPd(ArX)}][\mathrm{L}] - k_3[\mathrm{LPd(ArX)}] \qquad (1)$$

$$\frac{\mathrm{d}[\mathrm{PdL_2}]}{\mathrm{d}t} = 0 = k_6[\mathrm{PdL_3}] + k_{-2}[\mathrm{LPd(ArX)}][\mathrm{L}] - k_{-6}[\mathrm{PdL_2}][\mathrm{L}] - k_2[\mathrm{PdL_2}][\mathrm{ArX}] \qquad (2)$$

Solving for [LPd(ArX)],

$$[\mathrm{LPd(ArX)}] = \frac{k_2[\mathrm{PdL_2}][\mathrm{ArX}]}{k_{-2}[\mathrm{L}] + k_3} \qquad (3)$$

Adding equations (1) and (2),

$$0 = k_6[\mathrm{PdL_3}] - k_{-6}[\mathrm{PdL_2}][\mathrm{L}] - k_3[\mathrm{LPd(ArX)}]$$

Solving for [PdL_2],

$$[\mathrm{PdL_2}] = \frac{k_6[\mathrm{PdL_3}] - k_3[\mathrm{LPd(ArX)}]}{k_{-6}[\mathrm{L}]}$$

Substituting [PdL_2] into (3),

$$[\mathrm{LPd(ArX)}] = \frac{k_6 k_2[\mathrm{PdL_3}][\mathrm{ArX}] - k_2 k_3[\mathrm{LPd(ArX)}][\mathrm{ArX}]}{k_{-6}k_{-2}[\mathrm{L}]^2 + k_{-6}k_3[\mathrm{L}]}$$

Solving for [LPd(ArX)],

$$[\mathrm{LPd(ArX)}] = \frac{k_6 k_2[\mathrm{PdL_3}][\mathrm{ArX}]}{k_{-6}k_{-2}[\mathrm{L}]^2 + k_{-6}k_3[\mathrm{L}] + k_2 k_3[\mathrm{ArX}]}$$

$$rate = k_6[\mathrm{LPd(ArX)}] = \frac{k_6 k_2 k_3[\mathrm{PdL_3}][\mathrm{ArX}]}{k_{-6}k_{-2}[\mathrm{L}]^2 + k_{-6}k_3[\mathrm{L}] + k_2 k_3[\mathrm{ArX}]} = k_{obs}[\mathrm{PdL_3}]$$

Therefore,

$$k_{obs} = \frac{k_6 k_2 k_3[\mathrm{ArX}]}{k_{-6}k_{-2}[\mathrm{L}]^2 + k_{-6}k_3[\mathrm{L}] + k_2 k_3[\mathrm{ArX}]}$$

Path C

Under the steady state approximation,

$$\frac{\mathrm{d}[\mathrm{PdL}]}{\mathrm{d}t} = 0 = k_4[\mathrm{PdL_2}] - k_{-4}[\mathrm{PdL}][\mathrm{L}] - k_5[\mathrm{PdL}][\mathrm{ArX}] \quad (4)$$

$$\frac{\mathrm{d}[\mathrm{PdL_2}]}{\mathrm{d}t} = 0 = k_6[\mathrm{PdL_3}] + k_{-4}[\mathrm{PdL}][\mathrm{L}] - k_{-6}[\mathrm{PdL_2}][\mathrm{L}] - k_4[\mathrm{PdL_2}] \quad (5)$$

Solving for [PdL],

$$[\mathrm{PdL}] = \frac{k_4[\mathrm{PdL_2}]}{k_{-4}[\mathrm{L}] + \mathrm{k}_5[\mathrm{ArX}]} \quad (6)$$

Adding equations (4) and (5),

$$0 = k_6[\mathrm{PdL_3}] - k_{-6}[\mathrm{PdL_2}][\mathrm{L}] - k_5[\mathrm{PdL}][\mathrm{ArX}]$$

Solving for [PdL_2],

$$[\mathrm{PdL_2}] = \frac{k_6[\mathrm{PdL_3}] - k_5[\mathrm{ArX}][\mathrm{PdL}]}{k_{-6}[\mathrm{L}]}$$

Substituting [PdL_2] into (3),

$$[\mathrm{PdL}] = \frac{k_6 k_4[\mathrm{PdL_3}] - k_4 k_5[\mathrm{ArX}][\mathrm{PdL}]}{k_{-6}k_{-4}[\mathrm{L}]^2 + k_{-6}k_5[\mathrm{ArX}][\mathrm{L}]}$$

Solving for [PdL],

$$[\mathrm{PdL}] = \frac{k_6 k_4[\mathrm{PdL_3}]}{k_{-6}k_{-4}[\mathrm{L}]^2 + k_{-6}k_5[\mathrm{ArX}][\mathrm{L}] + k_4 k_5[\mathrm{ArX}]}$$

$$rate = k_5[\mathrm{PdL}][\mathrm{ArX}] = \frac{k_6 k_4 k_5[\mathrm{PdL_3}][\mathrm{ArX}]}{k_{-6}k_{-4}[\mathrm{L}]^2 + k_{-6}k_5[\mathrm{ArX}][\mathrm{L}] + k_4 k_5[\mathrm{ArX}]} = k_{obs}[\mathrm{PdL_3}]$$

Therefore,

$$k_{obs} = \frac{k_6 k_4 k_5[\mathrm{ArX}]}{k_{-6}k_{-4}[\mathrm{L}]^2 + k_{-6}k_5[\mathrm{ArX}][\mathrm{L}] + k_4 k_5[\mathrm{ArX}]}$$

X ray crystallographic data for $[(P^tBu_3)Pd(2\text{-}CF_3C_6H_4)(Cl)]_2$ (10)

Data Collection

A pale yellow plate crystal of $C_{38}H_{62}Cl_2F_6P_2Pd_2$ having approximate dimensions of 0.20 x 0.20 x 0.08 mm^3 was mounted with epoxy cement on the tip of a fine glass fiber. All measurements were made on a Nonius KappaCCD diffractometer with graphite monochromated Mo-Kα radiation.

Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions:

a = 8.2900(17) Å α = 90 °

b = 24.948(5) Å β = 106.86(3) °

c = 10.626(2) Å γ = 90 °

V = 2103.2(7) $Å^3$

For Z = 2 and F.W. = 978.52, the calculated density is 1.545 g/cm^3. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be $P2_1$ (#4).

The data were collected at a temperature of 173(2) K to a maximum 2θ value of 56.52 °. Four omega scans consisting of 108, 85, 101, and 42 data frames, respectively, were collected with a frame width of 0.7 ° and a detector-to-crystal distance, Dx, of 35.0 mm. Each frame was exposed twice (for the purpose of de-zingering) for a total of 84 s. The data frames were processed and scaled using the DENZO software package.[1]

Data Reduction

A total of 8016 reflections were collected of which 8016 were unique and observed (R_{int} = 0.000, Friedel pairs not merged). The linear absorption coefficient, μ, for Mo-Kα radiation is 11.11 cm^{-1}, and no absorption correction was applied. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods and expanded using Fourier techniques[2]. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were treated as idealized contributions. The final cycle of full-matrix least-squares refinement[3] on F was based on 8016 observed reflections ($I > 2.00\sigma(I)$) and 559 variable parameters and converged with unweighted and weighted agreement factors of:

$$R = \Sigma \, ||Fo| - |Fc|| \, / \, \Sigma \, |Fo| = 0.0427$$

$$R_W = \{\Sigma[w \, (F_o^2 - F_c^2)^2] \, / \, \Sigma[w(F_o^2)^2]\}^{1/2} = 0.1089$$

The maximum and minimum peaks on the final difference Fourier map corresponded to 1.301 and –0.838 $e^-/Å^3$ respectively.

Structural Description

The compound crystallized in the chiral monoclinic space group $P2_1$ with one molecule in the asymmetric unit and two molecules in the unit cell. Pd(1) and Pd(2) are separated by 3.61 Å and bridged by two μ_2-chloride ligands. The chloride ligands bond nearly symmetrically with the Pd-Cl bond distances ranging from 2.3913(16) to 2.4817(17) Å.

The mean deviations of the palladium coordination planes are 0.04 Å for Pd(1) and 0.11 Å for Pd(2) and these planes intersect at an angle of 145.6 ° as illustrated in Figure 1. The molecule possesses a pseudo-center of inversion but the molecular symmetry is disrupted by severe disorder. Although the environment about Pd(1) is well-ordered, the phosphine and aryl groups bonded to Pd(2) are disordered over several positions. Two of the *tert*-butyl groups, C(20-23) and C(24-27), were refined with alternate positions at occupancy factor ratios of 50:50. All components were refined with anisotropic displacement parameters. As illustrated in Figure 2 the alternate location of the aryl group is offset from the primary component by 180 °. The occupancy factor for this group was refined to 70:30 and the minor component was refined with isotropic displacement parameters.

The molecule was refined as a racemic twin and thus the absolute configuration could not be unambiguously determined. There are no significant intermolecular contacts.

X ray crystallographic data for $[(P^tBu_3)Pd(2\text{-}CF_3C_6H_4)(Cl)]_2$ (10)

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Figure S5

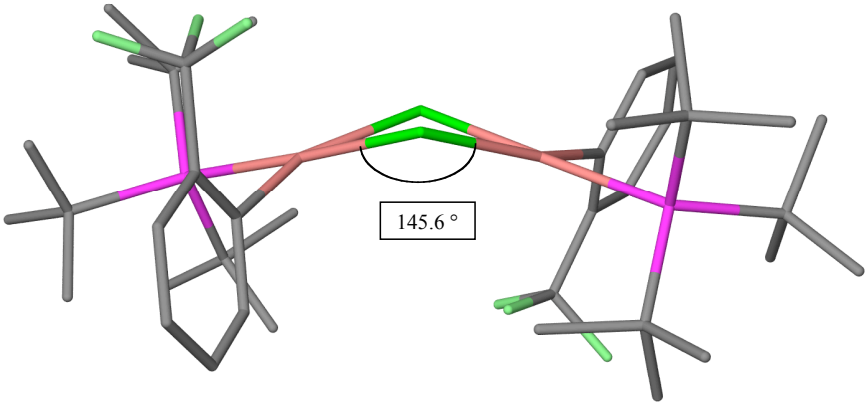

Figure S6

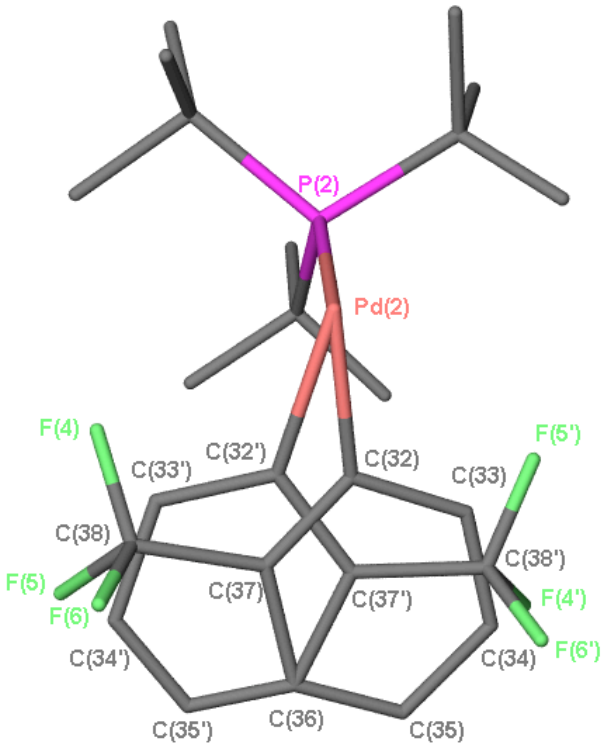

Table S1. Crystal data and structure refinement for $[(P^tBu_3)Pd(2\text{-}CF_3C_6H_4)(Cl)]_2$ (**10**)

Empirical formula	$C_{38}\ H_{62}\ Cl_2\ F_6\ P_2\ Pd_2$	
Formula weight	978.52	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 8.2900(17) Å	□= 90°.
	b = 24.948(5) Å	□= 106.86(3)°.
	c = 10.626(2) Å	□ = 90°.
Volume	2103.2(7) $Å^3$	
Z	2	
Density (calculated)	1.545 g/cm^3	
Absorption coefficient	11.11 cm^{-1}	
F(000)	1000	
Crystal size	0.20 x 0.20 x 0.08 mm^3	
Theta range for data collection	2.57 to 28.26°.	
Index ranges	-11<=h<=11, -33<=k<=23, -14<=l<=14	
Reflections collected	8016	
Independent reflections	8016 [R(int) = 0.0000]	
Completeness to theta = 28.26°	99.2 %	
Absorption correction	None	
Max. and min. transmission	0.9164 and 0.8084	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8016 / 1 / 559	
Goodness-of-fit on F^2	1.015	
Final R indices [I>2sigma(I)]	R1 = 0.0427, wR2 = 0.1089	
R indices (all data)	R1 = 0.0514, wR2 = 0.1146	
Absolute structure parameter	0.17(3)	
Largest diff. peak and hole	1.301 and -0.838 $e.Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for [(P^tBu_3)Pd(2-$CF_3C_6H_4$)(Cl)]$_2$ (**10**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	8676(1)	3424(1)	7418(1)	34(1)
Pd(2)	6889(1)	2167(1)	8043(1)	34(1)
P(1)	8705(2)	3967(1)	5601(1)	32(1)
P(2)	5695(2)	1789(1)	9609(2)	37(1)
Cl(2)	8147(2)	2513(1)	6442(2)	49(1)
Cl(1)	8672(2)	2899(1)	9300(2)	50(1)
F(1)	5627(5)	4686(2)	8326(6)	81(1)
F(2)	5733(6)	4126(3)	9872(5)	82(2)
F(3)	5743(4)	3851(2)	7980(4)	59(1)
C(1)	10203(6)	3610(3)	4771(6)	41(1)
C(2)	10712(8)	3965(3)	3724(7)	51(2)
C(3)	9451(8)	3102(3)	4075(7)	51(2)
C(4)	11777(7)	3460(3)	5894(6)	49(2)
C(5)	6488(6)	3968(3)	4385(6)	41(1)
C(6)	6386(8)	4090(3)	2955(7)	53(2)
C(7)	5686(6)	3418(3)	4459(7)	52(2)
C(8)	5367(7)	4375(3)	4827(7)	51(2)
C(9)	9430(8)	4709(3)	5852(7)	45(1)
C(10)	8931(9)	5035(3)	4580(8)	57(2)
C(11)	8651(9)	4993(3)	6826(7)	50(2)
C(12)	11352(8)	4741(3)	6505(7)	57(2)
C(13)	9295(7)	4007(2)	8740(6)	36(1)
C(14)	11062(7)	4090(3)	9296(7)	44(1)
C(15)	11692(9)	4441(3)	10334(7)	55(2)
C(16)	10605(10)	4714(3)	10880(7)	59(2)
C(17)	8897(9)	4615(3)	10382(6)	49(2)
C(18)	8244(8)	4271(3)	9333(6)	41(1)
C(19)	6369(8)	4231(3)	8863(7)	47(2)
C(20)	7540(9)	1576(3)	11071(7)	57(2)
C(21)	7440(40)	1450(20)	12370(40)	121(16)
C(22)	8110(30)	981(7)	10686(18)	73(5)

C(23)	9037(18)	1910(8)	11252(16)	65(4)
C(21')	6970(30)	1345(14)	12220(30)	75(8)
C(22')	8912(17)	1363(9)	10602(15)	67(4)
C(23')	8340(20)	2135(8)	11863(16)	72(4)
C(24)	4450(9)	2347(3)	10164(8)	56(2)
C(25)	3591(17)	2689(6)	9007(15)	53(3)
C(26)	3380(20)	2199(10)	11030(20)	50(5)
C(27)	5826(17)	2748(6)	11098(15)	47(3)
C(25')	2600(20)	2346(7)	9010(20)	72(5)
C(26')	4070(30)	2256(11)	11460(30)	72(7)
C(27')	5110(30)	2848(7)	10000(30)	88(6)
C(28)	4208(12)	1177(4)	9166(8)	69(2)
C(29)	3541(14)	984(4)	10269(10)	86(3)
C(30)	2740(20)	1286(8)	8033(15)	205(12)
C(31)	5120(30)	718(5)	8700(20)	184(11)
C(36)	4782(10)	1150(3)	4649(7)	53(2)
C(32)	5427(10)	1775(3)	6507(8)	35(2)
C(33)	3878(15)	2008(6)	5882(15)	60(3)
C(34)	2857(18)	1821(6)	4720(13)	67(3)
C(35)	3334(16)	1378(5)	4093(11)	69(3)
C(37)	5872(12)	1349(4)	5871(9)	43(2)
C(38)	7578(15)	1063(5)	6379(12)	55(3)
F(4)	8431(8)	1159(3)	7603(6)	70(2)
F(5)	7409(12)	537(3)	6287(10)	86(2)
F(6)	8597(10)	1179(3)	5626(8)	83(2)
C(32')	6210(20)	1559(8)	6737(19)	29(3)
C(33')	7210(30)	1112(8)	6840(20)	33(4)
C(34')	6990(40)	742(15)	5790(30)	58(7)
C(35')	5720(30)	766(10)	4750(30)	52(5)
C(37')	4880(20)	1578(8)	5583(18)	30(3)
C(38')	3640(40)	2029(11)	5220(30)	44(6)
F(4')	2071(19)	1826(8)	4940(20)	80(6)
F(5')	3742(17)	2385(7)	6145(14)	61(4)
F(6')	3670(20)	2297(6)	4169(14)	63(4)

Table S3. Bond lengths [Å] and angles [°] for [(P^tBu_3)Pd(2-$CF_3C_6H_4$)(Cl)]$_2$ (**10**).

Pd(1)-C(13)	1.984(6)	C(20)-C(22')	1.467(18)
Pd(1)-P(1)	2.3645(15)	C(20)-C(23)	1.461(19)
Pd(1)-Cl(1)	2.3913(16)	C(20)-C(21')	1.54(3)
Pd(1)-Cl(2)	2.4814(17)	C(20)-C(22)	1.645(18)
Pd(2)-C(32)	1.985(8)	C(20)-C(23')	1.66(2)
Pd(2)-C(32')	2.02(2)	C(24)-C(27')	1.40(2)
Pd(2)-P(2)	2.3650(15)	C(24)-C(25)	1.496(16)
Pd(2)-Cl(2)	2.3994(15)	C(24)-C(26)	1.50(2)
Pd(2)-Cl(1)	2.4817(17)	C(24)-C(26')	1.52(3)
P(1)-C(5)	1.916(6)	C(24)-C(27)	1.622(15)
P(1)-C(1)	1.937(5)	C(24)-C(25')	1.67(2)
P(1)-C(9)	1.940(7)	C(28)-C(30)	1.466(17)
P(2)-C(20)	1.913(7)	C(28)-C(29)	1.512(11)
P(2)-C(24)	1.923(7)	C(28)-C(31)	1.531(16)
P(2)-C(28)	1.933(7)	C(36)-C(35')	1.22(3)
F(1)-C(19)	1.338(8)	C(36)-C(35)	1.305(15)
F(2)-C(19)	1.350(8)	C(36)-C(37')	1.44(2)
F(3)-C(19)	1.328(8)	C(36)-C(37)	1.437(12)
C(1)-C(3)	1.508(10)	C(32)-C(33)	1.391(15)
C(1)-C(4)	1.537(8)	C(32)-C(37)	1.368(13)
C(1)-C(2)	1.573(8)	C(33)-C(34)	1.361(19)
C(5)-C(6)	1.527(9)	C(34)-C(35)	1.41(2)
C(5)-C(7)	1.536(10)	C(37)-C(38)	1.535(16)
C(5)-C(8)	1.539(9)	C(38)-F(4)	1.310(14)
C(9)-C(10)	1.529(10)	C(38)-F(5)	1.322(14)
C(9)-C(11)	1.542(9)	C(38)-F(6)	1.352(14)
C(9)-C(12)	1.545(9)	C(32')-C(37')	1.39(3)
C(13)-C(18)	1.382(8)	C(32')-C(33')	1.38(3)
C(13)-C(14)	1.427(8)	C(33')-C(34')	1.42(4)
C(14)-C(15)	1.385(10)	C(34')-C(35')	1.29(4)
C(15)-C(16)	1.384(12)	C(37')-C(38')	1.50(3)
C(16)-C(17)	1.382(10)	C(38')-F(4')	1.35(3)
C(17)-C(18)	1.387(9)	C(38')-F(6')	1.31(3)
C(18)-C(19)	1.492(9)	C(38')-F(5')	1.31(3)
C(20)-C(21)	1.44(4)		

C(13)-Pd(1)-P(1)	95.52(17)	C(6)-C(5)-C(8)	108.0(5)
C(13)-Pd(1)-Cl(1)	82.62(17)	C(7)-C(5)-C(8)	105.3(5)
P(1)-Pd(1)-Cl(1)	178.14(6)	C(6)-C(5)-P(1)	115.9(4)
C(13)-Pd(1)-Cl(2)	160.88(18)	C(7)-C(5)-P(1)	108.0(4)
P(1)-Pd(1)-Cl(2)	103.04(5)	C(8)-C(5)-P(1)	109.9(4)
Cl(1)-Pd(1)-Cl(2)	78.81(6)	C(10)-C(9)-C(11)	106.8(6)
C(32)-Pd(2)-C(32')	23.7(5)	C(10)-C(9)-C(12)	110.4(5)
C(32)-Pd(2)-P(2)	95.8(2)	C(11)-C(9)-C(12)	104.7(6)
C(32')-Pd(2)-P(2)	95.4(5)	C(10)-C(9)-P(1)	113.1(5)
C(32)-Pd(2)-Cl(2)	83.2(2)	C(11)-C(9)-P(1)	111.0(4)
C(32')-Pd(2)-Cl(2)	82.9(5)	C(12)-C(9)-P(1)	110.5(5)
P(2)-Pd(2)-Cl(2)	177.57(6)	C(18)-C(13)-C(14)	116.7(6)
C(32)-Pd(2)-Cl(1)	158.6(2)	C(18)-C(13)-Pd(1)	127.2(4)
C(32')-Pd(2)-Cl(1)	157.7(5)	C(14)-C(13)-Pd(1)	115.1(4)
P(2)-Pd(2)-Cl(1)	102.69(5)	C(15)-C(14)-C(13)	121.8(6)
Cl(2)-Pd(2)-Cl(1)	78.65(6)	C(14)-C(15)-C(16)	120.2(6)
C(5)-P(1)-C(1)	108.1(3)	C(15)-C(16)-C(17)	118.1(7)
C(5)-P(1)-C(9)	106.9(3)	C(16)-C(17)-C(18)	122.4(7)
C(1)-P(1)-C(9)	106.7(3)	C(13)-C(18)-C(17)	120.8(6)
C(5)-P(1)-Pd(1)	108.46(19)	C(13)-C(18)-C(19)	123.3(6)
C(1)-P(1)-Pd(1)	105.53(19)	C(17)-C(18)-C(19)	115.9(6)
C(9)-P(1)-Pd(1)	120.7(2)	F(3)-C(19)-F(1)	105.5(6)
C(20)-P(2)-C(24)	109.0(4)	F(3)-C(19)-F(2)	105.1(5)
C(20)-P(2)-C(28)	106.3(4)	F(1)-C(19)-F(2)	105.4(5)
C(24)-P(2)-C(28)	106.6(4)	F(3)-C(19)-C(18)	116.1(5)
C(20)-P(2)-Pd(2)	106.5(2)	F(1)-C(19)-C(18)	113.0(5)
C(24)-P(2)-Pd(2)	107.4(2)	F(2)-C(19)-C(18)	110.9(6)
C(28)-P(2)-Pd(2)	120.7(2)	C(21)-C(20)-C(22')	121(2)
Pd(2)-Cl(2)-Pd(1)	95.38(5)	C(21)-C(20)-C(23)	106.5(12)
Pd(1)-Cl(1)-Pd(2)	95.59(6)	C(22')-C(20)-C(23)	62.5(11)
C(3)-C(1)-C(4)	108.2(5)	C(21)-C(20)-C(21')	17.1(15)
C(3)-C(1)-C(2)	106.6(5)	C(22')-C(20)-C(21')	125.3(16)
C(4)-C(1)-C(2)	110.2(5)	C(23)-C(20)-C(21')	123.6(12)
C(3)-C(1)-P(1)	112.4(4)	C(21)-C(20)-C(22)	98(2)
C(4)-C(1)-P(1)	105.7(4)	C(22')-C(20)-C(22)	44.0(10)
C(2)-C(1)-P(1)	113.7(4)	C(23)-C(20)-C(22)	104.6(11)
C(6)-C(5)-C(7)	109.2(6)	C(21')-C(20)-C(22)	92.1(17)

C(21)-C(20)-C(23')	80.0(19)	C(31)-C(28)-P(2)	109.4(7)
C(22')-C(20)-C(23')	103.9(12)	C(35')-C(36)-C(35)	149.5(15)
C(23)-C(20)-C(23')	41.9(9)	C(35')-C(36)-C(37')	127.8(16)
C(21')-C(20)-C(23')	94.7(15)	C(35)-C(36)-C(37')	81.5(10)
C(22)-C(20)-C(23')	141.2(12)	C(35')-C(36)-C(37)	88.5(14)
C(21)-C(20)-P(2)	125.6(15)	C(35)-C(36)-C(37)	120.9(9)
C(22')-C(20)-P(2)	109.9(7)	C(37')-C(36)-C(37)	39.5(8)
C(23)-C(20)-P(2)	113.4(7)	C(33)-C(32)-C(37)	115.7(10)
C(21')-C(20)-P(2)	113.0(9)	C(33)-C(32)-Pd(2)	116.5(9)
C(22)-C(20)-P(2)	105.6(8)	C(37)-C(32)-Pd(2)	127.0(7)
C(23')-C(20)-P(2)	106.5(7)	C(32)-C(33)-C(34)	122.3(14)
C(27')-C(24)-C(25)	59.8(13)	C(33)-C(34)-C(35)	120.9(13)
C(27')-C(24)-C(26)	128.3(14)	C(36)-C(35)-C(34)	118.4(10)
C(25)-C(24)-C(26)	114.9(11)	C(32)-C(37)-C(36)	121.7(8)
C(27')-C(24)-C(26')	116.0(15)	C(32)-C(37)-C(38)	122.7(9)
C(25)-C(24)-C(26')	130.9(13)	C(36)-C(37)-C(38)	115.6(8)
C(26)-C(24)-C(26')	24.2(9)	F(4)-C(38)-F(5)	105.6(10)
C(27')-C(24)-C(27)	45.0(12)	F(4)-C(38)-F(6)	107.4(10)
C(25)-C(24)-C(27)	103.5(9)	F(5)-C(38)-F(6)	103.9(10)
C(26)-C(24)-C(27)	102.2(10)	F(4)-C(38)-C(37)	116.2(10)
C(26')-C(24)-C(27)	80.3(11)	F(5)-C(38)-C(37)	111.6(10)
C(27')-C(24)-C(25')	102.6(13)	F(6)-C(38)-C(37)	111.3(9)
C(25)-C(24)-C(25')	43.7(9)	C(37')-C(32')-C(33')	113.7(19)
C(26)-C(24)-C(25')	82.6(10)	C(37')-C(32')-Pd(2)	124.9(16)
C(26')-C(24)-C(25')	106.2(13)	C(33')-C(32')-Pd(2)	120.8(15)
C(27)-C(24)-C(25')	141.8(10)	C(34')-C(33')-C(32')	122(2)
C(27')-C(24)-P(2)	110.2(9)	C(33')-C(34')-C(35')	122(3)
C(25)-C(24)-P(2)	109.3(6)	C(36)-C(35')-C(34')	117(3)
C(26)-C(24)-P(2)	118.4(11)	C(32')-C(37')-C(36)	117.0(16)
C(26')-C(24)-P(2)	116.3(11)	C(32')-C(37')-C(38')	124(2)
C(27)-C(24)-P(2)	106.8(6)	C(36)-C(37')-C(38')	118.6(19)
C(25')-C(24)-P(2)	103.6(7)	F(4')-C(38')-F(6')	105(3)
C(30)-C(28)-C(29)	107.1(10)	F(4')-C(38')-F(5')	106(2)
C(30)-C(28)-C(31)	103.9(13)	F(6')-C(38')-F(5')	106(2)
C(29)-C(28)-C(31)	109.7(10)	F(4')-C(38')-C(37')	109(2)
C(30)-C(28)-P(2)	111.8(8)	F(6')-C(38')-C(37')	115.0(19)
C(29)-C(28)-P(2)	114.4(5)	F(5')-C(38')-C(37')	115(3)

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $[(P^tBu_3)Pd(2\text{-}CF_3C_6H_4)(Cl)]_2$ (**10**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	32(1)	34(1)	35(1)	1(1)	10(1)	-8(1)
Pd(2)	36(1)	33(1)	32(1)	3(1)	9(1)	-4(1)
P(1)	25(1)	37(1)	33(1)	1(1)	8(1)	-5(1)
P(2)	41(1)	35(1)	34(1)	1(1)	11(1)	-5(1)
Cl(2)	68(1)	40(1)	46(1)	-4(1)	29(1)	-16(1)
Cl(1)	64(1)	46(1)	37(1)	1(1)	12(1)	-21(1)
F(1)	56(2)	64(3)	113(4)	11(3)	9(2)	13(2)
F(2)	61(3)	136(5)	58(3)	-6(3)	33(2)	-8(3)
F(3)	37(2)	75(3)	66(3)	-14(2)	18(2)	-5(2)
C(1)	25(2)	53(4)	48(3)	3(3)	15(2)	0(2)
C(2)	39(3)	64(4)	54(4)	12(3)	23(3)	-2(3)
C(3)	52(3)	54(4)	57(4)	2(3)	30(3)	6(3)
C(4)	31(2)	59(4)	57(4)	13(4)	14(2)	7(3)
C(5)	24(2)	61(4)	37(3)	2(3)	6(2)	-1(2)
C(6)	39(3)	71(5)	42(4)	8(3)	1(3)	3(3)
C(7)	28(2)	70(4)	51(4)	-1(4)	3(2)	-16(3)
C(8)	29(3)	64(4)	58(4)	10(3)	12(3)	11(3)
C(9)	45(3)	39(3)	49(4)	11(3)	13(3)	-10(3)
C(10)	59(4)	50(4)	63(5)	15(4)	17(3)	-8(3)
C(11)	57(3)	32(3)	62(4)	3(3)	20(3)	2(3)
C(12)	56(4)	50(4)	59(4)	-12(4)	5(3)	-26(3)
C(13)	38(3)	36(3)	31(3)	-2(2)	8(2)	-4(2)
C(14)	34(3)	44(3)	46(4)	2(3)	-1(2)	-6(2)
C(15)	52(4)	52(4)	48(4)	9(3)	-5(3)	-10(3)
C(16)	75(5)	48(4)	43(4)	-2(3)	0(3)	-14(4)
C(17)	70(4)	40(3)	35(3)	1(3)	15(3)	-7(3)
C(18)	47(3)	39(3)	36(3)	2(3)	10(3)	-4(2)
C(19)	52(3)	41(4)	50(4)	1(3)	20(3)	3(3)
C(20)	59(4)	64(5)	45(4)	20(4)	9(3)	15(3)
C(21)	66(19)	230(40)	54(14)	9(17)	-1(13)	-80(20)
C(22)	98(13)	64(11)	61(10)	29(9)	28(9)	46(10)

C(23)	48(8)	91(12)	48(9)	6(9)	1(6)	13(7)
C(21')	37(11)	140(20)	30(10)	48(13)	-13(8)	-27(12)
C(22')	42(7)	95(13)	49(9)	26(9)	-9(6)	-1(8)
C(23')	89(11)	72(11)	45(8)	8(9)	3(8)	-5(10)
C(24)	62(4)	53(4)	59(4)	3(3)	30(4)	9(3)
C(25)	46(7)	53(8)	59(9)	-5(7)	14(6)	15(6)
C(26)	40(8)	67(12)	46(10)	-21(9)	19(7)	5(8)
C(27)	55(7)	41(7)	47(8)	-20(6)	16(6)	-7(6)
C(25')	56(8)	65(10)	99(14)	19(9)	28(9)	27(8)
C(26')	105(19)	53(11)	73(18)	-9(12)	50(14)	-5(14)
C(27')	95(14)	52(11)	130(20)	16(12)	52(15)	8(9)
C(28)	98(6)	64(5)	56(5)	-23(4)	38(4)	-47(4)
C(29)	118(8)	74(6)	80(6)	-15(5)	49(6)	-57(6)
C(30)	155(13)	260(20)	132(11)	70(13)	-69(10)	-177(16)
C(31)	250(20)	74(8)	320(30)	-98(12)	220(20)	-83(11)
C(36)	68(4)	57(4)	37(4)	-7(3)	22(3)	-17(3)
C(32)	34(4)	35(4)	32(4)	1(4)	3(3)	-4(3)
C(33)	62(7)	71(9)	43(7)	11(6)	10(5)	14(6)
C(34)	43(7)	82(9)	63(8)	1(7)	-6(6)	0(7)
C(35)	74(7)	74(8)	42(6)	-1(6)	-9(5)	-30(6)
C(37)	55(5)	37(5)	42(5)	3(4)	21(4)	-7(4)
C(38)	57(6)	63(8)	50(7)	3(6)	22(6)	-2(5)
F(4)	65(4)	89(5)	57(4)	-2(3)	20(3)	33(3)
F(5)	110(6)	47(4)	101(7)	0(4)	30(5)	17(4)
F(6)	90(5)	94(5)	86(5)	31(4)	58(4)	35(4)
F(4')	27(7)	97(13)	105(15)	20(10)	1(8)	17(8)
F(5')	65(8)	66(10)	43(8)	-1(7)	-2(6)	44(7)
F(6')	91(10)	62(9)	44(7)	0(6)	29(7)	3(7)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for [(P^tBu_3)Pd(2-$CF_3C_6H_4$)(Cl)]$_2$ (**10**).

	x	y	z	U(eq)
H(2A)	11467	3761	3343	76
H(2B)	11290	4289	4150	76
H(2C)	9697	4067	3026	76
H(3A)	10241	2940	3656	77
H(3B)	8392	3185	3404	77
H(3C)	9231	2850	4713	77
H(4A)	12597	3282	5531	73
H(4B)	11456	3216	6505	73
H(4C)	12280	3785	6363	73
H(6A)	5205	4084	2419	79
H(6B)	7022	3819	2630	79
H(6C)	6866	4445	2900	79
H(7A)	4543	3411	3852	77
H(7B)	5638	3355	5358	77
H(7C)	6367	3137	4216	77
H(8A)	4234	4371	4204	76
H(8B)	5853	4734	4856	76
H(8C)	5299	4277	5704	76
H(10A)	9310	5407	4770	86
H(10B)	7702	5029	4205	86
H(10C)	9460	4880	3950	86
H(11A)	9024	5367	6929	74
H(11B)	9015	4812	7680	74
H(11C)	7419	4980	6487	74
H(12A)	11697	5118	6630	86
H(12B)	11940	4566	5939	86
H(12C)	11639	4560	7360	86
H(14A)	11827	3901	8945	53
H(15A)	12873	4494	10672	65
H(16A)	11021	4962	11577	71
H(17A)	8143	4790	10773	58
H(21A)	8557	1353	12936	181

H(21B)	6664	1147	12316	181
H(21C)	7016	1762	12736	181
H(22A)	9061	850	11404	110
H(22B)	8457	1009	9880	110
H(22C)	7164	732	10544	110
H(23A)	9934	1782	12013	97
H(23B)	8762	2282	11401	97
H(23C)	9421	1891	10463	97
H(21D)	7964	1243	12938	112
H(21E)	6265	1028	11917	112
H(21F)	6323	1616	12531	112
H(22D)	9852	1255	11356	100
H(22E)	9294	1641	10101	100
H(22F)	8507	1052	10036	100
H(23D)	9295	2045	12625	108
H(23E)	7472	2319	12160	108
H(23F)	8725	2370	11269	108
H(25A)	2958	2973	9288	80
H(25B)	2816	2468	8335	80
H(25C)	4437	2849	8641	80
H(26A)	2827	2520	11232	74
H(26B)	4098	2043	11850	74
H(26C)	2532	1937	10579	74
H(27A)	5242	3040	11401	71
H(27B)	6547	2896	10598	71
H(27C)	6521	2549	11858	71
H(25D)	1870	2623	9207	108
H(25E)	2062	1995	8983	108
H(25F)	2771	2421	8150	108
H(26D)	3435	2563	11649	108
H(26E)	5124	2218	12169	108
H(26F)	3392	1930	11405	108
H(27D)	4464	3129	10283	131
H(27E)	5034	2901	9070	131
H(27F)	6292	2867	10530	131
H(29A)	2794	677	9966	130
H(29B)	2911	1274	10534	130

H(29C)	4486	877	11020	130
H(30A)	2021	968	7837	307
H(30B)	3126	1376	7268	307
H(30C)	2105	1588	8236	307
H(31A)	4360	408	8467	276
H(31B)	6125	618	9404	276
H(31C)	5444	833	7926	276
H(33A)	3519	2309	6279	72
H(34A)	1808	1992	4328	81
H(35A)	2619	1247	3282	82
H(33B)	8070	1049	7640	39
H(34B)	7812	468	5856	69
H(35B)	5520	496	4093	62

X ray crystallographic data for [(1-AdP^{t}Bu$_2$)Pd(Ph)(Cl)]$_2$ (11)

Data Collection

A pale yellow plate crystal of $C_{48}H_{76}Cl_2P_2Pd_2$ having approximate dimensions of 0.20 x 0.20 x 0.08 mm^3 was mounted with epoxy cement on the tip of a fine glass fiber. All measurements were made on a Nonius KappaCCD diffractometer with graphite monochromated Mo-Kα radiation.

Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions:

a = 15.251(3) Å α = 90 °

b = 14.575(3) Å β = 90.64(3) °

c = 20.401(4) Å γ = 90 °

V = 4534.3(16) Å^3

For Z = 4 and F.W. = 998.73, the calculated density is 1.463 g/cm^3. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be $P2_1/n$ (#14).

The data were collected at a temperature of 173(2) K to a maximum 2θ value of 56.58 °. Four omega scans consisting of 47, 47, 43, and 21 data frames, respectively, were collected with a frame width of 1.6 ° and a detector-to-crystal distance, Dx, of 35.0 mm. Each frame was exposed twice (for the purpose of de-zingering) for a total of 80 s. The data frames were processed and scaled using the DENZO software package.[3]

Data Reduction

A total of 17957 reflections were collected of which 11194 were unique and observed (R_{int} = 0.0282). The linear absorption coefficient, μ, for Mo-Kα radiation is 10.14 cm^{-1}, and no absorption correction was applied. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods and expanded using Fourier techniques[4]. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were treated as idealized contributions. The final cycle of full-matrix least-squares refinement[5] on F was based on 11194 observed reflections ($I > 2.00\sigma(I)$) and 487 variable parameters and converged with unweighted and weighted agreement factors of:

$$R = \Sigma \, ||Fo| - |Fc|| \, / \, \Sigma \, |Fo| = 0.0386$$

$$R_W = \{\Sigma[w \, (F_o^2 - F_c^2)^2] \, / \, \Sigma[w(F_o^2)^2]\}^{1/2} = 0.0954$$

The maximum and minimum peaks on the final difference Fourier map corresponded to 0.409 and –0.772 $e^-/Å^3$ respectively.

Structural Description

The compound crystallized in the monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit and four molecules in the unit cell. Pd(1) and Pd(2) are separated by 3.78 Å and bridged by two μ_2-chloride ligands that are separated by 3.12 Å. The chloride ligands possess dissimilar Pd-Cl bond distances with shorter Pd-Cl(1) bonds than Pd-Cl(2) on the order of 0.1 Å. This is probably caused by the steric congestion of the neighboring phosphine ligands. The mean deviations of the palladium coordination

planes are 0.06 Å for Pd(1) and 0.15 Å for Pd(2) and these planes intersect at an angle of 166.3 ° as illustrated in Figure 3. The molecule possesses a pseudo-mirror plane that bisects the Cl-Cl vector. The asymmetry is caused by slight differences in the palladium planes and the offsetting orientations of the their respective phenyl rings (88.1 vs. 99.5 °). There are no significant intermolecular contacts.

Figure S7

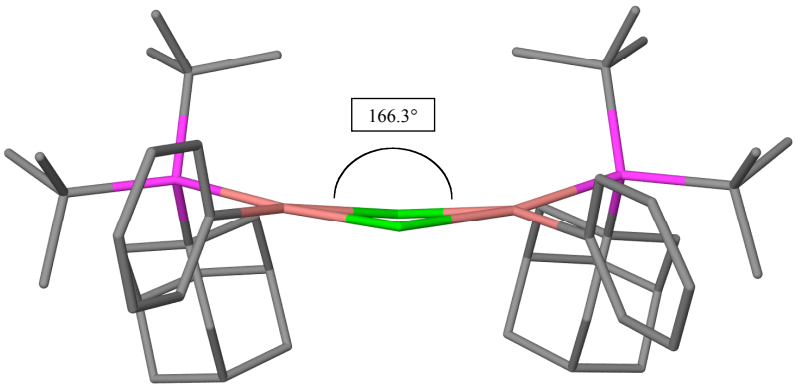

Table S6. Crystal data and structure refinement for $[(1\text{-AdP}^t\text{Bu}_2)\text{Pd(Ph)(Cl)}]_2$ (**11**).

Empirical formula	$C_{48}\ H_{76}\ Cl_2\ P_2\ Pd_2$	
Formula weight	998.73	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 15.251(3) Å	□= 90°.
	b = 14.575(3) Å	□= 90.64(3)°.
	c = 20.401(4) Å	□ = 90°.
Volume	4534.3(16) $Å^3$	
Z	4	
Density (calculated)	1.463 g/cm^3	
Absorption coefficient	10.14 cm^{-1}	
F(000)	2080	
Crystal size	0.20 x 0.08 x 0.08 mm^3	
Theta range for data collection	1.68 to 28.29°.	
Index ranges	-20<=h<=20, -19<=k<=19, -27<=l<=27	
Reflections collected	17957	
Independent reflections	11194 [R(int) = 0.0282]	
Completeness to theta = 28.29°	99.3 %	
Absorption correction	None	
Max. and min. transmission	0.9233 and 0.8229	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11194 / 0 / 487	
Goodness-of-fit on F^2	1.006	
Final R indices [I>2sigma(I)]	R1 = 0.0386, wR2 = 0.0954	
R indices (all data)	R1 = 0.0600, wR2 = 0.1042	
Largest diff. peak and hole	0.409 and -0.772 $e.Å^{-3}$	

Table S7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for [(1-AdP^{t}Bu$_2$)Pd(Ph)(Cl)]$_2$ (**11**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	59(1)	10049(1)	3337(1)	21(1)
Pd(2)	-1397(1)	7955(1)	3300(1)	19(1)
Cl(1)	-1300(1)	9467(1)	3775(1)	24(1)
Cl(2)	-129(1)	8615(1)	2686(1)	36(1)
P(1)	1428(1)	10607(1)	3012(1)	21(1)
P(2)	-1415(1)	6393(1)	3001(1)	19(1)
C(1)	1490(2)	10497(2)	2068(1)	23(1)
C(2)	598(2)	10827(2)	1785(2)	30(1)
C(3)	2240(2)	11029(2)	1731(2)	29(1)
C(4)	1602(2)	9485(2)	1861(1)	25(1)
C(5)	563(2)	10735(2)	1038(2)	35(1)
C(6)	1307(2)	11287(3)	732(2)	40(1)
C(7)	2190(2)	10919(3)	982(2)	37(1)
C(8)	2278(2)	9916(2)	795(2)	40(1)
C(9)	1543(2)	9372(2)	1109(2)	34(1)
C(10)	660(2)	9730(3)	859(2)	40(1)
C(11)	2280(2)	9811(2)	3423(2)	28(1)
C(12)	2402(2)	10094(2)	4147(2)	40(1)
C(13)	1912(2)	8828(2)	3431(2)	33(1)
C(14)	3186(2)	9792(2)	3101(2)	34(1)
C(15)	1777(2)	11855(2)	3207(2)	28(1)
C(16)	1595(2)	12156(2)	3913(2)	35(1)
C(17)	2768(2)	12008(2)	3102(2)	36(1)
C(18)	1241(2)	12534(2)	2776(2)	35(1)
C(19)	-161(2)	11112(2)	3917(1)	24(1)
C(20)	36(2)	11071(2)	4585(2)	29(1)
C(21)	-234(2)	11757(2)	5003(2)	35(1)
C(22)	-711(2)	12492(2)	4763(2)	43(1)
C(23)	-908(2)	12544(2)	4102(2)	39(1)
C(24)	-643(2)	11853(2)	3676(2)	29(1)

C(25)	-1244(2)	6347(2)	2065(1)	21(1)
C(26)	-1831(2)	7127(2)	1778(1)	24(1)
C(27)	-281(2)	6572(2)	1893(1)	25(1)
C(28)	-1471(2)	5433(2)	1718(1)	26(1)
C(29)	-1718(2)	7194(2)	1030(2)	29(1)
C(30)	-762(2)	7420(2)	887(2)	32(1)
C(31)	-173(2)	6647(2)	1144(2)	28(1)
C(32)	-420(2)	5748(2)	814(2)	33(1)
C(33)	-1366(2)	5522(2)	971(2)	29(1)
C(34)	-1969(2)	6279(2)	709(2)	33(1)
C(35)	-2421(2)	5625(2)	3184(2)	25(1)
C(36)	-2217(2)	4599(2)	3104(2)	37(1)
C(37)	-2777(2)	5746(2)	3886(2)	34(1)
C(38)	-3187(2)	5869(2)	2728(2)	29(1)
C(39)	-426(2)	5846(2)	3448(2)	28(1)
C(40)	332(2)	6543(2)	3457(2)	36(1)
C(41)	-660(2)	5680(3)	4168(2)	40(1)
C(42)	-86(2)	4943(2)	3156(2)	39(1)
C(43)	-2540(2)	7877(2)	3748(2)	25(1)
C(44)	-2579(2)	7828(2)	4431(2)	36(1)
C(45)	-3385(3)	7864(3)	4739(2)	50(1)
C(46)	-4145(3)	7975(2)	4381(2)	51(1)
C(47)	-4113(2)	8059(2)	3701(2)	43(1)
C(48)	-3303(2)	8014(2)	3385(2)	29(1)

Table S8. Bond lengths [Å] and angles [°] for [(1-AdP^tBu_2)Pd(Ph)(Cl)]$_2$ (**11**).

Pd(1)-C(19)	1.980(3)	C(21)-C(22)	1.382(5)
Pd(1)-P(1)	2.3436(9)	C(22)-C(23)	1.380(5)
Pd(1)-Cl(1)	2.4193(9)	C(23)-C(24)	1.393(4)
Pd(1)-Cl(2)	2.4922(9)	C(25)-C(28)	1.545(4)
Pd(2)-C(43)	1.979(3)	C(25)-C(27)	1.549(4)
Pd(2)-P(2)	2.3571(9)	C(25)-C(26)	1.557(4)
Pd(2)-Cl(1)	2.4110(8)	C(26)-C(29)	1.541(4)
Pd(2)-Cl(2)	2.5086(10)	C(27)-C(31)	1.541(4)
P(1)-C(11)	1.926(3)	C(28)-C(33)	1.540(4)
P(1)-C(1)	1.936(3)	C(29)-C(30)	1.527(4)
P(1)-C(15)	1.937(3)	C(29)-C(34)	1.532(4)
P(2)-C(39)	1.926(3)	C(30)-C(31)	1.530(5)
P(2)-C(25)	1.930(3)	C(31)-C(32)	1.519(4)
P(2)-C(35)	1.940(3)	C(32)-C(33)	1.518(4)
C(1)-C(4)	1.544(4)	C(33)-C(34)	1.529(4)
C(1)-C(3)	1.548(4)	C(35)-C(38)	1.528(4)
C(1)-C(2)	1.548(4)	C(35)-C(36)	1.536(4)
C(2)-C(5)	1.530(4)	C(35)-C(37)	1.546(4)
C(3)-C(7)	1.537(4)	C(39)-C(42)	1.537(4)
C(4)-C(9)	1.545(4)	C(39)-C(41)	1.534(4)
C(5)-C(10)	1.518(5)	C(39)-C(40)	1.539(4)
C(5)-C(6)	1.529(5)	C(43)-C(48)	1.387(4)
C(6)-C(7)	1.532(5)	C(43)-C(44)	1.396(4)
C(7)-C(8)	1.517(5)	C(44)-C(45)	1.387(5)
C(8)-C(9)	1.519(5)	C(45)-C(46)	1.373(6)
C(9)-C(10)	1.526(5)	C(46)-C(47)	1.393(6)
C(11)-C(13)	1.539(4)	C(47)-C(48)	1.403(4)
C(11)-C(14)	1.538(4)		
C(11)-C(12)	1.542(5)	C(19)-Pd(1)-P(1)	93.18(9)
C(15)-C(16)	1.534(4)	C(19)-Pd(1)-Cl(1)	84.39(8)
C(15)-C(17)	1.545(4)	P(1)-Pd(1)-Cl(1)	174.68(3)
C(15)-C(18)	1.550(4)	C(19)-Pd(1)-Cl(2)	162.88(8)
C(19)-C(24)	1.392(4)	P(1)-Pd(1)-Cl(2)	103.74(3)
C(19)-C(20)	1.393(4)	Cl(1)-Pd(1)-Cl(2)	78.96(3)
C(20)-C(21)	1.380(4)	C(43)-Pd(2)-P(2)	93.28(8)

C(43)-Pd(2)-Cl(1)	85.28(8)	C(8)-C(9)-C(4)	109.1(3)
P(2)-Pd(2)-Cl(1)	170.91(3)	C(10)-C(9)-C(4)	109.7(3)
C(43)-Pd(2)-Cl(2)	160.06(9)	C(5)-C(10)-C(9)	109.7(3)
P(2)-Pd(2)-Cl(2)	104.30(3)	C(13)-C(11)-C(14)	108.5(3)
Cl(1)-Pd(2)-Cl(2)	78.80(3)	C(13)-C(11)-C(12)	106.2(3)
Pd(2)-Cl(1)-Pd(1)	102.81(3)	C(14)-C(11)-C(12)	108.3(3)
Pd(1)-Cl(2)-Pd(2)	98.04(3)	C(13)-C(11)-P(1)	108.7(2)
C(11)-P(1)-C(1)	110.11(14)	C(14)-C(11)-P(1)	115.4(2)
C(11)-P(1)-C(15)	107.05(14)	C(12)-C(11)-P(1)	109.3(2)
C(1)-P(1)-C(15)	105.41(13)	C(16)-C(15)-C(17)	106.1(3)
C(11)-P(1)-Pd(1)	105.47(10)	C(16)-C(15)-C(18)	104.5(3)
C(1)-P(1)-Pd(1)	107.86(9)	C(17)-C(15)-C(18)	109.9(3)
C(15)-P(1)-Pd(1)	120.75(10)	C(16)-C(15)-P(1)	114.2(2)
C(39)-P(2)-C(25)	109.91(13)	C(17)-C(15)-P(1)	112.0(2)
C(39)-P(2)-C(35)	106.66(14)	C(18)-C(15)-P(1)	109.9(2)
C(25)-P(2)-C(35)	106.67(13)	C(24)-C(19)-C(20)	119.0(3)
C(39)-P(2)-Pd(2)	105.67(10)	C(24)-C(19)-Pd(1)	119.2(2)
C(25)-P(2)-Pd(2)	106.79(9)	C(20)-C(19)-Pd(1)	121.0(2)
C(35)-P(2)-Pd(2)	120.91(10)	C(21)-C(20)-C(19)	120.8(3)
C(4)-C(1)-C(3)	105.8(2)	C(20)-C(21)-C(22)	120.1(3)
C(4)-C(1)-C(2)	107.1(2)	C(23)-C(22)-C(21)	119.8(3)
C(3)-C(1)-C(2)	109.3(2)	C(22)-C(23)-C(24)	120.6(3)
C(4)-C(1)-P(1)	110.93(19)	C(19)-C(24)-C(23)	119.8(3)
C(3)-C(1)-P(1)	116.4(2)	C(28)-C(25)-C(27)	106.6(2)
C(2)-C(1)-P(1)	107.0(2)	C(28)-C(25)-C(26)	109.4(2)
C(5)-C(2)-C(1)	111.4(3)	C(27)-C(25)-C(26)	107.6(2)
C(7)-C(3)-C(1)	111.1(3)	C(28)-C(25)-P(2)	116.8(2)
C(1)-C(4)-C(9)	111.6(2)	C(27)-C(25)-P(2)	110.87(19)
C(10)-C(5)-C(6)	109.5(3)	C(26)-C(25)-P(2)	105.25(19)
C(10)-C(5)-C(2)	108.8(3)	C(29)-C(26)-C(25)	110.4(2)
C(6)-C(5)-C(2)	110.0(3)	C(31)-C(27)-C(25)	110.7(2)
C(5)-C(6)-C(7)	109.5(3)	C(33)-C(28)-C(25)	110.8(2)
C(8)-C(7)-C(6)	109.5(3)	C(30)-C(29)-C(34)	109.9(3)
C(8)-C(7)-C(3)	110.3(3)	C(30)-C(29)-C(26)	108.7(2)
C(6)-C(7)-C(3)	109.1(3)	C(34)-C(29)-C(26)	109.7(2)
C(7)-C(8)-C(9)	109.2(3)	C(29)-C(30)-C(31)	109.6(3)
C(8)-C(9)-C(10)	109.5(3)	C(32)-C(31)-C(30)	110.0(3)

C(32)-C(31)-C(27)	110.4(3)	C(42)-C(39)-C(40)	108.3(3)
C(30)-C(31)-C(27)	108.8(2)	C(41)-C(39)-C(40)	106.0(3)
C(31)-C(32)-C(33)	109.0(3)	C(42)-C(39)-P(2)	115.9(2)
C(32)-C(33)-C(34)	109.8(3)	C(41)-C(39)-P(2)	109.2(2)
C(32)-C(33)-C(28)	109.6(3)	C(40)-C(39)-P(2)	108.4(2)
C(34)-C(33)-C(28)	109.7(2)	C(48)-C(43)-C(44)	119.7(3)
C(33)-C(34)-C(29)	109.5(2)	C(48)-C(43)-Pd(2)	118.9(2)
C(38)-C(35)-C(36)	108.4(2)	C(44)-C(43)-Pd(2)	120.7(2)
C(38)-C(35)-C(37)	105.3(2)	C(45)-C(44)-C(43)	119.8(4)
C(36)-C(35)-C(37)	106.5(2)	C(46)-C(45)-C(44)	120.7(4)
C(38)-C(35)-P(2)	110.4(2)	C(45)-C(46)-C(47)	120.0(3)
C(36)-C(35)-P(2)	112.3(2)	C(46)-C(47)-C(48)	119.7(4)
C(37)-C(35)-P(2)	113.5(2)	C(43)-C(48)-C(47)	
C(42)-C(39)-C(41)	108.6(3)		
120.0(3)			

Table S9. Anisotropic displacement parameters ($Å^2 x\ 10^3$) [(1-AdP^{t}Bu$_2$)Pd(Ph)(Cl)]$_2$ (**11**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	21(1)	18(1)	23(1)	-2(1)	1(1)	-3(1)
Pd(2)	19(1)	19(1)	20(1)	-2(1)	2(1)	-3(1)
Cl(1)	23(1)	20(1)	30(1)	-4(1)	4(1)	-2(1)
Cl(2)	35(1)	31(1)	41(1)	-15(1)	18(1)	-15(1)
P(1)	20(1)	20(1)	23(1)	1(1)	-1(1)	-2(1)
P(2)	19(1)	18(1)	20(1)	-1(1)	1(1)	0(1)
C(1)	23(1)	23(2)	22(2)	2(1)	-1(1)	-2(1)
C(2)	27(2)	30(2)	32(2)	5(1)	-3(1)	0(1)
C(3)	26(2)	33(2)	30(2)	6(1)	3(1)	-3(1)
C(4)	24(2)	28(2)	25(2)	2(1)	2(1)	1(1)
C(5)	30(2)	44(2)	30(2)	5(2)	-8(1)	2(2)
C(6)	45(2)	48(2)	28(2)	13(2)	0(2)	2(2)
C(7)	35(2)	47(2)	29(2)	11(2)	4(1)	-8(2)
C(8)	42(2)	55(2)	22(2)	2(2)	6(1)	5(2)
C(9)	38(2)	37(2)	26(2)	-4(1)	-2(1)	2(2)
C(10)	48(2)	47(2)	24(2)	-1(2)	-7(2)	-5(2)
C(11)	25(2)	30(2)	30(2)	5(1)	-4(1)	4(1)
C(12)	47(2)	45(2)	27(2)	1(2)	-8(2)	9(2)
C(13)	35(2)	28(2)	35(2)	9(1)	1(1)	4(1)
C(14)	25(2)	36(2)	41(2)	0(2)	-5(1)	7(1)
C(15)	27(2)	24(2)	33(2)	-2(1)	2(1)	-7(1)
C(16)	33(2)	31(2)	42(2)	-9(2)	-2(1)	-10(1)
C(17)	32(2)	35(2)	40(2)	-1(2)	1(1)	-16(1)
C(18)	40(2)	19(2)	47(2)	1(1)	2(2)	-3(1)
C(19)	24(2)	20(1)	27(2)	-2(1)	2(1)	-5(1)
C(20)	36(2)	26(2)	25(2)	4(1)	2(1)	-1(1)
C(21)	43(2)	35(2)	27(2)	-7(1)	1(1)	-6(2)
C(22)	46(2)	35(2)	49(2)	-16(2)	9(2)	-1(2)
C(23)	33(2)	23(2)	59(2)	-6(2)	-5(2)	5(1)
C(24)	25(2)	25(2)	37(2)	-1(1)	-2(1)	-2(1)
C(25)	22(1)	21(1)	21(2)	-2(1)	1(1)	0(1)

C(26)	25(2)	22(2)	25(2)	-3(1)	2(1)	2(1)
C(27)	26(2)	26(2)	22(2)	-3(1)	3(1)	0(1)
C(28)	29(2)	19(2)	29(2)	-2(1)	1(1)	-1(1)
C(29)	34(2)	27(2)	26(2)	3(1)	-4(1)	3(1)
C(30)	43(2)	31(2)	23(2)	1(1)	8(1)	-5(2)
C(31)	28(2)	32(2)	25(2)	1(1)	9(1)	-2(1)
C(32)	41(2)	32(2)	25(2)	-6(1)	6(1)	4(2)
C(33)	36(2)	26(2)	24(2)	-8(1)	0(1)	-3(1)
C(34)	39(2)	35(2)	23(2)	-6(1)	-4(1)	0(2)
C(35)	26(2)	23(2)	27(2)	0(1)	6(1)	-7(1)
C(36)	45(2)	22(2)	44(2)	1(2)	7(2)	-3(2)
C(37)	38(2)	30(2)	35(2)	6(1)	11(1)	-7(1)
C(38)	19(1)	33(2)	35(2)	-10(1)	3(1)	-7(1)
C(39)	27(2)	32(2)	25(2)	2(1)	-4(1)	6(1)
C(40)	23(2)	53(2)	31(2)	-5(2)	-7(1)	5(2)
C(41)	40(2)	51(2)	28(2)	6(2)	-3(2)	8(2)
C(42)	37(2)	40(2)	41(2)	6(2)	2(2)	15(2)
C(43)	24(2)	20(2)	30(2)	-3(1)	9(1)	-5(1)
C(44)	41(2)	38(2)	28(2)	-5(1)	11(1)	-11(2)
C(45)	62(3)	44(2)	44(2)	-16(2)	31(2)	-20(2)
C(46)	42(2)	36(2)	77(3)	-16(2)	39(2)	-11(2)
C(47)	28(2)	25(2)	77(3)	-5(2)	9(2)	-4(1)
C(48)	25(2)	19(2)	42(2)	1(1)	5(1)	0(1)

Table S10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for [(1-AdP^{t}Bu$_2$)Pd(Ph)(Cl)]$_2$ (**11**).

	x	y	z	U(eq)
H(2A)	121	10459	1978	36
H(2B)	505	11477	1908	36
H(3A)	2199	11688	1845	35
H(3B)	2812	10797	1894	35
H(4A)	1141	9110	2068	31
H(4B)	2178	9258	2019	31
H(5A)	-13	10969	870	42
H(6A)	1248	11943	851	48
H(6B)	1275	11236	249	48
H(7A)	2675	11277	778	45
H(8A)	2853	9677	948	47
H(8B)	2245	9850	312	47
H(9A)	1603	8709	992	41
H(10A)	622	9658	376	48
H(10B)	180	9371	1056	48
H(12A)	2835	9691	4357	59
H(12B)	1841	10041	4373	59
H(12C)	2608	10731	4169	59
H(13A)	2337	8418	3644	49
H(13B)	1804	8622	2980	49
H(13C)	1361	8818	3673	49
H(14A)	3575	9379	3347	50
H(14B)	3435	10412	3102	50
H(14C)	3126	9574	2649	50
H(16A)	1787	12792	3975	53
H(16B)	1916	11757	4219	53
H(16C)	965	12112	3997	53
H(17A)	2919	12645	3209	54
H(17B)	2911	11884	2643	54
H(17C)	3104	11593	3387	54
H(18A)	1418	13164	2881	53
H(18B)	615	12458	2864	53

H(18C)	1352	12410	2313	53
H(20A)	359	10566	4754	35
H(21A)	-92	11723	5457	42
H(22A)	-902	12961	5052	52
H(23A)	-1227	13055	3936	46
H(24A)	-791	11887	3223	35
H(26A)	-2453	7002	1879	29
H(26B)	-1667	7719	1984	29
H(27A)	-108	7158	2102	29
H(27B)	109	6083	2066	29
H(28A)	-1079	4943	1886	31
H(28B)	-2082	5259	1818	31
H(29A)	-2104	7692	852	35
H(30A)	-598	8005	1102	39
H(30B)	-682	7492	409	39
H(31A)	452	6795	1045	34
H(32A)	-31	5250	975	39
H(32B)	-349	5802	334	39
H(33A)	-1529	4927	758	34
H(34A)	-2586	6129	809	39
H(34B)	-1912	6327	228	39
H(36A)	-2741	4238	3205	55
H(36B)	-1739	4426	3404	55
H(36C)	-2041	4478	2651	55
H(37A)	-3282	5341	3947	51
H(37B)	-2957	6385	3949	51
H(37C)	-2316	5589	4205	51
H(38A)	-3691	5479	2829	43
H(38B)	-3015	5770	2272	43
H(38C)	-3346	6514	2790	43
H(40A)	843	6273	3680	53
H(40B)	150	7097	3692	53
H(40C)	485	6704	3006	53
H(41A)	-157	5406	4398	60
H(41B)	-1163	5264	4190	60
H(41C)	-809	6266	4375	60
H(42A)	421	4729	3412	59

H(42B)	88	5045	2701	59
H(42C)	-551	4479	3168	59
H(44A)	-2055	7770	4684	43
H(45A)	-3410	7812	5202	60
H(46A)	-4694	7993	4597	62
H(47A)	-4638	8146	3453	52
H(48A)	-3276	8077	2922	35

X ray crystallographic data for $[(CyP^tBu_2)Pd(Ph)(Br)]_2$ (15)

Data Collection

A pale yellow block crystal of $C_{40}H_{68}Br_2P_2Pd_2$ having approximate dimensions of 0.25 x 0.2 x 0.2 mm was mounted on a glass fiber. All measurements were made on a Nonius KappaCCD diffractometer with graphite monochromated Mo-Kα radiation.

Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions:

a = 14.549(3) Å $\alpha = 90^o$

b = 14.689(3) Å $\beta = 97.19(3)^o$

c = 20.017(4) Å $\gamma = 90^o$

V = 4244.3(15) $Å^3$

For Z = 4 and F.W. = 983.5, the calculated density is 1.539 g/cm^3. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be: $P2_1/c$ (#14)

The data were collected at a temperature of 296(2)K to a maximum 2θ value of 55.94^o. Three omega scans consisting of 68, 68, and 49 data frames, respectively, were collected with a frame width of 1.5° and a detector-to-crystal distance, Dx, of 35 mm. Each frame was exposed twice (for the purpose of de-zingering) for 20s. The data frames were processed and scaled using the DENZO software package.[3]

Data Reduction

A total of 18273 reflections were collected of which 10077 were unique and observed (R_{int} = 0.0610). The linear absorption coefficient, μ, for Mo-Kα radiation is 28.31 cm^{-1} and no absorption correction was applied. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods and expanded using Fourier techniques[4]. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined isotropically. The final cycle of full-matrix least-squares refinement[5] on F was based on 10077 observed reflections ($I > 2.00\sigma(I)$) and 415 variable parameters and converged with unweighted and weighted agreement factors of:

$$R = \Sigma \, ||Fo| - |Fc|| \, / \, \Sigma \, |Fo| = 0.0419$$

$$R_W = [\Sigma \, w \, (|Fo| - |Fc|)^2 \, / \, \Sigma \, w \, Fo^2]^{1/2} = 0.0827$$

The maximum and minimum peaks on the final difference Fourier map corresponded to 0.459 and -0.561 $e^-/Å^3$, respectively.

Structural Description

The compound crystallized in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit and four in the unit cell. The geometry about the palladium atoms is square planar with acute Br-Pd-Br angles measured at 82.787(18) and 82.526(18)˚. The planes defined by Pd(1), C(1), P(1), Br(1), Br(2) and Pd(2), C(21), P(2), Br(1), Br(2) have mean deviations of 0.0578 and 0.0820Å respectively and are offset by 20.7˚ (see Figure 4).

Most interesting is the presence of a pseudo-mirror plane with the phosphine ligands in a "*cis*-like" arrangement. The Pd-Br bond lengths are asymmetric with Br(1) possessing lengths ~0.1Å longer than Br(2) which is certainly a direct effect of the pseudo-mirror plane and the steric bulk imparted by the phosphine ligands. A search of the Cambridge Crystallographic Database (v. 5.23, April 2002) yielded only three examples $[(PR_x)(R)Pd(\mu\text{-}X)]_2$ with a similar "cis-like" arrangement. Two of the examples involve bulky P-C-chelating ligands while the third is a fragment of a more complicated tetramer.

Figure S8

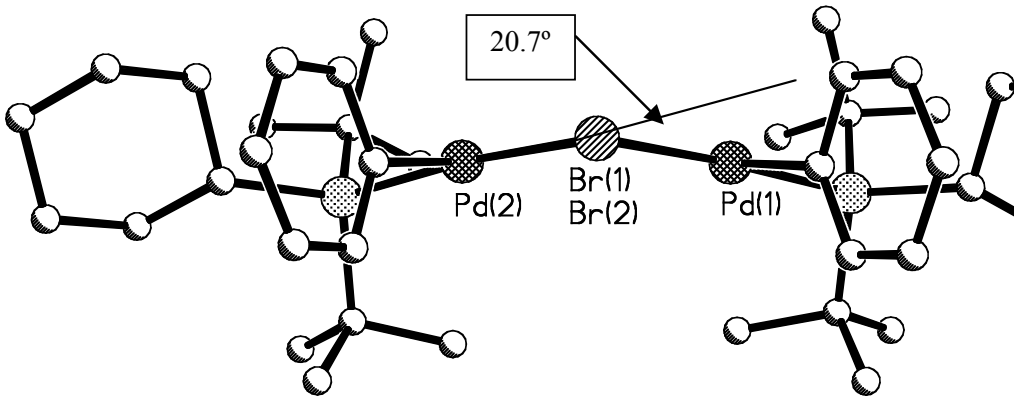

Table S11. Crystal data and structure refinement for $[(CyP^tBu_2)Pd(Ph)(Br)]_2$ (**15**).

Empirical formula	$C_{40}\ H_{68}\ Br_2\ P_2\ Pd_2$	
Formula weight	983.50	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 14.549(3) Å	□= 90°.
	b = 14.689(3) Å	□= 97.19(3)°.
	c = 20.017(4) Å	□ = 90°.
Volume	4244.3(15) $Å^3$	
Z	4	
Density (calculated)	1.539 g/cm^3	
Absorption coefficient	28.31 mm^{-1}	
F(000)	2000	
Crystal size	0.25 x 0.20 x 0.20 mm^3	
Theta range for data collection	2.31 to 27.97°.	
Index ranges	-19<=h<=19, -17<=k<=19, -26<=l<=26	
Reflections collected	18273	
Independent reflections	10077 [R(int) = 0.0610]	
Completeness to theta = 27.97°	98.4 %	
Absorption correction	None	
Max. and min. transmission	0.6013 and 0.5379	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10077 / 0 / 415	
Goodness-of-fit on F^2	0.914	
Final R indices [I>2sigma(I)]	R1 = 0.0419, wR2 = 0.0677	
R indices (all data)	R1 = 0.1119, wR2 = 0.0827	
Largest diff. peak and hole	0.459 and -0.561 $e.Å^{-3}$	

Table S12. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for [(CyP^{t}Bu$_2$)Pd(Ph)(Br)]$_2$ (**15**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	2851(1)	9501(1)	2515(1)	35(1)
Pd(2)	1891(1)	11689(1)	3139(1)	34(1)
Br(1)	1875(1)	9968(1)	3459(1)	51(1)
Br(2)	2439(1)	11073(1)	2090(1)	54(1)
P(2)	1531(1)	12370(1)	4124(1)	33(1)
P(1)	3358(1)	8061(1)	2884(1)	33(1)
C(1)	3437(3)	9404(2)	1667(2)	37(1)
C(2)	2867(3)	9271(3)	1068(2)	48(1)
C(3)	3223(4)	9265(3)	463(2)	60(1)
C(4)	4151(4)	9407(3)	435(2)	67(2)
C(5)	4716(4)	9566(3)	1025(2)	62(1)
C(6)	4370(3)	9572(3)	1636(2)	47(1)
C(7)	3860(3)	7407(3)	2215(2)	41(1)
C(8)	3136(3)	7140(3)	1620(2)	49(1)
C(9)	3603(4)	6879(3)	1008(2)	71(2)
C(10)	4290(4)	6114(3)	1170(2)	75(2)
C(11)	4995(4)	6351(3)	1769(2)	67(1)
C(12)	4522(3)	6602(3)	2378(2)	50(1)
C(13)	2397(3)	7344(3)	3175(2)	42(1)
C(14)	1517(3)	7529(3)	2685(2)	61(1)
C(15)	2605(3)	6320(3)	3173(2)	58(1)
C(16)	2176(3)	7601(3)	3883(2)	59(1)
C(17)	4330(3)	8199(3)	3599(2)	46(1)
C(18)	4082(3)	8955(3)	4079(2)	58(1)
C(19)	5188(3)	8539(3)	3297(2)	59(1)
C(20)	4577(3)	7328(3)	4011(2)	63(1)
C(21)	1893(3)	12876(2)	2651(2)	34(1)
C(22)	1130(3)	13101(3)	2199(2)	44(1)
C(23)	1118(4)	13862(3)	1799(2)	57(1)
C(24)	1887(4)	14413(3)	1826(2)	62(1)
C(25)	2663(4)	14187(3)	2247(2)	56(1)

C(26)	2670(3)	13424(3)	2654(2)	44(1)
C(27)	1110(3)	13568(2)	3986(2)	36(1)
C(28)	173(3)	13633(3)	3544(2)	46(1)
C(29)	7(3)	14595(3)	3280(2)	60(1)
C(30)	25(4)	15273(3)	3858(2)	62(1)
C(31)	914(3)	15189(3)	4334(2)	52(1)
C(32)	1110(3)	14232(3)	4586(2)	45(1)
C(33)	617(3)	11712(3)	4523(2)	41(1)
C(34)	1040(3)	10871(3)	4906(2)	54(1)
C(35)	-116(3)	11386(3)	3958(2)	57(1)
C(36)	136(3)	12286(3)	5030(2)	61(1)
C(37)	2644(3)	12436(3)	4727(2)	43(1)
C(38)	3239(3)	13193(3)	4469(2)	57(1)
C(39)	2531(3)	12637(3)	5471(2)	55(1)
C(40)	3185(3)	11547(3)	4687(2)	59(1)

Table S13. Bond lengths [Å] and angles [°] for $[(CyP^tBu_2)Pd(Ph)(Br)]_2$ (**15**).

Pd(1)-C(1)	1.998(4)	C(23)-C(24)	1.377(6)
Pd(1)-P(1)	2.3306(11)	C(24)-C(25)	1.362(6)
Pd(1)-Br(2)	2.5067(6)	C(25)-C(26)	1.387(5)
Pd(1)-Br(1)	2.5939(8)	C(27)-C(28)	1.533(5)
Pd(2)-C(21)	1.999(4)	C(27)-C(32)	1.548(5)
Pd(2)-P(2)	2.3286(11)	C(28)-C(29)	1.517(5)
Pd(2)-Br(2)	2.5052(7)	C(29)-C(30)	1.525(5)
Pd(2)-Br(1)	2.6082(7)	C(30)-C(31)	1.511(6)
P(2)-C(27)	1.872(4)	C(31)-C(32)	1.509(5)
P(2)-C(37)	1.897(4)	C(33)-C(35)	1.532(5)
P(2)-C(33)	1.900(4)	C(33)-C(34)	1.541(5)
P(1)-C(7)	1.870(4)	C(33)-C(36)	1.552(5)
P(1)-C(17)	1.893(4)	C(37)-C(40)	1.532(5)
P(1)-C(13)	1.899(4)	C(37)-C(38)	1.537(5)
C(1)-C(2)	1.385(5)	C(37)-C(39)	1.548(5)
C(1)-C(6)	1.389(6)		
C(2)-C(3)	1.376(5)	C(1)-Pd(1)-P(1)	92.96(11)
C(3)-C(4)	1.374(7)	C(1)-Pd(1)-Br(2)	83.53(10)
C(4)-C(5)	1.371(6)	P(1)-Pd(1)-Br(2)	175.15(3)
C(5)-C(6)	1.380(5)	C(1)-Pd(1)-Br(1)	165.65(11)
C(7)-C(12)	1.535(5)	P(1)-Pd(1)-Br(1)	100.94(3)
C(7)-C(8)	1.539(5)	Br(2)-Pd(1)-Br(1)	82.787(18)
C(8)-C(9)	1.523(5)	C(21)-Pd(2)-P(2)	93.01(10)
C(9)-C(10)	1.511(6)	C(21)-Pd(2)-Br(2)	83.45(10)
C(10)-C(11)	1.518(7)	P(2)-Pd(2)-Br(2)	173.39(3)
C(11)-C(12)	1.520(6)	C(21)-Pd(2)-Br(1)	165.06(10)
C(13)-C(15)	1.534(5)	P(2)-Pd(2)-Br(1)	101.44(3)
C(13)-C(14)	1.537(6)	Br(2)-Pd(2)-Br(1)	82.526(18)
C(13)-C(16)	1.539(5)	Pd(1)-Br(1)-Pd(2)	93.111(18)
C(17)-C(19)	1.537(6)	Pd(2)-Br(2)-Pd(1)	97.807(19)
C(17)-C(18)	1.540(5)	C(27)-P(2)-C(37)	106.48(18)
C(17)-C(20)	1.540(5)	C(27)-P(2)-C(33)	107.85(18)
C(21)-C(22)	1.381(5)	C(37)-P(2)-C(33)	110.14(18)
C(21)-C(26)	1.387(5)	C(27)-P(2)-Pd(2)	112.55(11)
C(22)-C(23)	1.374(5)	C(37)-P(2)-Pd(2)	107.25(13)

C(33)-P(2)-Pd(2)	112.42(12)	C(26)-C(21)-Pd(2)	123.6(3)
C(7)-P(1)-C(17)	106.01(19)	C(23)-C(22)-C(21)	121.8(4)
C(7)-P(1)-C(13)	107.70(18)	C(22)-C(23)-C(24)	120.2(5)
C(17)-P(1)-C(13)	109.64(18)	C(25)-C(24)-C(23)	119.2(4)
C(7)-P(1)-Pd(1)	112.10(13)	C(24)-C(25)-C(26)	120.4(5)
C(17)-P(1)-Pd(1)	108.59(13)	C(25)-C(26)-C(21)	121.3(4)
C(13)-P(1)-Pd(1)	112.58(13)	C(28)-C(27)-C(32)	108.8(3)
C(2)-C(1)-C(6)	118.0(4)	C(28)-C(27)-P(2)	113.3(3)
C(2)-C(1)-Pd(1)	118.2(3)	C(32)-C(27)-P(2)	120.6(3)
C(6)-C(1)-Pd(1)	123.3(3)	C(29)-C(28)-C(27)	110.5(4)
C(3)-C(2)-C(1)	120.9(4)	C(28)-C(29)-C(30)	111.0(3)
C(4)-C(3)-C(2)	120.9(4)	C(31)-C(30)-C(29)	110.9(4)
C(5)-C(4)-C(3)	118.6(4)	C(32)-C(31)-C(30)	113.4(4)
C(4)-C(5)-C(6)	121.2(5)	C(31)-C(32)-C(27)	110.2(3)
C(5)-C(6)-C(1)	120.4(4)	C(35)-C(33)-C(34)	108.3(3)
C(12)-C(7)-C(8)	108.7(3)	C(35)-C(33)-C(36)	108.9(4)
C(12)-C(7)-P(1)	122.3(3)	C(34)-C(33)-C(36)	107.2(3)
C(8)-C(7)-P(1)	113.2(3)	C(35)-C(33)-P(2)	107.9(3)
C(9)-C(8)-C(7)	110.8(4)	C(34)-C(33)-P(2)	111.1(3)
C(10)-C(9)-C(8)	111.4(4)	C(36)-C(33)-P(2)	113.3(3)
C(9)-C(10)-C(11)	111.2(4)	C(40)-C(37)-C(38)	106.5(3)
C(10)-C(11)-C(12)	111.1(4)	C(40)-C(37)-C(39)	109.2(3)
C(11)-C(12)-C(7)	110.5(3)	C(38)-C(37)-C(39)	108.5(3)
C(15)-C(13)-C(14)	108.7(3)	C(40)-C(37)-P(2)	109.1(3)
C(15)-C(13)-C(16)	107.9(3)	C(38)-C(37)-P(2)	107.2(3)
C(14)-C(13)-C(16)	106.9(4)	C(39)-C(37)-P(2)	116.0(3)
C(15)-C(13)-P(1)	112.9(3)		
C(14)-C(13)-P(1)	107.1(3)		
C(16)-C(13)-P(1)	113.2(3)		
C(19)-C(17)-C(18)	106.0(3)		
C(19)-C(17)-C(20)	109.5(4)		
C(18)-C(17)-C(20)	108.9(3)		
C(19)-C(17)-P(1)	107.6(3)		
C(18)-C(17)-P(1)	109.8(3)		
C(20)-C(17)-P(1)	114.6(3)		
C(22)-C(21)-C(26)	116.9(4)		
C(22)-C(21)-Pd(2)	118.6(3)		

Table S14. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $[(CyP^tBu_2)Pd(Ph)(Br)]_2$ (**15**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	47(1)	30(1)	29(1)	0(1)	8(1)	2(1)
Pd(2)	42(1)	30(1)	30(1)	-1(1)	8(1)	0(1)
Br(1)	79(1)	35(1)	43(1)	2(1)	25(1)	5(1)
Br(2)	93(1)	34(1)	38(1)	4(1)	25(1)	15(1)
P(2)	36(1)	36(1)	29(1)	-3(1)	7(1)	-3(1)
P(1)	37(1)	31(1)	31(1)	3(1)	5(1)	-1(1)
C(1)	55(3)	25(2)	33(2)	0(2)	13(2)	8(2)
C(2)	62(3)	43(3)	39(3)	0(2)	7(2)	8(2)
C(3)	97(4)	50(3)	34(3)	1(2)	10(3)	15(3)
C(4)	112(5)	52(3)	44(3)	6(2)	38(3)	7(3)
C(5)	71(4)	56(3)	66(3)	9(3)	30(3)	-2(3)
C(6)	64(3)	39(3)	41(2)	3(2)	20(2)	-2(2)
C(7)	48(3)	37(3)	41(2)	4(2)	9(2)	2(2)
C(8)	68(3)	34(3)	46(3)	1(2)	11(2)	5(2)
C(9)	108(5)	57(3)	49(3)	0(2)	12(3)	18(3)
C(10)	114(5)	53(3)	68(3)	-1(3)	42(3)	25(3)
C(11)	79(4)	50(3)	78(4)	2(3)	28(3)	17(3)
C(12)	56(3)	36(3)	58(3)	4(2)	12(2)	11(2)
C(13)	48(3)	32(2)	49(3)	2(2)	14(2)	-5(2)
C(14)	42(3)	65(3)	76(3)	-3(3)	4(3)	-11(3)
C(15)	68(4)	35(3)	73(3)	2(2)	22(3)	-12(3)
C(16)	75(4)	43(3)	64(3)	2(2)	30(3)	-6(3)
C(17)	47(3)	45(3)	45(2)	4(2)	-3(2)	-7(2)
C(18)	70(4)	62(3)	39(2)	-1(2)	-5(2)	-12(3)
C(19)	46(3)	64(3)	65(3)	6(2)	-3(2)	-12(3)
C(20)	69(4)	62(3)	55(3)	18(2)	-12(2)	0(3)
C(21)	45(3)	29(2)	30(2)	-4(2)	11(2)	6(2)
C(22)	53(3)	45(3)	34(2)	0(2)	9(2)	1(2)
C(23)	68(4)	63(3)	40(3)	7(2)	8(2)	22(3)
C(24)	97(5)	37(3)	55(3)	11(2)	24(3)	21(3)
C(25)	74(4)	36(3)	63(3)	-3(2)	28(3)	-5(3)

C(26)	48(3)	41(3)	46(3)	-1(2)	14(2)	3(2)
C(27)	39(3)	37(2)	35(2)	-6(2)	16(2)	-3(2)
C(28)	47(3)	48(3)	43(2)	-12(2)	2(2)	7(2)
C(29)	72(4)	57(3)	49(3)	-1(2)	3(2)	14(3)
C(30)	92(4)	41(3)	53(3)	1(2)	13(3)	13(3)
C(31)	68(3)	43(3)	50(3)	-15(2)	24(3)	2(2)
C(32)	55(3)	44(3)	39(2)	-10(2)	16(2)	-1(2)
C(33)	46(3)	41(3)	39(2)	-3(2)	17(2)	-9(2)
C(34)	66(3)	48(3)	50(3)	7(2)	16(2)	-7(3)
C(35)	48(3)	58(3)	66(3)	-3(2)	7(2)	-18(3)
C(36)	66(4)	62(3)	62(3)	-2(2)	36(3)	-7(3)
C(37)	37(3)	55(3)	37(2)	-6(2)	0(2)	-1(2)
C(38)	40(3)	75(4)	53(3)	-9(2)	-1(2)	-10(3)
C(39)	62(3)	67(3)	33(2)	-7(2)	-6(2)	-3(3)
C(40)	46(3)	67(3)	60(3)	-4(2)	-4(2)	7(3)

Table S15. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for [(CyP^{t}Bu$_2$)Pd(Ph)(Br)]$_2$ (**15**).

	x	y	z	U(eq)
H(2A)	2234	9186	1074	57
H(3A)	2830	9162	66	72
H(4A)	4390	9396	26	80
H(5A)	5344	9672	1012	75
H(6A)	4765	9688	2029	56
H(7A)	4245	7858	2019	50
H(8A)	2772	6631	1749	59
H(8B)	2719	7648	1506	59
H(9A)	3136	6691	646	85
H(9B)	3922	7405	856	85
H(10A)	4607	5994	781	90
H(10B)	3961	5565	1269	90
H(11A)	5371	6858	1652	81
H(11B)	5401	5834	1878	81
H(12A)	4987	6763	2751	60
H(12B)	4179	6082	2514	60
H(14A)	1014	7176	2816	92
H(14B)	1622	7361	2237	92
H(14C)	1365	8164	2695	92
H(15A)	2100	5992	3325	87
H(15B)	3163	6198	3468	87
H(15C)	2682	6131	2724	87
H(16A)	1689	7217	4004	89
H(16B)	1982	8225	3885	89
H(16C)	2720	7521	4202	89
H(18A)	4577	9024	4441	87
H(18B)	3522	8795	4259	87
H(18C)	3992	9518	3836	87
H(19A)	5694	8613	3649	89
H(19B)	5051	9114	3078	89
H(19C)	5354	8104	2975	89
H(20A)	5075	7453	4360	95

H(20B)	4763	6862	3720	95
H(20C)	4045	7125	4209	95
H(22A)	611	12727	2164	52
H(23A)	587	14006	1508	69
H(24A)	1877	14934	1561	74
H(25A)	3190	14547	2260	68
H(26A)	3207	13276	2936	53
H(27A)	1548	13841	3709	43
H(28A)	162	13214	3168	56
H(28B)	-318	13461	3805	56
H(29A)	-589	14625	3003	72
H(29B)	482	14755	3001	72
H(30A)	-30	15887	3679	74
H(30B)	-499	15162	4103	74
H(31A)	1425	15395	4105	63
H(31B)	879	15587	4716	63
H(32A)	642	14047	4863	54
H(32B)	1708	14213	4861	54
H(34A)	565	10551	5103	80
H(34B)	1515	11062	5254	80
H(34C)	1304	10476	4599	80
H(35A)	-587	11051	4148	86
H(35B)	170	11000	3656	86
H(35C)	-390	11902	3716	86
H(36A)	-316	11919	5215	92
H(36B)	-164	12801	4802	92
H(36C)	590	12493	5387	92
H(38A)	3809	13247	4765	85
H(38B)	2909	13759	4458	85
H(38C)	3372	13043	4024	85
H(39A)	3131	12660	5733	83
H(39B)	2169	12164	5642	83
H(39C)	2224	13211	5501	83
H(40A)	3749	11576	4991	88
H(40B)	3328	11462	4236	88
H(40C)	2816	11046	4809	88

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5. Least Squares function minimized:
   $\Sigma w(F_o^2 - F_c^2)^2$