Supporting Information for:

Detailed Study of C–O and C–C Bond-Forming Reductive Elimination from Stable $C_2N_2O_2$-Ligated Pd(IV) Complexes

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General Procedures

NMR spectra were obtained on a Varian Inova 500 (499.90 MHz for ^{1}H; 125.70 MHz for ^{13}C), a Varian Inova 400 (399.96 for ^{1}H), or a Varian MR 400 (399.54 for ^{1}H; 61.484 for ^{2}H). Kinetics data were obtained on a Bruker AMX 500 (500.14 MHz for ^{1}H) spectrometer or on Varian Inova 500 or MR 400 instruments. ^{1}H NMR chemical shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak used as an internal reference. ^{19}F NMR spectra were referenced using the residual solvent peak in the ^{1}H NMR spectrum. ^{13}C NMR spectra were obtained on a Varian MR 400 (100.460) instrument and the chemical shifts are reported in parts per million (ppm) relative to TMS. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), doublet of doublet of doublets (ddd), doublet of triplets (dt), triplet (t), triplet of doublets (td), triplet of triplets (tt), multiplet (m), and broad band resonance (br). IR spectra were obtained on a Perkin-Elmer spectrum BX FT-IR spectrometer. Mass spectral data were obtained on a Micromass magnetic sector mass spectrometer or on a Micromass LCT mass spectrometer with an electrospray ionization mode.

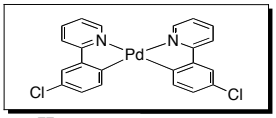
Materials and Methods

Diethylsulfide and 2-phenylpyridine were purchased from Lancaster, 7,8-benzoquinoline from Pfaltz & Bauer, $PhI(OAc)_2$ and *n*-BuLi from Acros, and $Pd(Cl)_4(NH_4)_2$ from Strem Chemicals. The carboxylate oxidants $PhI(O_2CR)_2$ were prepared by reaction of $PhI(OAc)_2$ with RCO_2H.[1] The tetrabutylammonium salts $[Bu_4N(O_2CR)]$ were synthesized by reaction of $NBu_4(OH)$ with RCO_2H. *trans*-$(Et_2S)_2PdCl_2$ was prepared from $Pd(Cl)_4(NH_4)_2$ and SEt_2.[2] The ligand precursor 2'-bromo-5'-methyl-2-phenylpyridine was prepared by Pd-catalyzed bromination of 3'-methyl-2-phenylpyridine.[3] Organic solvents were obtained from Fisher Scientific and used without further purification. All syntheses were carried out under ambient atmosphere unless otherwise stated. NMR solvents were obtained from Cambridge Isotopes, and stored under nitrogen. Acetone was purified by distillation from calcium sulfate. All other NMR solvents were passed through basic alumina and stored over sieves. The synthesis of substrates and characterization of compounds **1**, **3**, **5**, **6, 7-18**, **22**, **31**, **42**, **64, 65** has been reported previously, in a preliminary communication of this work.[4] Flash chromatography was performed on EM Science silica gel 60 (0.040-0.063 mm particle size, 230-400 mesh) and thin layer chromatography was performed on Merck TLC plates pre-coated with silica gel 60 F_{254}.

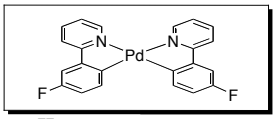
Experimental Details

Synthesis of Pd^{II} Complexes S1-S4[5]

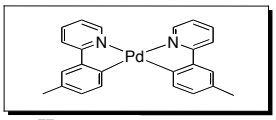
General Procedure. A solution of the aryl bromide (2-3 equiv relative to Pd) in THF or diethyl ether was cooled to –78 ºC in a dry ice/acetone bath. *n*-BuLi (1 equiv relative to ligand) or *t*-BuLi (2 equiv relative to ligand) was added dropwise. After stirring at –78 ºC for 5-10 min, a solution of $(Et_2S)_2PdCl_2$ in diethyl ether was added. The resulting mixture was stirred at –78 ºC for 30-120 min, then the reaction was quenched with water. The reaction mixture was diluted with water, and the palladium(II) product was extracted into CH_2Cl_2 or toluene. The organic extracts were filtered through a plug of aluminum oxide (certified, anhydrous, Fisher A591), the solvent volume was reduced to ~5 mL, and hexanes was added to precipitate the product. The resulting yellow solid was collected by filtration and dried under vacuum to afford the desired bis-cyclometallated complex.



Pd^{II}(Cl-Arpy)$_2$, S1: This complex was synthesized according to the general procedure above. The aryl bromide was dissolved in diethyl ether, *n*-BuLi was used as the lithiating reagent, and the extraction was carried out with CH_2Cl_2. Complex **S1** was obtained in 41% yield as a yellow solid. ^{1}H NMR ($CDCl_3$): δ 8.63 (d, J = 5.5 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.88 (td, J = 8.5, 2.5 Hz, 1H), 7.85 (d, J = 7.0 Hz, 1H), 7.61 (d, J = 2.5 Hz, 1H), 7.32 (ddd, J = 7.0, 5.5, 1.5 Hz, 1H), 7.26 (dd, J = 8.0, 2.5 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 164.28, 159.23, 148.32, 148.07, 139.87, 138.60, 130.25, 129.62, 123.34, 122.66, 119.62.

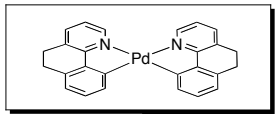


Pd^{II}(F-Arpy)$_2$, S2: This complex was synthesized according to the general procedure above. The aryl bromide was dissolved in diethyl ether, *n*-BuLi was used as the lithiating reagent, and the extraction was carried out with CH_2Cl_2. Complex **S2** was obtained in 43% yield as a yellow solid. ^{1}H NMR ($CDCl_3$): δ 8.64 (d, J = 5.5 Hz, 1H), 7.94 (dd, J = 8.5, 6.5 Hz, 1H), 7.89 (td, J = 7.5, 1.5 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.36 (dd, J = 11.0, 2.0 Hz, 1H), 7.32 (ddd, J = 7.5, 5.0, 1.5 Hz, 1H), 7.05 (td, J = 9.0, 2.5 Hz, 1H). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 162.81 (d, J = 4 Hz), 160.40 (d, J = 238 Hz), 156.12 (d, J = 3 Hz), 149.04, 147.77 (d, J = 6 Hz), 139.28, 138.76 (d, J = 6 Hz), 123.52, 119.85, 115.77 (d, J = 19 Hz), 110.18 (d, J = 21 Hz). ^{19}F NMR ($CDCl_3$): δ –120.48 (dt, J = 9.5 Hz, 6.5 Hz).



Pd^{II}(Me-Arpy)$_2$, S3: This complex was synthesized according to the general procedure above. The aryl bromide was dissolved in diethyl ether, *n*-BuLi was used as the lithiating reagent, and

the extraction was carried out with CH_2Cl_2. Complex **S3** was obtained in 55% yield as a yellow solid. Characterization data matched with those reported previously in the literature.[4]

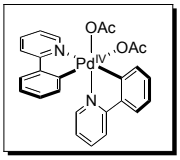


$Pd^{II}(BzqH_2)_2$, S4: This complex was synthesized according to the general procedure above. The aryl bromide was dissolved in THF, *n*-BuLi was used as the lithiating reagent, and the extraction was carried out with CH_2Cl_2. Complex **S4** was obtained in 71% yield as a yellow solid. ^{1}H NMR ($CDCl_3$): δ 8.47 (d, J = 4.5 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 7.5 Hz, 1H), 7.21 (t, J = 7.5 Hz, 1H), 7.15 (dd, J = 7.5, 5.5 Hz, 1H), 6.91 (d, J = 7.0 Hz, 1H), 3.00 (dd, J = 11.5, 4.0 Hz, 2H), 2.96 (dd, J = 11.5, 4.0 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 162.35, 159.76, 145.97, 144.14, 136.90, 136.64, 136.47, 132.52, 129.89, 123.29, 121.68, 28.09, 28.00.

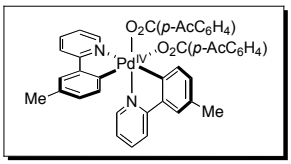
Synthesis of Pd^{IV} Complexes 2, 2-d_6, 47-49,62-64, 69

General Procedure. The appropriate bis-cyclometalated Pd^{II} starting material (0.24 mmol, 1 equiv) and oxidant (1.0-1.1 equiv) were combined in a 50 mL round bottomed flask equipped with a stir bar. CH_2Cl_2 (30 mL) was added, and the mixture was stirred at 25 ºC for between 10 min and 1 h. The solvent was evaporated to a volume of ~5 mL and hexanes (2-5 mL) was added to precipitate the product. The precipitate was collected and then suspended in Et_2O (5-10 mL) and sonicated, leaving a finely suspended powder. This material was collected at the top of a pipette-sized column of Celite and washed with Et_2O (5 mL). The product was then eluted with CH_2Cl_2, and the solvent was removed under vacuum. The Pd^{IV} products were isolated as off-white to yellow powders. If the resulting product was a tacky solid, the solid was washed with hexanes (2 mL) to the remove residual impurities.

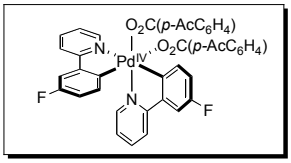
Notably, all Pd^{IV} complexes were stored at –35 ºC. HRMS data are reported for each compound and showed loss of one carboxylate ligand (*trans* to the σ-aryl group). The characterization of complexes **7-18, 64** was reported previously.[4] In general the Pd^{IV} complexes were insufficiently soluble and/or insufficiently stable to obtain ^{13}C NMR spectral data.



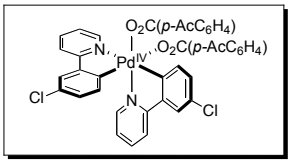
Complex **2:** Yield: 81%. ^1H NMR (acetone-d_6): δ 9.45 (d, J = 5.5 Hz, 1H), 8.27 (d, J = 8.0 Hz, 1H), 8.20 (t, 8.5, 1H), 8.09-8.06 (multiple peaks, 2H), 7.95-7.92 (multiple peaks, 2H), 7.87 (d, J = 8.0 Hz, 1H), 7.62 (t, J = 6.0 Hz, 1H), 7.58 (d, J = 6.0 Hz, 1H), 7.51(t, J = 7.5 Hz, 1H), 7.46 (t, J = 7.5 Hz, 1H), 7.10-7.08 (multiple peaks, 2H), 6.85 (t, J = 8.5 Hz, 1H), 6.30 (d, J = 8.5 Hz, 1H), 1.75 (s, 3H), 1.62 (s, 3H). FTIR (KBr): 1654, 1604, 1569, 1484, 1441, 1419, 1366, 1291, 1006, 759 cm^{-1}. HRMS-electrospray (m/z): $[M - OAc]^+$ calcd for $C_{24}H_{19}N_2O_2Pd$, 473.0481; Found, 473.0495.



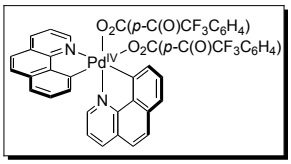
Complex **47**: Yield: 63%. ^1H NMR ($CDCl_3$): δ 9.49 (dt, J = 5.5, 1.0 Hz, 1H), 8.07-8.02 (multiple peaks, 5H), 7.98 (app. d, J = 8.5 Hz, 2H), 7.88 (dt, J = 8.5, 1.5 Hz, 2H), 7.82 (app. d, J = 8.0 Hz, 2H), 7.80-7.78 (multiple peaks, 2H), 7.58 (d, J = 6.0 Hz, 1H), 7.54 (d, J = 2.0 Hz, 1H), 7.51 (dd, J = 9.0, 5.0 Hz, 1H), 7.49 (d, J = 2.0 Hz, 1H), 7.31 (dd, J = 8.0, 2.0 Hz, 1H), 6.97 (td, J = 6.0, 2.5 Hz, 1H), 6.74 (dd, J = 8.0, 1.5 Hz, 1H), 6.39 (d, J = 8.0 Hz, 1H), 2.59 (s, 3H), 2.56 (s, 3H), 2.48 (s, 3H), 2.29 (s, 3H). FTIR (KBr): 1683, 1652, 1603, 1558, 1483, 1426, 1260 cm^{-1}. HRMS-electrospray (m/z): $[M - O_2C(p\text{-}AcC_6H_4)]^+$ calcd for $C_{42}H_{34}N_2O_6Pd$ 605.1056; Found, 605.1076.



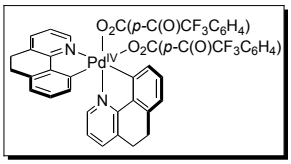
Complex **48**: Yield: 77%. ^{1}H NMR ($CDCl_3$): δ 9.50 (dd, J = 5.5, 1.0 Hz, 1H), 8.15-8.11 (multiple peaks, 2H), 8.04 (d, J = 8.0 Hz, 1H), 8.01 (d, J = 8.0 Hz, 2H), 7.98 (d, J = 8.5 Hz, 2H), 7.89 (d, J = 8.0 Hz, 2H), 7.87 (m, 1H), 7.84 (d, J = 8.0 Hz, 2H), 7.79 (d, J = 8.0 Hz, 1H), 7.47 (dd, J = 9.5, 3.0 Hz, 1H), 7.44 (dd, J = 9.0, 2.5 Hz, 1H), 7.27 (td, J = 9.0, 3.0 Hz, 1H), 7.06 (td, J = 7.0, 1.5 Hz, 1H), 6.72 (td, J = 9.0, 3.0 Hz, 1H), 6.44 (dd, J = 9.0, 5.5 Hz, 1H), 2.59 (s, 3H), 2.57 (s, 3H). ^{19}F NMR ($CDCl_3$): δ –114.72 (dt, J = 9.0, 6.0 Hz), –116.69 (dt, J = 9.0, 6.0 Hz). FTIR (KBr): 1683, 1652, 1604, 1564, 1484, 1464, 1426, 1261 cm^{-1}. HRMS-electrospray (m/z): [M – $O_2C(p\text{-}AcC_6H_4)$]$^+$ calcd for $C_{40}H_{28}F_2N_2O_6Pd$ 613.0555; Found, 613.0559.



Complex **49**: Yield: 70%. ^{1}H NMR ($CDCl_3$): δ 9.48 (dd, J = 5.5, 1.0 Hz, 1H), 8.13 (td, J = 7.5, 1.5 Hz, 1H), 8.10 (d, J = 8.5 Hz, 1H), 8.07 (app. d, J = 8.0 Hz, 1H), 8.01 (d, J = 8.5 Hz, 2H), 7.98 (d, J = 8.5 Hz, 2H), 7.89 (d, J = 8.5 Hz, 2H), 7.87 (dd, J = 8.0, 1.5 Hz, 1H), 7.84 (d, J = 8.0 Hz, 2H), 7.81 (dd, J = 8.0, 1.5 Hz, 1H), 7.72 (d, J = 2.5 Hz, 1H), 7.70 (d, J = 2.5 Hz, 1H), 7.59 (ddd, J = 7.5, 5.5, 1.5 Hz, 1H), 7.57 (dd, J = 6.0, 1.0 Hz, 1H), 7.49 (dd, J = 8.5, 2.5 Hz, 1H), 7.07 (ddd, J = 7.5, 6.0, 1.5 Hz, 1H), 6.94 (dd, J = 9.0, 2.5 Hz, 1H), 6.43 (d, J = 8.5 Hz, 1H), 2.60 (s, 3H), 2.57 (s, 3H). FTIR (KBr): 1683, 1652, 1604, 1558, 1482, 1422, 1262 cm^{-1}. HRMS-electrospray (m/z): [M – $O_2C(p\text{-}AcC_6H_4)$]$^+$ calcd for $C_{40}H_{28}Cl_2N_2O_6Pd$ 644.9964; Found, 644.9960.

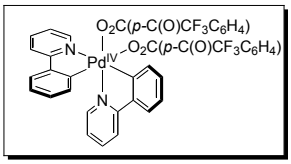


Complex **64**: Yield: 91%. ^{1}H NMR (acetone-d_6): δ 9.97 (dd, J = 5.0, 1.6 Hz, 1H), 8.76 (dd, J = 8.0, 1.5 Hz, 1H), 8.54 (dd, J = 8.0, 1.5 Hz, 1H), 8.44 (d, J = 7.0 Hz, 1H), 8.14-7.87 (multiple peaks, 12H), 7.66 (d, J = 7.6 Hz, 1H), 7.40 (dd, J = 8.0, 6.0 Hz, 1H), 7.14 (t, J = 8.0, 1H), 6.44 (d, J = 7.6, 1H). ^{19}F NMR: (acetone-d_6): δ –72.46 (s, 3F), –72.52 (s, 3F). FTIR (KBr): 1718, 1658, 1620, 1568, 1490, 1455, 1406, 1319 cm^{-1}. HRMS-electrospray (m/z): [M – $O_2C[(p\text{-}C(O)CF_3)C_6H_4]$ + CH_3OH]$^+$ calcd for $C_{44}H_{24}F_6N_2O_6Pd$, 711.0723; Found, 711.0735.

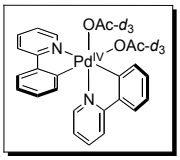


Complex **63**: Yield: 82%. ^{1}H NMR ($CDCl_3$): δ 9.33 (d, J = 4.5 Hz, 1H), 8.09-8.07 (multiple peaks, 2H), 8.01-8.00 (ap. d, J = 9 Hz, 4H), 7.94-7.92 (multiple peaks, 2H), 7.86 (d, J = 8.5 Hz,

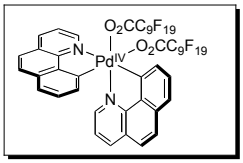
1H), 7.80 (d, J = 7.0 Hz, 1H), 7.53 (d, J = 8.0 Hz, 1H), 7.47-7.41 (multiple peaks, 2H), 7.35 (d, J = 5.5 Hz, 1H), 7.19 (d, J = 7.5 Hz, 1H), 6.92-6.83 (multiple peaks, 3H), 6.34 (d, J = 8.0 Hz, 1H). ^{19}F NMR: (acetone-d_6): δ –72.35 (s, 3F), –72.42 (s, 3F). HRMS-electrospray (m/z): [M – $O_2C[(p\text{-}C(O)CF_3)C_6H_4]$ + $CH_3OH]^+$ calcd for $C_{44}H_{28}F_6N_2O_6Pd$, 715.1036; Found, 715.1046.



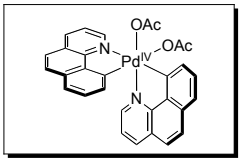
Complex **62**: Yield: 71%. ^{1}H NMR (acetone-d_6): δ 9.56 (d, J = 5.6 Hz, 1H), 8.38 (d, J = 8.4 Hz, 1H), 8.27 (td, J = 7.2, 1.6 Hz, 1H), 8.22-8.17 (multiple peaks, 2H), 8.11 (d, J = 6.8 Hz, 2H), 8.09-7.30 (multiple peaks, 9H), 7.70 (d, J = 5.2 Hz, 1H), 7.70 (dd, J = 7.6, 5.6 Hz, 1H), 7.56-7.48 (multiple peaks, 2H), 7.22 (td, J = 6.0, 1.6 Hz, 1H), 7.16 (t, J = 7.2 Hz, 1H), 6.94 (td, J = 8.6, 1.6 Hz, 1H), 6.48 (d, J = 8.0 Hz, 1H). ^{19}F NMR (acetone-d_6): δ –72.36 (s, 3F), –72.43 (3F, s). FTIR (KBr): 1717, 1604, 1569, 1485, 1442, 1335, 1185 cm^{-1}. HRMS-electrospray (m/z): [M – $O_2C[(p\text{-}C(O)CF_3)C_6H_4]$ + $CH_3OH]^+$ calcd for $C_{40}H_{24}F_6N_2O_6Pd$ 663.0711; Found, 663.0723.



Complex **2-d_6**: Yield: 73%. ^{1}H NMR ($CDCl_3$): δ 9.36 (d, J = 4.8 Hz, 1H), 8.12 (dd, J = 7.8, 1.0 Hz, 1H), 8.10-8.00 (multiple peaks, 2H), 7.76-7.73 (multiple peaks, 2H), 7.55-7.49 (multiple peaks, 3H), 7.44 (td, J = 7.5, 1.2 Hz, 1H), 7.07 (td, J = 7.5, 1.0 Hz, 1H), 6.90 (m, 1H), 6.85 (ddd, J = 8.0, 7.0, 1.5 Hz, 1H), 6.38 (dd, J = 8.0, 1.0 Hz, 1H). ^{2}D NMR ($CHCl_3$): δ 1.93 (s, 3H), 1.86 (s, 3H). FTIR (KBr): 1648, 1604, 1570, 1484, 1442, 1353, 1309, 1286, 1007, 760 cm^{-1}. HRMS-electrospray (m/z): [M – OAc-d_3]$^+$ calcd for $C_{24}H_{16}D_3N_2O_2Pd$, 476.0670; Found, 476.0677.



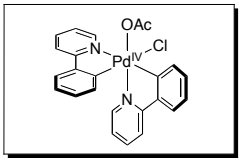
Complex **69**: Under the general procedure conditions (above), a mixture of products was formed. Therefore, the reaction was carried out in dry acetone at 45 °C and then worked up according to the general procedure above. Yield: 64%. ^{1}H NMR (acetone-d_6): δ 9.73 (d, J = 5.0 Hz, 1H), 8.94 (d, J = 8.0 Hz, 1H), 8.62 (d, J = 8.0 Hz, 1H), 8.19-8.16 (multiple peaks, 4H), 8.12 (d, J = 9.0 Hz, 1H), 8.00-7.94 (multiple peaks, 3H), 7.95 (d, J = 9.0 Hz, 1H), 7.86 (d, J = 6.0 Hz, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.43 (d, J = 5.0 Hz, 1H), 7.41 (d, J = 5.0 Hz, 1H), 7.17 (t, J = 8.0 Hz, 1H), 6.38 (d, J = 8.0 Hz, 1H). ^{19}F NMR (acetone- d_6): δ –81.79 to – 81.85 (multiple peaks, 6F), –116.6 to – 116.80 (multiple peaks, 4F), –122.48 to –123.38 (multiple peaks, 24F), –126.88 (br. s, 4F). FTIR (KBr): 1726, 1699, 1660, 1569, 1456, 1408, 1364, 1322, 1210 cm^{-1}. HRMS-electrospray (m/z): [M – $O_2CC_9F_{19}$]$^+$ calcd for $C_{46}H_{16}F_{38}N_2O_4Pd$ 974.9943; Found, 974.9966.



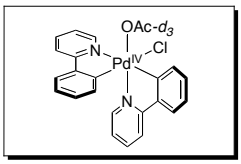
Complex **74**: Yield: 71%. ^{1}H NMR (acetone-d_6): δ 9.83 (d, J = 5.0 Hz, 1H), 8.77 (d, J = 8.0 Hz, 1H), 8.42 (d, J = 8.0 Hz, 1H), 8.24 (d, J = 8.0 Hz, 1H), 8.08-7.83 (multiple peaks, 7H), 7.69 (d, J = 6.0 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.26 (multiplet, 1H), 7.03 (t, J = 8.0 Hz, 1H), 6.24 (d, J = 8.0 Hz, 1H), 1.73 (s, 3H), 1.57 (s, 3H). FTIR (KBr): 1646, 1616, 1558, 1405, 1353, 1309, 1283, 914, 836, 667 cm^{-1}. HRMS-electrospray (m/z): $[M - O_2C_2H_3]^+$ calcd for $C_{30}H_{22}N_2O_4Pd$ 521.0481; Found, 521.0489.

Synthesis of (Phpy)$_2$Pd(Cl)(OAc) (21), (Phpy)$_2$Pd(Cl)(OAc-d_3) (S21-d_3) and (Bzq)$_2$Pd(Cl)(OAc) (**73**).

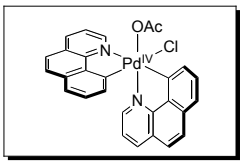
General Procedure. The appropriate Pd^{IV} complex [either (Phpy)$_2$Pd(OAc)$_2$ or (Phpy)$_2$Pd(OAc-d_3)$_2$] (0.12 mmol, 1.0 equiv) was dissolved in THF (10 mL). LiCl (52 mg, 1.2 mmol, 10 equiv) was added, and the reaction was stirred for 30 min. The precipitate from the reaction was collected on a frit, washed with THF, and dried under vacuum. The resulting off-white solid was dissolved in acetone (12 mL), and HCl (1 M solution in Et_2O, 100 μL, 0.10 mmol, 0.84 equiv) was added. The mixture was stirred for 3 h, and then the solvent was removed under vacuum to afford the product as a light yellow solid.



(Phpy)$_2$Pd(Cl)(OAc) (**21**). Yield: 31%. ^{1}H NMR (DMSO-d_6): δ 9.62 (d, J = 4.0 Hz, 1H), 8.39 (d, J = 8.0 Hz, 1H), 8.31-8.27 (multiple peaks, 2H), 8.08-8.04 (multiple peaks, 2H), 7.97 (d, J = 6.5 Hz, 1H), 7.89 (d, J = 8.5 Hz, 1H), 7.76 (t, J = 7.0 Hz, 1H), 7.51 (t, J = 8.0 Hz, 1H), 7.22-7.18 (multiple peaks, 2H), 7.12 (t, J = 7.0 Hz, 1H), 6.92 (t, J = 7.0, 1H), 6.19 (d, J = 8.0 Hz, 1H), 1.72 (s, 3H). FTIR (KBr): 1758, 1650, 1603, 1567, 1464, 1421, 1294 cm^{-1}. HRMS-electrospray (m/z): $[M - Cl]^+$ calcd for $C_{24}H_{19}ClN_2O_2Pd$ 473.0481; Found, 473.0478.



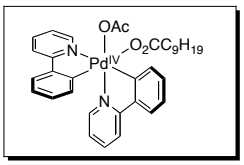
(Phpy)$_2$Pd(Cl)(OAc-d_3) (**S21-d_3**). Yield: 43%. ^{1}H NMR (DMSO-d_6): δ 9.61 (d, J = 4.0 Hz, 1H), 8.39 (d, J = 8.0 Hz, 1H), 8.31-8.24 (multiple peaks, 2H), 8.07-8.02 (multiple peaks, 2H), 7.96 (d, J = 7.5 Hz, 1H), 7.88 (d, J = 8.5 Hz, 1H), 7.75 (t, J = 6.0 Hz, 1H), 7.57 (t, J = 8.0 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 7.23-7.19 (multiple peaks, 2H), 7.11 (t, J = 7.5 Hz, 1H), 6.92 (t, J = 8.0 Hz, 1H), 6.19 (d, J = 8.0 Hz, 1H). ^{2}H NMR (DMSO): δ 1.99 (s, 3D). FTIR (KBr): 1640, 1602, 1579, 1567, 1484, 1439, 1410, 1305 cm^{-1}. HRMS-electrospray (m/z): $[M - Cl]^+$ calcd for $C_{24}H_{16}D_3ClN_2O_2Pd$ 476.0670; Found, 476.0679.



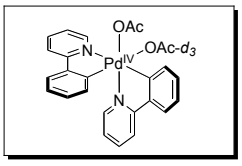
(Bzq)$_2$Pd(Cl)(OAc) (**71**). Yield: 96%. ^{1}H NMR (DMSO-d_6): δ 9.91 (d, J = 5.0 Hz, 1H), 8.92 (d, J = 8.0 Hz, 1H), 8.60 (d, J = 8 Hz, 1H), 8.21-8.15 (multiple peaks, 4H), 8.09 (d, J = 9.0 Hz, 1H), 8.03 (t, J = 8.0 Hz, 1H), 7.98-7.95 (multiple peaks, 2H), 7.67 (d, J = 7.5 Hz, 1H), 7.42-7.40 (multiplet, 1H), 7.35 (d, J = 6.0 Hz, 1H), 7.14 (t, J = 8.0 Hz, 1H), 6.20 (d, J = 8.0 Hz, 1H), 1.74 (s, 3H). FTIR (KBr): cm^{-1}. HRMS-electrospray (m/z): [M – Cl]$^+$ calcd for $C_{28}H_{19}ClN_2O_2Pd$ 521.0481; Found, 521.0488.

Synthesis of Pd^{IV} Complexes 2a-d_3, 2b-d_3 and 6 Containing Mixed Carboxylate Ligands

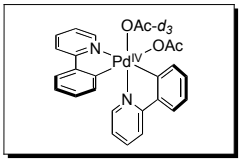
General Procedure. Complex **21** or **S21-d_3** (0.074 mmol, 1 equiv) and AgO_2CR (0.082 mmol, 1.1 equiv) were dissolved in a 50/50 solution of CH_2Cl_2/EtOAc (16 mL). The reaction mixture was stirred for 1.5 h, and was then filtered through a plug of Celite. The filtrate was concentrated to afford the product as a yellow powder.



(Phpy)$_2$Pd($O_2CC_9H_{19}$)(OAc) (**19**). Yield: 74%. ^{1}H NMR ($CDCl_3$): δ 9.39 (d, J = 5.0 Hz, 1H), 8.08 (d, J = 8.0 Hz, 1H), 8.02-7.98 (multiple peaks, 2H), 7.70 (multiple peaks, J = 4.0 Hz, 2H), 7.65-7.61 (multiple peaks, 2H), 7.54 (d, J = 6.0 Hz, 1H), 7.50-7.38 (multiple peaks, 2H), 7.40 (t, J = 7.0 Hz, 1H), 7.04 (t, J = 7.0 Hz, 1H), 6.87-6.82 (multiple peaks, 2H), 6.35 (d, J = 8.0 Hz, 1H), 2.07 (t, J = 8.0 Hz, 2H), 1.93 (s, 3H), 1.33-0.99 (multiple peaks, 14H), 0.85 (t, J = 7.0 Hz, 3H). HRMS-electrospray (m/z): [M – $O_2CC_9H_{19}$]$^+$ calcd for $C_{24}H_{19}N_2O_2Pd$, 473.0481; Found, 473.0480.



(Phpy)$_2$Pd(OAc-d_3)(OAc) (**2a-d_3**). Yield: 53%. ^{1}H NMR (acetone-d_6): δ 9.44 (d, J = 5.0 Hz, 1H), 8.26 (d, J = 8.0 Hz, 1H), 8.19 (t, J = 8.0 Hz, 1H), 8.07-8.05 (multiple peaks, 2H), 7.94-7.91 (multiple peaks, 2H), 7.86 (d, J = 8.0 Hz, 1H), 7.60 (t, J = 5.5 Hz, 1H), 7.57 (d, J = 5.5 Hz, 1H), 7.50 (t, J = 7.5 Hz, 1H), 7.46-7.43 (multiple peaks, 2H), 7.07 (multiple peaks, 2H), 6.84 (t, J = 8.5 Hz, 1H), 6.29 (d, J = 8.5 Hz, 1H), 1.73 (s, 3H). ^{2}H NMR ($CHCl_3$): δ 1.86 (s, 3D). HRMS-electrospray (m/z): [M – OAc-d_3]$^+$ calcd for $C_{26}H_{19}D_3N_2O_4Pd$ 473.0481; Found, 473.0491.



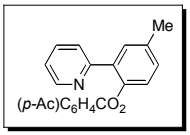
(Phpy)$_2$Pd(OAc)(OAc-d_3) (**2b-d_3**). Yield: 51%. ^{1}H NMR (acetone-d_6): δ 9.42 (d, J = 5.0 Hz, 1H), 8.24 (dd, J = 7.0 Hz, 1H), 8.17 (t, J = 8.0 Hz, 1H), 8.06-8.03 (multiple peaks, 2H), 7.93-7.88 (multiple peaks, 2H), 7.85 (d, J = 8.0 Hz, 1H), 7.60-7.54 (multiple peaks, 2H), 7.50-7.41 (multiple peaks, 2H), 7.07-7.02 (multiple peaks, 2H), 6.82 (t, J = 7.0 Hz, 1H), 6.28 (d, J = 8.0 Hz, 1H), 1.60 (s, 3H). ^{2}H NMR ($CHCl_3$): δ 1.94 (s, 3D). HRMS-electrospray (m/z): $[M - OAc]^+$ calcd for $C_{26}H_{19}D_3N_2O_4Pd$ 476.0670; Found, 476.0675.

Characterization of Organic Products of C–O Bond-Forming Reductive Elimination

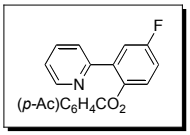
The organic reductive elimination products were challenging to purify from the crude reaction mixtures. As a result they were synthesized independently according to the general procedure below. In all cases, the products were spectroscopically identical to those observed by ^{1}H NMR spectroscopy in the reductive elimination reactions. Compounds **3**,[6] **4**,[7] and **66**[8] have been previously reported and characterized by our group. For compounds **65**, **S5** and **S6** the compounds were characterized by converting the benzoate substituent to the alcohol product due to competitive hydrolysis of the CF_3 carbonyl upon isolation of the desired product.

General Procedure. The appropriate arylpyridine substrate (1.7 mmol, 1.0 equiv), PhI[O_2C(*p*-AcC_6H_4)]$_2$ (3.4 mmol, 2.0 equiv), and $Pd(OAc)_2$ (0.05 mmol, 3 mol %) were dissolved in CH_3CN (18 mL) in a 20 mL vial. The vial was sealed with a Teflon-lined cap, and the reaction mixture was heated at 80°C for 12 h. The solvent was removed under vacuum, and the resulting brown residue was re-dissolved in CH_2Cl_2 (15 mL). The organic layer was extracted with saturated $NaHCO_3$ (2 x 30 mL) and then dried over $MgSO_4$. The products were purified by column chromatography.

For **65**, **S5**, and **S6** the compounds were stirred in an NaOH/MeOH solution and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$.

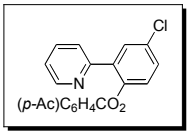


2-(2,5-*p*-acetylbenzoate-methylphenyl)pyridine (53): Yield: 72% of an off-white tacky solid. R_f = 0.1 in 79% hexanes/20% ethyl acetate/1% triethylamine. ^{1}H NMR ($CDCl_3$): δ 8.55 (dd, *J* = 4.8, 1.2 Hz, 1H), 8.15 (d, *J* = 8.0 Hz, 2H), 7.99 (d, *J* = 8.0 Hz, 2H), 7.60 (td, *J* = 7.5, 2.0 Hz, 1H), 7.56 (d, *J* = 2.0 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.28 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.14 (ddd, *J* =8.0, 4.8, 1.2 Hz, 1H), 2.64 (s, 3H), 2.43 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 197.74, 164.77, 155.84, 149.82, 146.06, 140.76, 136.62, 136.42, 133.59, 132.93, 131.57, 130.65, 130.61, 128.48, 123.81, 123.10, 122.38, 27.15, 21.20. FTIR (KBr): 2361, 1742, 1684, 1653, 1463, 1264, 1184, 1065, 1013, 858, 773, 761 cm^{-1}. HRMS-electrospray (m/z): $[M - H]^+$ calcd for $C_{21}H_{17}NO_3$ 332.1287; Found, 332.1280.

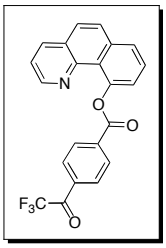


2-(2,5-*p*-acetylbenzoate-fluorophenyl)pyridine (54): Yield: 86% of an off-white tacky solid. R_f = 0.1 in 79% hexanes/20% ethyl acetate/1% triethylamine. ^{1}H NMR ($CDCl_3$): δ 8.55 (d, *J* = 5.0 Hz, 1H), 8.16 (d, *J* = 7.0 Hz, 2H), 8.02 (d, *J* = 7.0 Hz, 2H), 7.64 (td, *J* = 7.5, 1.5 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.50 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.29 (d, *J* = 4.5 Hz, 1H), 7.27 (d, *J* = 4.5 Hz, 1H), 7.20-7.18 (multiple peaks, 2H), 2.66 (s, 3H). ^{19}F NMR ($CDCl_3$): δ –115.67 (app. t, *J* = 8.0 Hz, 1F). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 197.08, 164.05, 161.43, 158.99, 154.01, 149.37, 143.58 (d, J_{CF} = 12 Hz), 140.35, 136.10, 134.37 (d, J_{CF} = 31 Hz), 132.66, 130.07, 127.96, 124.42 (d, J_{CF} = 34 Hz), 122.73 (d, J_{CF} = 300 Hz), 117.09 (d, J_{CF} = 99 Hz), 116.14 (d, J_{CF} = 93 Hz), 26.58. FTIR

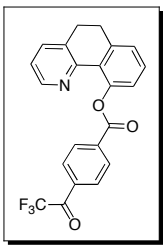
(KBr): 1734, 1684, 1496, 1284, 1265, 1177, 1087, 859, 782, 744, 688 cm^{-1}. HRMS-electrospray (m/z): $[M - Na]^+$ calcd for $C_{20}H_{14}FNO_3$ 358.0855; Found, 358.0861.



2-(2,5-*p*-acetylbenzoate-chlorophenyl)pyridine (55): Yield: 27% of an off-white tacky solid. R_f = 0.1 in 79% hexanes/20% ethyl acetate/1% triethylamine. ^1H NMR ($CDCl_3$): δ 8.56 (dd, *J* = 5.0, 3.0 Hz, 1H), 8.15 (d, *J* = 8.0 Hz, 2H), 8.02 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 2.0 Hz, 1H), 7.65 (td, *J* = 8.0, 2.0 Hz, 1H), 7.53 (d, *J* = 8.0, 1.0 Hz, 1H), 7.46 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.19 (dd, *J* = 5.0, 3.0 Hz, 1H), 2.66 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 197.61, 164.36, 154.41, 149.92, 146.77, 140.91, 136.66, 134.75, 133.07, 132.27, 130.98, 130.63, 129.88, 128.51, 124.86, 123.73, 122.92, 27.12. FTIR (KBr): 1739, 1691, 1590, 1491, 1458, 1274, 1191, 1081, 878, 787, 744, 692 cm^{-1}. HRMS-electrospray (m/z): $[M - Na]^+$ calcd for $C_{20}H_{14}ClNO_3$ 374.0560; Found, 374.0544.

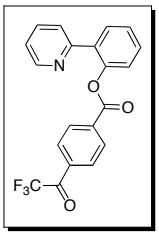


Benzo[h]quinolin-10-yl-4-(2,2,2-trifluoroacetyl)benzoate (65): Yield: 37% of an off-white tacky solid. R_f = 0.1 in 59% hexanes/40% ethyl acetate/1% triethylamine. ^1H NMR ($CDCl_3$): δ 8.54 (d, *J* = 4.0 Hz, 1H), 8.33 (dd, *J* = 4.5, 1.5 Hz, 1H), 8.3 (d, *J* = 8.0 Hz, 2H), 8.14 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.93 (d, *J* = 7.0 Hz, 1H) 7.9 (d, *J* = 9.0 Hz, 1H), 7.76 (t, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 9.0 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.39 (dd, *J* = 8.0, 4.5, 1H). ^{19}F NMR ($CDCl_3$): δ –71.55 (s, 3F). FTIR (KBr): 1741, 1718, 1595, 1410, 1270, 1190, 1087, 942, 836, 716 cm^{-1}. When this compound was dissolved in DMSO-d_6 (required for sufficient solubility to obtain a ^{13}C NMR spectrum), partial hydration of the trifluoromethylketone was observed. The reductive elimination products from **64** were further characterized by treatment with a solution of NaOH in methanol to convert. As expected, this reaction generated 10-hydroxybenzo[h]quinoline, which matched the previously reported characterization data.[9]

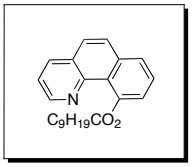


(5,6-Dihydrobenzo[*h*]quinolin-10-yl 4-(2,2,2-trifluoroacetyl)benzoate (S5): Isolated directly from reductive elimination of **63** (0.028 mmol) at 80°C in CH_3CN (1.8 mL) and purified via column chromatography. Yield: 78% of an off-white tacky solid. R_f = 0.2 in 59% hexanes/40% ethyl acetate/1% triethylamine. ^1H NMR ($CDCl_3$): δ 8.38-8.35 (multiple peaks, 2H), 8.18 (d, *J* =

8.0 Hz, 2H), 7.89 (dd, J = 5.0, 2.0 Hz, 1H), 7.44 (dd, J = 8.0, 2.0 Hz, 1H), 7.36 (t, J = 8.0 Hz, 1H), 7.21 (dd, J = 6.5, 1.0 Hz, 1H), 7.13 (dd, J = 8.0, 1.0 Hz, 1H), 6.95 (dd, J = 5.0, 3.0 Hz, 1H), 2.95-2.91 (multiple peaks, 4H). ^{19}F NMR ($CDCl_3$): δ –71.38 (s, 3F). FTIR (KBr): 1744, 1718, 1278, 1227, 1202, 1179, 1141, 1091, 941, 802, 720 cm^{-1}. When this compound was dissolved in DMSO-d_6 (required for sufficient solubility to obtain a ^{13}C NMR spectrum), partial hydration of the trifluoromethylketone was observed. The reductive elimination products were further characterized by treatment with a solution of NaOH in methanol to convert **S5** to 5,6-dihydrobenzo[h]quinolin-10-ol. ^{1}H NMR ($CDCl_3$): δ 14.01 (s, 1H), 8.30 (d, J = 4.5 Hz, 1H), 7.56 (d, J = 7.0 Hz, 1H), 7.20-7.16 (multiple peaks, 2H), 6.86 (d, J = 8.0 Hz, 1H), 6.69 (d, J = 7.0 Hz, 1H), 2.89 (multiplet, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 159.47, 154.68, 144.11, 138.99, 136.34, 131.93, 131.04, 121.52, 118.39, 116.61, 116.01, 28.19, 27.95. HRMS-electrospray (*m/z*): [M + H]$^+$ calcd for $C_{13}H_{11}NO$ 198.0919; Found, 198.0914.



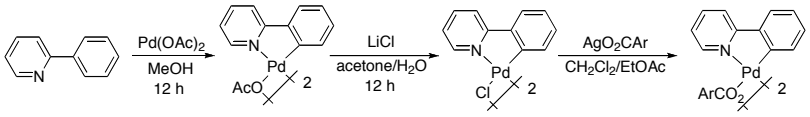
2-(pyridin-2-yl)phenyl 4-(2,2,2-trifluoroacetyl)benzoate (S6): Yield: 26% of an off-white tacky solid. R_f = 0.1 in 59% hexanes/40% ethyl acetate/1% triethylamine. ^{1}H NMR ($CDCl_3$): δ 8.51 (d, J = 6.0, 2.0 Hz, 1H), 8.24 (d, J = 8.0 Hz, 2H), 8.24 (d, J = 8.0 Hz, 2H), 7.74 (dd, J = 6.0, 2.0 Hz, 1H), 7.67 (td, J = 8.0, 2.0, 1H), 7.55-7.50 (multiple peaks, 2H), 7.44 (td, J = 8.0, 1.0 Hz, 1H), 7.33 (dd, J = 8.0, 1.0 Hz, 1H), 7.16 (ddd, J = 5.0, 3.0, 1.0 Hz, 1H). ^{19}F NMR ($CDCl_3$): δ –71.64 (3F, s). FTIR (KBr): 1733, 1469, 1270, 1180, 1116, 1072, 1053, 1016, 923, 859, 755, 709 cm^{-1}. When this compound was dissolved in DMSO-d_6 (required for sufficient solubility to obtain a ^{13}C NMR spectrum), partial hydration of the trifluoromethylketone was observed. The reductive elimination products were further characterized by treatment with a solution of NaOH in methanol to convert **S6** to 2-(pyridine-2-yl)phenol, which matched the previously reported characterization data.[10]



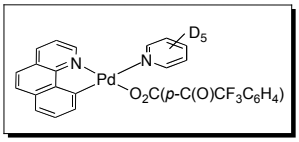
Benzo[*h*]quinolin-10-yl deconate (68): Yield: 36% of a yellow oil. R_f = 0.2 in 79% hexanes/20% ethyl acetate/1% triethylamine. ^{1}H NMR (acetone-d_6): δ 8.99 (dd, J = 4.0, 2.0 Hz, 1H), 8.36 (dd, J = 8.0, 2.0 Hz, 1H), 7.97-7.94 (multiple peaks, 2H), 7.85 (d, J = 9.0 Hz, 1H) 7.74 (t, J = 8.0 Hz, 1H), 7.62 (dd, J = 8.0, 4.0 Hz, 1H), 7.40 (dd, J = 8.0, 1.0 Hz, 1H), 2.89 (t, J = 7.5 Hz, 2H), 1.83 (m, 2H), 1.54 (m, 2H), 1.42-1.29 (multiple peaks, 10H), 0.88 (t, J = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 173.77, 149.01, 148.18, 145.89, 136.20, 135.87, 128.25, 128.22, 127.43, 126.77, 126.51, 123.63, 122.43, 121.67, 35.06, 32.11, 29.71, 29.67, 29.65, 29.53, 24.90, 22.89, 14.34. FTIR (KBr): 3048, 2925, 2853, 1757, 1622, 1593, 1444, 1403, 1142, 834, 806, 746, 721 cm^{-1}. HRMS-electrospray (*m/z*): [M + H]$^+$ calcd 350.2120 for $C_{23}H_{27}NO_2$; Found, 350.2126.

Characterization of Inorganic Products of C–O Bond-Forming Reductive Elimination

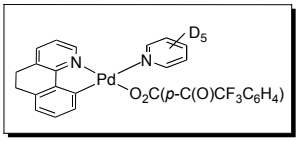
The inorganic reductive elimination products were challenging to purify cleanly from the crude reaction mixtures. As a result they were synthesized independently according to the following three step sequence. In all cases, the products were spectroscopically identical to those observed by ^{1}H NMR spectroscopy in the reductive elimination reactions.



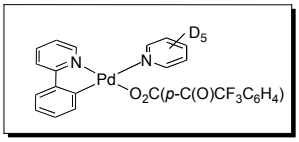
General Procedure. *Step 1:* The appropriate N~C ligand (0.56 mmol, 1.0 equiv) and $Pd(OAc)_2$ (0.56 mmol, 1.0 equiv) were dissolved in MeOH (8 mL). The orange reaction mixture was allowed to stir for 12 h. The resulting solid precipitate was collected on a frit and washed with hexanes. For further purification, the solid was re-dissolved in CH_2Cl_2, precipitated with hexanes and dried under vacuum to afford the products as bright yellow solids. *Step 2:* The yellow solid from step 1 (0.30 mmol, 1.0 equiv) was combined with LiCl (1.45 mmol, 4.8 equiv) in acetone (3.25 mL) and water (325 μL). The reaction mixture was stirred for 12 h. A precipitate was formed and collected on a frit. The product washed with hexanes and dried under vacuum to afford a pale yellow solid. *Step 3:* The solid from step 2 (0.25 mmol, 1.0 equiv) was combined with $Ag(O_2CAr)$ (0.62 mmol, 2.5 equiv) in a mixture of CH_2Cl_2 (12 mL) and EtOAc (8 mL). The reaction mixture was stirred for 12 h, then filtered through a plug of celite. The solvent was removed under vacuum, and the resulting residue was recrystallized from CH_2Cl_2/hexanes to afford a bright yellow solid.



BzqPd(C_5D_5N)OBz$_{C(O)CF3}$ (S7): Yield: 56%. ^{1}H NMR ($CDCl_3$ containing 20% C_5D_5N): δ 8.71 (d, J = 4.8 Hz, 1H), 8.30 (dd, J = 8.4, 1.2 Hz, 1H), 8.26 (d, J = 8.0 Hz, 2H), 8.07 (d, J = 8.0 Hz, 2H), 7.76 (d, J = 8.4 Hz, 1H), 7.63-7.58 (multiple peaks, 2H), 7.45 (dd, J = 8.0, 5.2 Hz, 1H), 7.30 (d, J = 7.2 Hz, 1H), 6.47 (d, J = 7.6 Hz, 1H). ^{19}F NMR ($CDCl_3$): δ –71.44 (s, 3F). FTIR (KBr): 1599, 1555, 1485, 1397, 1205, 1185, 1141, 941, 752 cm^{-1}.



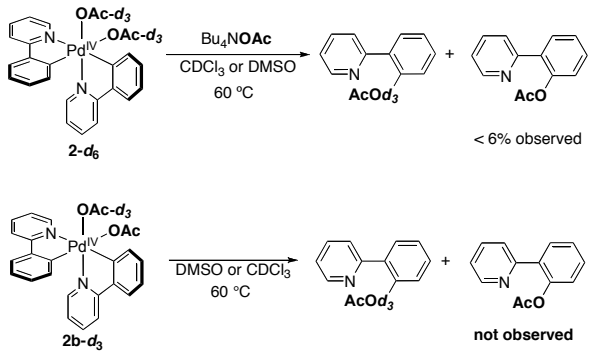
BzqH$_2$Pd(C_5D_5N)OBz$_{C(O)CF3}$ (S8): Yield: 51%. ^{1}H NMR ($CDCl_3$ containing 20% C_5D_5N): δ 8.27 (d, J = 8.8 Hz, 1H), 8.07 (d, J = 8.4 Hz, 1H), 7.50 (d, J = 7.6 Hz, 2H), 7.00 (t, J = 6.4 Hz, 2H), 6.90-6.86 (multiple peaks, 3H), 6.08 (d, J = 6.4 Hz, 1H), 2.93 (app. s, 4H). ^{19}F NMR ($CDCl_3$): δ –71.57. FTIR (KBr): 1599, 1564, 1479, 1411, 1318, 1159, 720, 534 cm^{-1}.



(Phpy)$_2$Pd(C$_5$D$_5$N)OBz$_{C(O)CF3}$ (S9): Yield: 43%. ^{1}H NMR ($CDCl_3$ containing 20% C_5D_5N): δ 8.51 (d, *J* = 4.4 Hz, 1H), 8.21 (d, *J* = 7.6 Hz, 2H), 8.05 (d, *J* = 7.6 Hz, 2H), 7.80 (td, *J* = 8.0, 1.2 Hz, 1H), 7.68-7.65 (multiple peaks, 2H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.10-7.07 (multiple peaks, 2H), 6.94 (t, *J* = 7.8 Hz, 1H), 6.25 (d, *J* = 8.0 Hz, 1H). ^{19}F NMR ($CDCl_3$): δ –71.50 (s, 3F). FTIR (KBr): 1600, 1556, 1384, 1319, 1164, 1065, 941, 712, 532 cm^{-1}.

Attempts to isolate clean samples of the dimeric Pd^{II} species observed in the reductive elimination of Pd^{IV} complexes **58-60** were hindered by the hazards associated with working with $Ag(O_2C(p\text{-}C(O)AcC_6H_4)$. ***Although the explosive nature of this salt has not been reported previously, it was found that when dried and exposed to a minor amount of friction, it readily underwent detonation.***

General Procedure for Crossover studies:

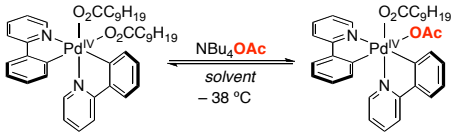


Complex **2-*d*$_6$** or **2b-*d*$_3$** (6.2 mg, 0.012 mmol) was dissolved in DMSO or $CHCl_3$ (0.8 mL) in a 4 mL vial in a N_2-filled drybox. If appropriate, $NBu_4(OAc)$ (18 mg, 0.060 mmol, 5.0 equiv) was added to this solution. The vial was sealed with a Teflon-lined cap, removed from the drybox, and heated at 60 °C for 5 h. The resulting mixture was evaporated to dryness, redissolved in CH_2Cl_2 (3 mL), then filtered through a pipette plug containing 25% poly-4-vinylpyridine and 75% silica gel. The plug was washed with a 9 : 1 solution of hexanes : ethyl acetate that contained 1% triethylamine (~20 mL total volume). The solvent was then removed under vacuum, and the organic products were analyzed by ^1H and ^2H NMR spectroscopy. The ratio of **3-*d*$_3$** to **3** was determined by integration of H6 of the pyridine (8.68 ppm) relative to the methyl group of the acetate (2.17 ppm) in $CDCl_3$. Each experiment was carried out in triplicate, and the results reported in the manuscript represent an average of three runs.

Sources of Error in Kinetics Experiments

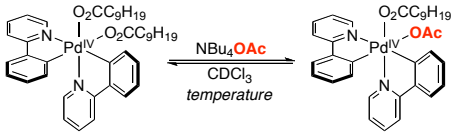
Error in the kinetics experiments most likely arises from a slight temperature instability in the NMR spectrometer. Additionally minor inconsistencies in the amount of pyridine added to the reaction have been shown to affect the rate of C–O bond formation. In the case of the carboxylate exchange reactions, the close proximity of the resonances associated with the starting materials and products leads to some error in the intergration valuaes. The error was calculated by taking an average of the trials. The standard deviation of the average was then calculated. The average was added to the standard deviation, and the difference and sum of these values were taken against the average to obtain the plus/minus values.

General Procedure for Solvent Study of Kinetics of Carboxylate Exchange:



Complex **7** (5.8 mg, 0.0076 mmol, 1.0 equiv) was dissolved in an appropriate deuterated solvent (0.25 mL) in a screw cap NMR tube in a N_2-filled drybox. The NMR tube was sealed with a Teflon-lined cap fitted with a septum, and removed from the drybox. Bu_4NOAc (2.4 mg, 0.0076 mmol, 1.0 equiv) was dissolved in the appropriate deuterated solvent (0.25 mL) in a 4 mL vial, and the vial was sealed with a Teflon-lined cap fitted with a septum and removed from the glovebox. The solution in the NMR tube was frozen in liquid nitrogen, and the [Bu_4NOAc] solution was added via syringe. The NMR tube was placed in the NMR spectrometer where the probe had been pre-cooled to –38 ºC. The sample was allowed to equilibrate in the spectrometer for six minutes before acquiring spectra. The rate of carboxylate exchange was then studied by ^{1}H NMR spectroscopy at –38 ºC by monitoring the disappearance of the most downfield resonance (9.51 ppm in acetone-d_6, 9.33 in CD_3CN, 9.27 in $CDCl_3$, 9.82 in toluene-d_8). The reaction was followed until it reached equilibrium and then fitted to a first order kinetics plot for a reversible reaction.[11] Each experiment was carried out in duplicate, and the *k* values represent an average of two runs. Notably, when the experiment was run in toluene, no exchange was observed over the course of approximately 6 h at –38 ºC.

General procedure for Eyring Plot for Carboxylate Exchange:



Complex **7** (5.8 mg, 0.0076 mmol, 1.0 equiv) was dissolved in $CDCl_3$ (0.25 mL) in a screw cap NMR tube in a N_2-filled drybox. The NMR tube was sealed with a Teflon-lined cap fitted with a septum, and removed from the drybox. Bu_4NOAc (2.4 mg, 0.0076 mmol, 1.0 equiv) was dissolved in the appropriate deuterated solvent (0.25 mL) in a 4 mL vial, and the vial was sealed with a Teflon-lined cap fitted with a septum and removed from the glovebox. The solution in the NMR tube was frozen in liquid nitrogen, and the [Bu_4NOAc] solution was added via syringe. The NMR tube was placed in the NMR spectrometer where the probe had been pre-cooled to the appropriate temperature. The sample was allowed to equilibrate in the spectrometer for six minutes before acquiring spectra. The rate of carboxylate exchange was then studied by ^{1}H NMR spectroscopy at –58 ºC, –53 ºC, –50 ºC, –48 ºC and –38 ºC by monitoring the disappearance of the most downfield resonance (9.27 ppm in $CDCl_3$). The reaction was followed until it reached equilibrium and then fitted to a first order kinetics plot for a reversible reaction.[11] The rates shown in Table S2 below are an average of two trials.

Table S1. Rate Data for Carboxylate Exchange at Complex **7** as a Function of Solvent

Solvent	k_{obs} (s^{-1} x 10^4)[a]
toluene-d_8	<0.1
acetone-d_6	3.6 ± 0.1
CD_3CN	7.6 ± 0.1
$CDCl_3$	70 ± 0.1

[a] Values represent an average of two kinetics runs

Figure S1. Representative Kinetics Data for Carboxylate Exchange at **7** in CH_3CN at –38 °C

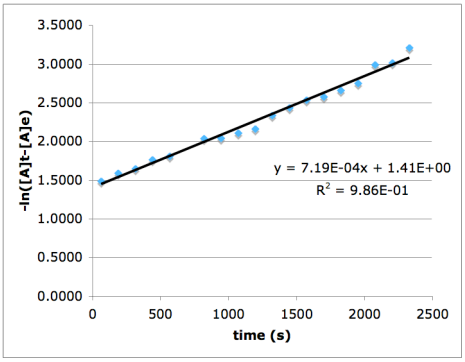
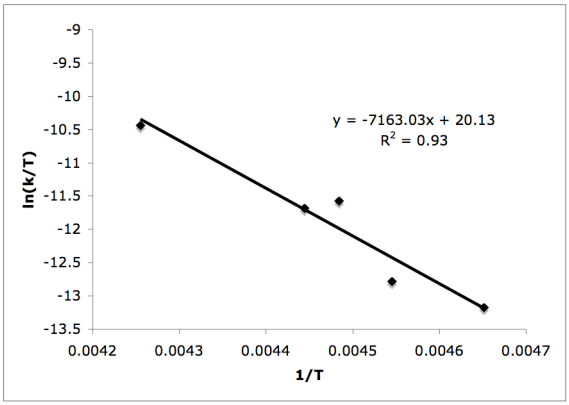


Table S2. Rate Data for Carboxylate Exchange at Complex **7** as a Function of Temperature

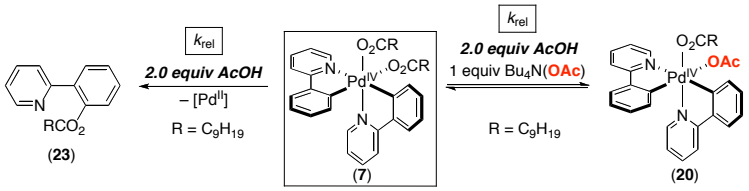
Temperature	k_{obs} (s^{-1} x 10^4)[a]
–58 ºC	4.1± 0.1
–53 ºC	5.4± 0.0
–50 ºC	20 ± 0.4
–48 ºC	19 ± 0.5
–38 ºC	70 ± 0.1

[a] Values represent an average of two kinetics runs

Figure S2. Erying Plot for Carboxylate Exchange at **7**

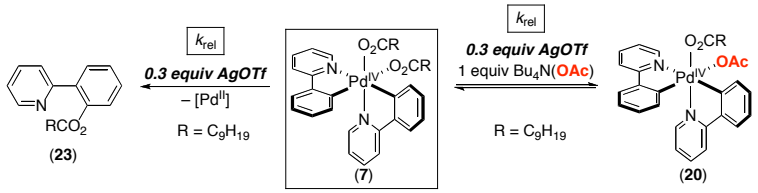


General Procedure for Kinetics with Acidic Additives



Carboxylate Exchange (HOAc). Complex **7** (5.8 mg, 0.0076 mmol, 1.0 equiv) was dissolved in acetone-d_6 (0.25 mL) in a screw cap NMR tube in a N_2-filled drybox. The NMR tube was sealed with a Teflon-lined cap fitted with a septum, and removed from the drybox. Bu_4NOAc (2.4 mg, 0.0076 mmol, 1.0 equiv) and a stock solution of AcOH (0.25 mL of a 14 mM stock solution in acetone-d_6, 0.0035 mmol, 0.5 equiv) was dissolved in the acetone-d_6 (0.25 mL) in a 4 mL vial, and the vial was sealed with a Teflon-lined cap fitted with a septum and removed from the glovebox. The solution in the NMR tube was frozen in liquid nitrogen, and the [Bu_4NOAc]/acid solution was added via syringe. The NMR tube was quickly shaken and placed in the NMR spectrometer where the probe had been pre-cooled to –35 ºC. The sample was allowed to equilibrate in the spectrometer for six minutes before acquiring spectra. Carboxylate exchange was studied by ^{1}H NMR spectroscopy by monitoring the disappearance of the most downfield signal (at 9.51 ppm in acetone-d_6). The reaction was followed until it reached equilibrium and then the data was fitted to a first order kinetics plot for a reversible reaction.[11] Each experiment was carried out in duplicate, and the *k* values represent an average of two runs.

Reductive Elimination (HOAc). Complex **7** (5.8 mg, 0.0076 mmol, 1.0 equiv) was dissolved acetone-d_6 (0.5 mL) in a screw cap NMR tube in a N_2-filled drybox. AcOH (0.5 mL of a 7 mM stock solution in acetone-d_6, 0.0035 mmol, 0.5 equiv) was then added. The tube was sealed with a Teflon-lined cap, shaken, and removed from the drybox. The tube was quickly placed in the NMR spectrometer, and the reaction was allowed to equilibrate for six minutes in the spectrometer before acquisition was started. The kinetics of reductive elimination was studied by ^{1}H NMR spectroscopy by monitoring the disappearance of the most downfield signal (at 9.51 ppm in acetone at 40 °C). The data was fit to a first order kinetics plot. Each experiment was carried out in duplicate, and the *k* values represent an average of two runs.



Carboxylate Exchange (AgOTf). Complex **7** (5.8 mg, 0.0076 mmol, 1.0 equiv) was dissolved in $CDCl_3$ (0.25 mL) in a 4 mL vial in a N_2-filled drybox. AgOTf was added to a screw cap NMR tube as a stock solution in THF (40 μL of a 50 mM stock solution, 0.50 mg, 0.002 mmol, 0.3 equiv). The solvent was then removed from the tube under high vacuum. The NMR tube was then transferred into a N_2-filled drybox and Bu_4NOAc (2.4 mg, 0.0076 mmol, 1.0 equiv) dissolved in 0.25 mL of $CDCl_3$ was added to the NMR tube, which was then sealed with a Teflon-lined cap fitted with a septum, and removed from the drybox. This solution was frozen in liquid N_2, and complex **7** (5.8 mg, 0.0076 mmol, 1.0 equiv) was dissolved in $CDCl_3$ (0.25 mL) and added to the NMR tube via syringe. The NMR tube was quickly shaken and placed in the NMR spectrometer where the probe had been pre-cooled to –53 ºC. The sample was allowed to equilibrate in the spectrometer for six minutes before acquiring spectra. Carboxylate exchange was studied by ^{1}H NMR spectroscopy by monitoring the disappearance of the most downfield signal (9.42 ppm in $CDCl_3$). The reaction was followed until it reached equilibrium and then the data was fitted to a first order kinetics plot for a reversible reaction.[11] Each experiment was carried out in duplicate, and the *k* values represent an average of two runs.

Reductive Elimination (AgOTf). AgOTf was added to a screw cap NMR tube as a stock solution in THF (40 μL of a 50 mM stock solution, 0.50 mg, 0.002 mmol, 0.3 equiv). The solvent was then removed from the tube under high vacuum. The NMR tube was transferred into a N_2-filled drybox. Complex **7** (5.8 mg, 0.0076 mmol, 1.0 equiv) was dissolved in $CDCl_3$ (0.5 mL) in a 4 mL vial and then transferred to the screw cap NMR tube that contained the AgOTf. The tube was sealed with a Teflon-lined cap, shaken, and removed from the drybox. The tube was quickly placed in the NMR spectrometer, and the reaction was allowed to equilibrate for six minutes in the spectrometer before acquisition was started. The kinetics of reductive elimination were studied by ^{1}H NMR spectroscopy by monitoring the disappearance of the most downfield signal (9.42 ppm in $CDCl_3$ at 23 °C). The data was fit to a first order kinetics plot. Each experiment was carried out in duplicate, and the *k* values represent an average of two runs.

Table S3. Effect of AcOH on C–O Bond-Forming Reductive Elimination and Carboxylate Exchange at **7**

Entry	Acid	k_{obs} C–O coupling, k (s^{-1} x 10^4)[a]	k_{obs} exchange, k (s^{-1} x 10^4)[b]
1	none	0.82 ± 0.0	0.33± 0.0
2	HOAc	2.9 ± 0.1	1.5± 1.5

[a] 40 ºC in acetone-d_6; [b] –35 ºC in acetone-d_6;

Table S4. Effect of AgOTf on C–O Bond-Forming Reductive Elimination and Carboxylate Exchange at **7**

Entry	Acid	k_{obs} C–O coupling, k (s^{-1} x 10^4)[a]	k_{obs} exchange, k (s^{-1} x 10^4)[b]
1	none	4.0 ± 0.2	54± 0.0
2	AgOTf	0.26± 0.1	6.2± 0.1

[a] 23 ºC in $CDCl_3$; [b] –53 ºC in $CDCl_3$

Figure S3. Representative Kinetics Data for Reductive Elimination of **7** with AcOH

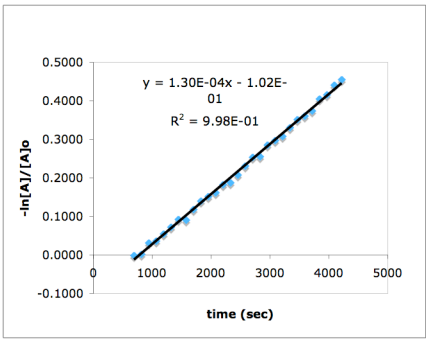
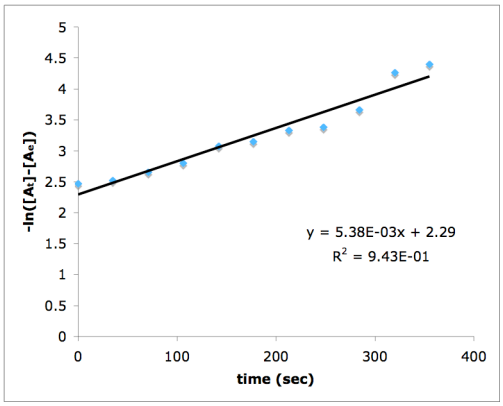
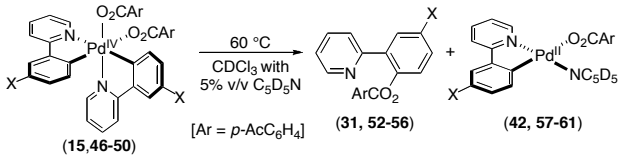


Figure S4. Representative Kinetics Data for Carboxylate Exchange at **7** with AgOTf



General Procedure for Studies of Arylpyridine Electronics



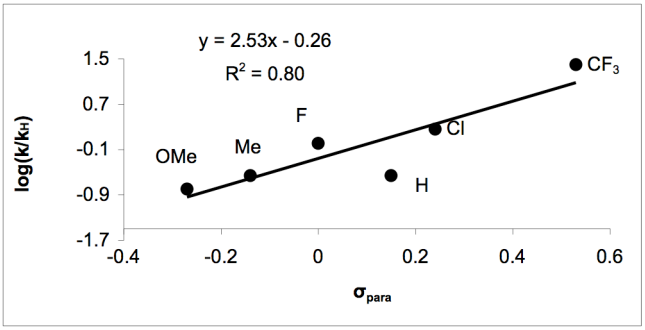
The Pd^{IV} complex (0.0076 mmol) was dissolved in $CDCl_3$ containing 5% by volume pyridine-d_5 (0.5 mL) in a screw cap NMR tube in a N_2-filled drybox. The tube was sealed with a Teflon-lined cap and removed from the drybox. The kinetics of carboxylate exchange were studied by ^1H NMR spectroscopy at 60 ºC by monitoring the disappearance of the most downfield resonance and the most upfield aromatic resonance of each complex. The rates of disappearance from these peaks were averaged. The data are summarized in Table S5. The data was fitted to a Hammett Plot with σ_{para} but only gave a moderate R squared value.

Table S5. Data for Hammett Plot of Arylpyridine Electronics

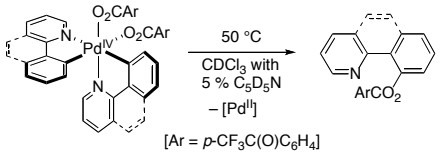
Compound	k_{obs} (s^{-1} x 10^5)	σ_{para}
*OMe	3.08	–0.27
Me	4.81	–0.14
H	20.0	0.00
F	3.64	0.15
Cl	36.9	0.24
*CF_3	323	1.4

* These complexes were studied but clean samples were not obtained.

Figure S5. Hammett Plot with σ_{para}



General Procedure for Rigidity Kinetics and C-O vs. C-C Product Formation:



Effect of Ligand Rigidity on Rate of Reductive Elimination. The Pd^{IV} complex (0.0076 mmol) was dissolved in $CDCl_3$ containing 5% by volume pyridine-d_5 (0.5 mL) in a screw cap NMR tube in a N_2-filled drybox. The tube was sealed with a Teflon-lined cap and removed from the drybox. The kinetics of reductive elimination was studied by ^1H NMR spectroscopy at 50 ºC by monitoring the disappearance of the most downfield resonance associated with each Pd^{IV} complex. Two trials were run and the rates of disappearance from the runs were averaged. The data are summarized in Table S6.

Table S6. Data for Ligand Rigidity Kinetics

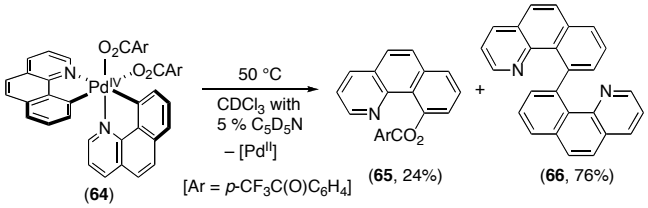
Substrate	k_{obs} (s^{-1} x 10^5)	k_{rel}
62	1.96 ± 0.1	1.9
63	1.06 ± 0.1	1.0
64	N/A	~0.1*

* The slow reaction rate along with competing C–C bond-formation prevented quantitative rate measurement in this system.

Competing C–C and C–O Bond-Forming Reductive Elimination

Observation of Competing C–O and C–C Bond-Forming Reductive Elimination from 64. Complex **64** (0.0076 mmol) was dissolved in $CHCl_3$ containing 5% by volume pyridine (0.5 mL) in a 4 mL vial in a drybox. The vial was sealed with a Teflon-lined cap, removed from the drybox, and heated at 50 ºC for 4 d. The solvent was removed under vacuum, and the resulting residue was taken up in CH_2Cl_2 (1 mL) and filtered through a plug containing 25% poly-4-vinylpyridine and 75% Celite. The plug was washed with CH_2Cl_2 (10 mL), the solvent was removed under vacuum, and the reaction was analyzed by ^1H NMR spectroscopy in $CDCl_3$. The ratio of C–O to C–C products for reductive elimination from **64** was determined by integration of signals at 8.54 ppm for **65** (C–O) and at 7.74 ppm for **66** (C–C). The results listed below represent the average of two trials.

Table S7. Competing C–O and C–C Bond-Forming Reductive Elimination from **64**



Complex	yield 65 : yield 66
64	24% : 76%

* average of two trials

Effect of Solvent on the Ratio of C–C versus C–O Bond-Forming Reductive Elimination

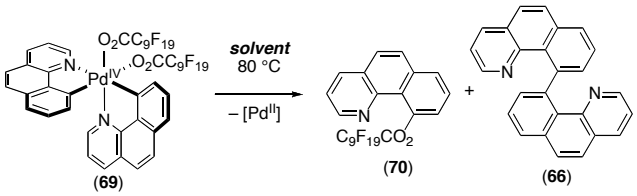
Complex **67** (6.1 mg, 0.0076 mmol) was dissolved in the appropriate solvent (0.5 mL) in a 4 mL vial in a drybox. The vial was sealed with a Teflon-lined cap, removed from the drybox, and heated at 80 ºC for 4 h. The solvent was removed under vacuum, and the resulting residue was taken up in CH_2Cl_2 (1 mL), and filtered through a plug containing 25% poly-4-vinylpyridine and 75% Celite. The plug was washed with CH_2Cl_2 (10 mL), the solvent was removed under vacuum, and the reaction was analyzed by ^{1}H NMR spectroscopy in acetone-d_6. The ratio of C–C to C–O products was determined by integration of signals at 8.93 ppm for **68** (C–O) and at 7.98-8.08 ppm for **66** (C–C). The results listed below represent the average of two trials.

Table S8. Effect of Solvent on the Product Ratio of Reductive Elimination from **67**

Solvent	Ratio 66 : 68
CH_3CN	0.25 : 1.0
$CHCl_3$	0.77 : 1.0
nitrobenzene	2.2 : 1.0
DMSO	3.3 : 1.0
acetone	13 : 1.0
benzene	> 20 : 1

* average of two trials

Effect of Carboxylate on the Ratio of C–C versus C–O Bond-Forming Reductive Elimination



(**69**) (**70**) (**66**)

Complex **69** (11.3 mg, 0.0076 mmol) was dissolved in the appropriate solvent (0.5 mL) in a 4 mL vial in a drybox. The vial was sealed with a Teflon-lined cap, removed from the drybox, and heated at 80 ºC for 8 d. The solvent was removed under vacuum, and the resulting residue was taken up in CH_2Cl_2 (1 mL), and filtered through a plug containing 25% poly-4-vinylpyridine and 75% Celite. The plug was washed with CH_2Cl_2 (10 mL), the solvent was removed under vacuum, and the reaction was analyzed by ^{1}H NMR spectroscopy in acetone-d_6. In all cases, the sole product observed was **66** (C–C).

Table S9. Solvent Effects on Product Distribution of Reductive Elimination from Complex **69**

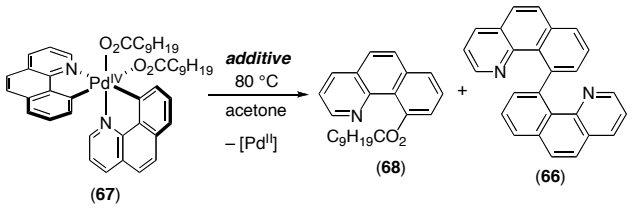
Solvent	Product
pyridine-d_5	**66**
acetone-d_6	**66**
DMSO-d_6	**66**
CD_3CN	**66**

Effect of Additives on the Relative Rates of C–C versus C–O Bond-Forming Reductive Elimination

Additive = AcOH. Complex **67** (6.1 mg, 0.0076 mmol, 1.0 equiv) was dissolved in acetone (0.5 mL) in a 4 mL vial in a drybox. AcOH (2.2 μL, 0.038 mmol, 5 equiv) was added, and then the vial was sealed with a Teflon-lined cap, removed from the drybox, and heated at 80 ºC for 3 h. The solvent was removed under vacuum, and the resulting residue was taken up in CH_2Cl_2 (1 mL), and filtered through a plug containing 25% poly-4-vinylpyridine and 75% Celite. The plug was washed with CH_2Cl_2 (10 mL), the solvent was removed under vacuum, and the reaction was analyzed by ^{1}H NMR spectroscopy in acetone-d_6. The ratio of C–C to C–O products was determined by integration of signals at 8.93 ppm for **68** (C–O) and at 7.98-8.08 ppm for **66** (C–C). The results listed below represent the average of two trials.

Additive = AgOTf. AgOTf was transferred to a 4 mL vial as a stock solution in THF (15.5 μL of a 50 mM stock solution, 0.20 mg, 0.00078 mmol, 0.1 equiv). The THF was removed under vacuum and then this vial was taken into the glove box. Complex **67** (6.1 mg, 0.0076 mmol, 1.0 equiv) and acetone were added to the vial, which was then sealed with a Teflon-lined cap, removed from the drybox, and heated at 80 ºC for 3 h. The solvent was removed under vacuum, and the resulting residue was taken up in CH_2Cl_2 (1 mL), and filtered through a plug containing 25% poly-4-vinylpyridine and 75% Celite. The plug was washed with CH_2Cl_2 (10 mL), the solvent was removed under vacuum, and the reaction was analyzed by ^{1}H NMR spectroscopy in acetone-d_6. The ratio of C–C to C–O products was determined by integration of signals at 8.93 ppm for **68** (C–O) and at 7.98-8.08 ppm for **66** (C–C). The results shown in Table S10 represent the average of two trials.

Table S10. Effect of Acidic Additives on the Product Ratio of Reductive Elimination from **67**



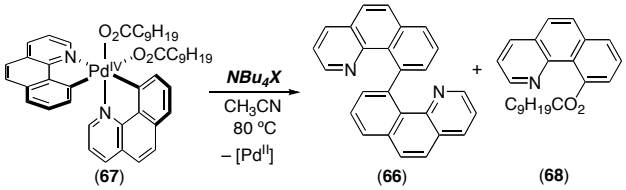
Entry	Additive	Ratio 66 : 68
1	none	13 : 1
2	AcOH (5.0 equiv)	3.6 : 1
3	AgOTf (0.1 equiv)	0.10 : 1

* average of two trials

Additive = NBu$_4$X. Complex **67** (6.1 mg, 0.0076 mmol, 1.0 equiv) was dissolved in CH_3CN (0.5 mL) in a 4 mL vial in a drybox. BuN_4X (0.0076 mmol, 1.0 equiv) was added. The vial was sealed with a Teflon-lined cap, removed from the drybox, and heated at 80 ºC for 3 h. The solvent was removed under vacuum, and the resulting residue was taken up in CH_2Cl_2 (1 mL), and filtered through a plug containing 25% poly-4-vinylpyridine and 75% Celite. The plug was

washed with CH_2Cl_2 (10 mL), the solvent was removed under vacuum, and the reaction was analyzed by ^{1}H NMR spectroscopy in acetone-d_6. The ratio of C–C to C–O products was determined by integration of signals at 8.93 ppm for **68** (C–O) and at 7.98-8.08 ppm for **66** (C–C). The results listed in Table S11 represent the average of two trials.

Table S11. Effect of $NBu_4(O_2CC_9H_{19})$ on the Product Distribution for Reductive Elimination from **67**

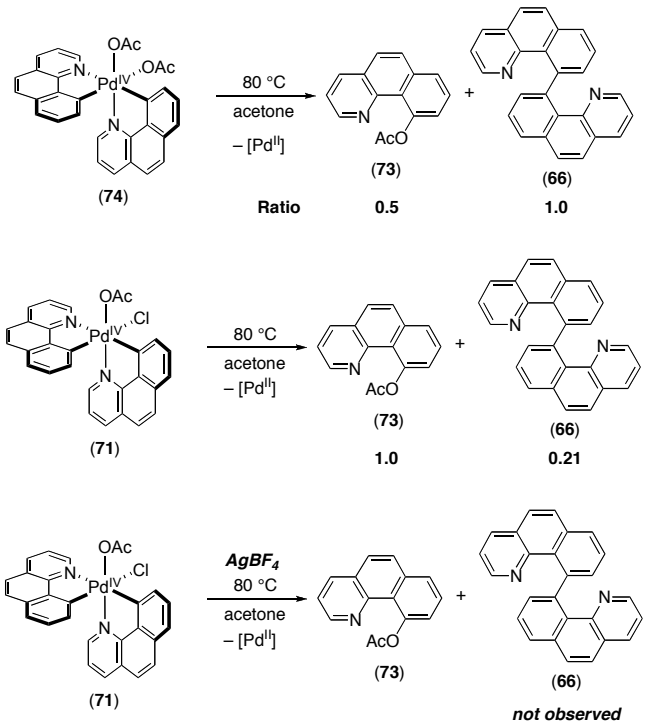


(**67**) (**66**) (**68**)

Entry	Additive	Ratio 66 : 68
1	none	0.2 : 1
2	$Bu_4N(O_2CC_9H_{19})$	2 : 1
3	$Bu_4N(PF_6)$	0.2 : 1

* average of two trials

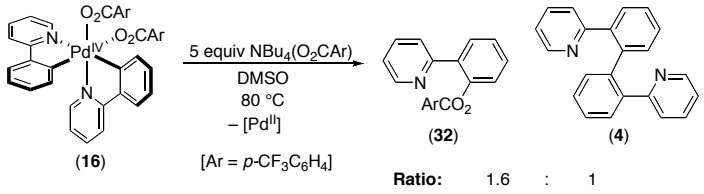
Study of the Reductive Elimination from 71 with $AgBF_4$



Complex **71** (4.2 mg, 0.0076 mmol, 1.0 equiv) or complex **74** (4.4 mg, 0.0076 mmol, 1.0 equiv) was dissolved in acetone (0.5 mL) in a 4 mL vial. The vial was sealed with a Teflon-lined cap and heated at 80 ºC for 3 h. The solvent was removed under vacuum, and the resulting residue was taken up in CH_2Cl_2 (1 mL), and filtered through a plug containing 25% poly-4-vinylpyridine and 75% Celite. The plug was washed with CH_2Cl_2 (10 mL), the solvent was removed under vacuum, and the reaction was analyzed by ^1H NMR spectroscopy in $CDCl_3$. The ratio of C–C to C–O products was determined by integration of signals at 7.61 ppm for **68** (C–O) and at 7.98-8.08 ppm for **66** (C–C). The hydrolysis product was observed in varying quantities after workup, when this was the case the integral at 8.84 ppm (for the OH product) was added to the peak for product **68**. The ratios listed represent the average of two trials.

Complex **73** (4.2 mg, 0.0076 mmol, 1.0 equiv) was dissolved in acetone (0.5 mL) in a 4 mL vial. $AgBF_4$ (1.5 mg, 0.0076 mmol, 1.0 equiv) was added to the vial and then, was sealed with a Teflon-lined cap and heated at 80 ºC for 3 h. The solvent was removed under vacuum, and the resulting residue was taken up in CH_2Cl_2 (1 mL), and filtered through a plug containing 25% poly-4-vinylpyridine and 75% Celite. The plug was washed with CH_2Cl_2 (10 mL), the solvent was removed under vacuum, and the reaction was analyzed by ^1H NMR spectroscopy in $CDCl_3$. The ratio of C–C to C–O products was determined by integration of signals at 7.61 ppm for **68** (C–O) and at 7.98-8.08 ppm for **66** (C–C). The hydrolysis product was observed in varying quantities after workup, when this was the case the integral at 8.84 ppm (for the OH product) was added to the peak for product **68**. The ratios listed represent the average of two trials.

Observation of C–C Bond-Forming Reductive Elimination at Phenylpyridine Complex 16



Complex **16** (6.8 mg, 0.0080 mmol, 1.0 equiv) was dissolved in DMSO (0.5 mL) in a 4 mL vial in a drybox. $Bu_4N(O_2C(p\text{-}CF_3C_6H_4))$ (19 mg, 0.039, 5.0 equiv) was added. The vial was sealed with a Teflon-lined cap, removed from the drybox, and heated at 80 ºC for 5 h. The solvent was removed under vacuum, and the resulting residue was taken up in CH_2Cl_2 (2 mL), and filtered through a plug containing 25% poly-4-vinylpyridine and 75% Celite. The plug was washed with CH_2Cl_2 (12 mL), the solvent was removed under vacuum, and the reaction was analyzed by ^1H NMR spectroscopy in acetone-d_6. The ratio of C–C to C–O products was determined by integration of signals at 8.48 ppm for **32** (C–O) and at 8.36 ppm for **4** (C–C). The results listed below represent the average of two trials.

Table S12. Data for C-C vs. C-O Product Formation with Additive

Trial	Ratio 32 : 4
Additive	1.0 : 1.6
No Additive	0.0 : 1.0

* average of two trials

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