Autocatalytic Oxidative Addition of PhBr to $Pd(P^tBu_3)_2$ via $Pd(P^tBu_3)_2(H)(Br)$

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

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

Supporting information.

General methods. All manipulations were conducted in an inert atmosphere dry box or using standard Schlenk techniques unless otherwise specified. ^1H spectra were recorded on a 400 or 500 MHz spectrometer; ^{13}C spectra were recorded at 125 MHz with solvent resonances as reference; $^{31}P\{^1H\}$ NMR spectra were recorded at 160 or 200 MHz with external H_3PO_4 as a reference. Toluene, dichloromethane, THF, diethyl ether, and pentane were dried with a solvent purification system by percolation through neutral alumina under positive pressure of argon. 2-butanone was purchased from Aldrich (ACS grade) and dried over anhydrous calcium sulphate. The complexes $Pd(P^tBu_3)_2$[1] (**1**), $(P^tBu_3)Pd(Ph)(Br)$[2] (**2**), and $(P^tBu_3)_2Pd(H)(Br)$[3] (**3**) were prepared by published procedures. The complex $[(P^tBu_3)Pd(\mu\text{-}Br)]_2$[4] (**4**) was obtained from Johnson Matthey. All other reagents were obtained from commercial sources and used without further purification.

Independent synthesis of P^tBu_3·HBr (6). P^tBu_3 (100 mg, 0.49 mmol) and pyridinium bromide (72 mg, 0.45 mmol) were weighed into a small vial. Acetonitrile (2 mL) was added, and the mixture was stirred until the solution was homogeneous, at which time 5 mL of ether were added. Upon addition of the ether, a white solid precipitated immediately. The product was

separated by filtration, rinsed with ether, and dried under vacuum to give 117 mg of the phosphonium salt (92 % yield). ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 8.57 (d, J = 472 Hz, 1H), 1.63 (d, J = 14.9 Hz, 27H); ^{13}C NMR (CD_2Cl_2, 125 MHz) δ 37.28 (d, J = 28.0 Hz), 30.44; ^{31}P{^{1}H} NMR (CD_2Cl_2, 165 MHz) δ 40.97. Anal. calcd. for $C_{12}H_{28}BrP$: C, 50.89; H, 9.96. Found: C, 50.84; H, 10.16.

Independent synthesis of [Pd(P(*t*-Bu)$_3$)$_2$(C(CH$_3$)$_2$CH$_2$)(μ-Br)]$_2$ (5).[3,5] Inside the glove box, the palladium(I) dimer [Pd(P^{t}Bu$_3$)(μ-Br)]$_2$ (**4**) (200 mg, 0.26 mmol) was weighed into a small vial and dissolved in 2.0 mL of dry toluene. The solution was stirred at 80 °C for 2 h. The vial was then opened to air, and the reaction mixture was filtered through a plug of Celite to separate the dark solid from the orange solution. The solvent was evaporated under vacuum to yield an orange residue. The residue was dissolved in CH_2Cl_2, and the resulting solution flushed through a plug of silica. The methylene chloride solution was concentrated to about 0.5 ml, layered with pentane, and placed in the freezer at -35 °C overnight. Yellow crystalline product formed, which was collected by filtration and dried under vacuum to afford 81 mg of dimeric complex (40% yield). ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 1.56 (d, J = 14.0 Hz, 18H), 1.48 (d, J = 14.5 Hz, 6H), 1.15 (b, 2H); ^{13}C NMR (C_6D_6, 125 MHz) δ 50.12 (d, J = 18.7 Hz), 38.83 (d, J = 9.4 Hz), 32.45 (d, J = 2.8 Hz), 31.52, 14.18 (d, J = 27.2 Hz); ^{31}P{^{1}H} NMR (CD_2Cl_2, 165 MHz) δ -8.44. Anal. Calcd. for $C_{12}H_{26}BrPPd$: C, 37.18; H, 6.76. Found: C, 37.35; H, 6.55.

Independent synthesis of (HP^{t}Bu$_3$)$_2$[PdBr$_4$] (7). Into a small vial was weighed P^{t}Bu$_3$·HBr (**6**) (42 mg, 0.15 mmol) and $PdBr_2$ (18 mg, 0.068 mmol). The solids were mixed with 2 mL of THF and 100 μL of MeCN. The reaction mixture was stirred at room temperature, and the orange

product precipitated from solution. The reaction should be stirred until the dark starting palladium salt can no longer be observed (approximately 1 h). After this time, the orange solid was isolated by filtration, rinsed with pentane, and dried under vacuum to afford 49 mg of product (87 % yield). ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 8.19 (d, J = 467.0 Hz, 1H), 1.77 (d, J = 15.0 Hz, 27H) ; ^{13}C NMR (CD_2Cl_2, 125 MHz) δ 37.97 (d, J = 28.0 Hz), 30.90; ^{31}P{^{1}H} NMR (CD_2Cl_2, 165 MHz) δ 44.52. Anal. calcd. for $C_{24}H_{56}Br_4P_2Pd$: C, 34.62; H, 6.78. Found: C, 34.34; H, 6.71.

General procedure for kinetic experiments. The amounts and reagents used to prepare each sample are described below. The solvents and bromoarenes were added to the samples with a micropipette or microliter syringe. The sample solutions were transferred to a screw top NMR tube and sealed with a cap containing a Teflon-lined septum. A sealed capillary tube with a THF or DMF solution of H_3PO_4 (0.35 M) was placed inside the NMR tube as an external standard for calculation of yields and conversions. 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.

Representative procedure for the reaction of PhBr with 1. Complex $Pd(P^tBu_3)_2$ (**1**) was weighed into a small vial (10 mg, 0.020 mmol) and dissolved in a mixture of 400 μL of THF (or

toluene) and 100 μL PhBr (0.95 mmol). The sample was handled following the general procedure for the kinetic experiments described above. The reaction was performed at 70 °C.

Reaction of PhBr with 1 in 2-butanone. Complex $Pd(P^tBu_3)_2$ (**1**) was weighed into a small vial (10 mg, 0.020 mmol) and a mixture of 400 μL of 2-butanone and 100 μL PhBr (0.95 mmol) was then added. The mixture was heated briefly with a heat gun to facilitate dissolution of **1** and immediately transferred to an NMR tube. A sealed capillary tube with a DMF solution of H_3PO_4 (0.35 M) was placed inside the NMR tube to be used as an external standard for calculation of yields and conversions. The reaction was performed at 70 °C.

Representative procedure for the reaction of 1 with PhBr in the presence of additives. Into a small vial, 8 mg (0.01 mmol) of $[Pd(P^tBu_3)(\mu\text{-}Br)]_2$ (**4**) were weighed. This material was dissolved in 1.0 mL of toluene to prepare a 0.010 M stock solution. Into a separate vial, was weighed 10 mg (0.020 mmol) of $Pd(P^tBu_3)_2$ (**1**). To this vial was added 100 μL of the stock solution of $[Pd(P^tBu_3)(\mu\text{-}Br)]_2$ (0.001 mmol), 300 μL of toluene and 100 μL PhBr (0.95 mmol). The sample was handled following the general procedure for the kinetic experiments described above. The reaction was heated at 70 °C.

Representative procedure for the reaction of 1 with PhBr in the presence of tetraalkylammonium salt. $Pd(P^tBu_3)_2$ (**1**) (10 mg, 0.020 mmol) and $N(butyl)_4Br$ (3 mg, 0.01 mmol) were weighed into a small vial and dissolved in 400 μL of THF and 100 μL PhBr (0.95 mmol). The sample was handled following the general procedure for the kinetic experiments described above and the reaction was heated at 70 °C.

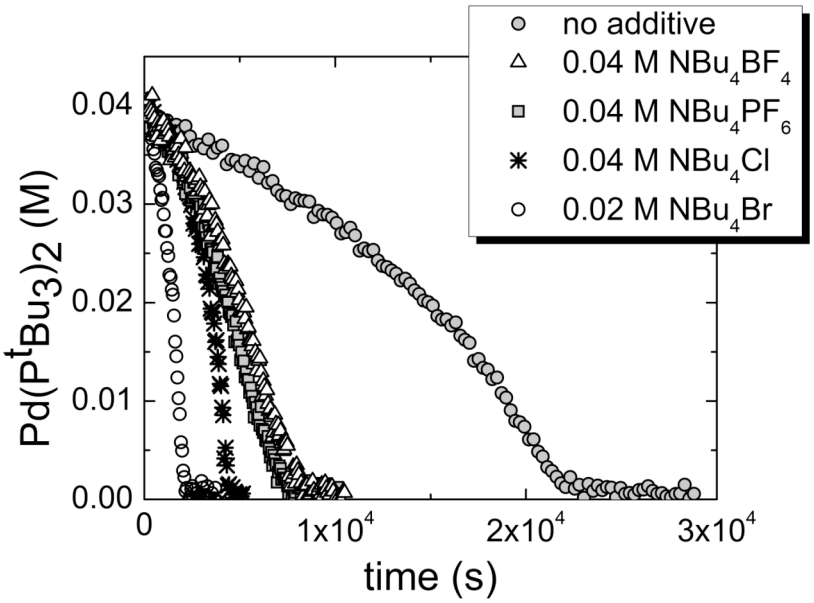

Figure S1. Decay of $Pd(P^tBu_3)_2$ (**1**) (0.039 M) during the oxidative addition of PhBr (0.95 M) in toluene at 70 °C in the presence of additives.

Representative procedure for the reaction of 1 with PhBr in the presence of trialkylammonium salts. NEt_3·HBr (4 mg, 0.02 mmol) was weighed into a small vial and dissolved in 2.0 mL of THF to prepare a 0.010 M stock solution. Into a separate vial was weighed 10 mg (0.02 mmol) of $Pd(P^tBu_3)_2$ (**1**). To this vial was added 100 μL of the stock solution of NEt_3·HBr (0.001 mmol), 300 μL of THF, and 100 μL PhBr (0.95 mmol). The sample was handled following the general procedure for the kinetic experiments described above. The reaction was heated at 70 °C.

Reaction of PhBr with a 1:1 mixture of 1 and 3. Into a small vial, was weighed 10 mg of **1** (0.020 mmol) and 12 mg of **3** (0.020 mmol). The complexes were dissolved in 400 μL of toluene and 100 μL PhBr. The sample was handled following the general procedure for the kinetic

experiments described above, and the reaction was heated at 70 °C. A plot of the concentrations of **1** and **3** vs time is shown in Figure S1.

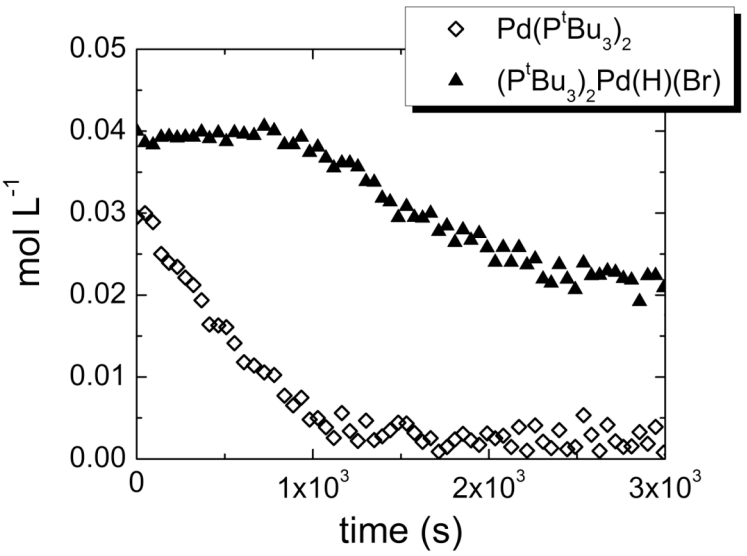

Figure S2. Decay of a 1:1 mixture of Pd(P^{t}Bu$_3$)$_2$ (**1**) (0.039 M) and (P^{t}Bu$_3$)$_2$Pd(H)(Br) (**3**) (0.041 M) during oxidative addition of PhBr (0.95 M) in toluene at 70 ^{o}C.

Thermolysis of arylpalladium halide complex 2: Complex **2** (10 mg, 0.020 mmol) and 1,3,5-trimethoxybenzene (2 mg, 0.012 mmol) were dissolved in 500 μL toluene-d_8 and heated in a sealed NMR tube at 50 ^{o}C. Degradation of the starting complex was monitored by ^{1}H and ^{31}P NMR spectroscopy. After 2.5 hours approximately 49% conversion of **2** occurred by ^{1}H NMR, and the μ-Br dimer **4** was the major new species observed by ^{31}P NMR, present in a 1:1.29 ratio with unreacted **2**. The complexes **1** and **3** were also observed in minor amounts (0.12:1 and 0.07:1 ratios versus unreacted **2**, respectively). Additionally, several organic products of decomposition were observed by ^{1}H NMR: benzene (6%), bromobenzene (4%), and biphenyl (20%) based on **2**.

Representative procedure for the reaction of PhBr with 3. ($P^tBu_3)_2Pd(H)(Br)$ (**3**) (12 mg, 0.020 mmol) was weighed into a small vial and dissolved in 400 μL of degassed toluene (or THF or MEK) and 100 μL PhBr (0.95 mmol). The sample was handled following the general procedure for the kinetic experiments described above. The reaction was heated at 70 °C. During the course of the reaction in toluene, a dark orange crystalline solid formed in the NMR tube. After cooling, the solid was isolated by removal of solvent from the tube via syringe. The solid was then triturated with 1 mL of toluene followed by 4x1 mL triturations with pentane. The solid was then removed from the NMR tube and dried under vacuum giving 5 mg (18%) $(HP^tBu_3)_2[PdBr_4]$ (**7**). ^{1}H NMR (acetone-d_6, 500 MHz) δ 8.27 (d, J = 465.0 Hz, 1H), 1.86 (d, J = 15.0 Hz, 27H) ; $^{31}P\{^1H\}$ NMR (acetone-d_6, 200 MHz) δ 45.90. Anal. calcd. for $C_{24}H_{56}Br_4P_2Pd$: C, 34.62; H, 6.78. Found: C, 34.62; H, 6.75.

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