Oxidative Addition of Phenyl Bromide to Pd(BINAP) vs Pd(BINAP)(amine). Evidence for Faster Adddition to Pd(BINAP)

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Supporting Information

Experimental Section.

General Considerations. All manipulations were conducted in an inert atmosphere glovebox. UV-visible spectra were collected on a Varian Cary 3E spectrophotometer equipped with a thermostated multicell block. Unless stated otherwise, all reagents were purchased from commercial suppliers and used without further purification. $Pd(BINAP)_2$ was prepared using a literature procedure.[16] THF was distilled from a purple solution of sodium benzophenone ketyl. Octylamine and *N*-methylpiperazine were distilled from CaH_2. Bromobenzene was distilled and filtered through basic alumina prior to use.

Kinetic Measurements of the Oxidative Addition of PhBr to $[Pd(BINAP)_2]$ by UV-VIS spectroscopy. Separate stock solutions of 1.7 x 10^{-4} M $[Pd(BINAP)_2]$ and 2.05 x 10^{-2} M BINAP were prepared. For experiments to determine the order of the reaction of $[Pd(BINAP)_2]$ with PhBr in the concentration of BINAP in the *absence* of amine, 1 mL of the solution of $[Pd(BINAP)_2]$ (1.7 x 10^{-7} mol), and 3.0 μL [PhBr] (2.8 x 10^{-5} mol) were added to a 5 ml volumetric flask. To these solutions were added 4000-1400 μL samples of the solution of BINAP. To the resulting solution was added enough toluene to bring the volume to the 5 mL mark. The final concentrations were then 3.4 x 10^{-5} M $[Pd(BINAP)_2]$, 5.7 x 10^{-3} M PhBr and 1.6 x 10^{-3} M – 5.7 x 10^{-3} M BINAP.

For experiments to determine the order of the reaction of $[Pd(BINAP)_2]$ with PhBr in the concentration of BINAP in the *presence* of amine, 1 μL of the solution of $[Pd(BINAP)_2]$ (1.7 x 10^{-7} mol), and 3.0 μL of [PhBr] (2.8 x 10^{-5} mol), and 275 μL of *N*-methylpiperazine were added to a 5 ml volumetric flask. To these solutions were added 300-2000 μL samples of the solution of BINAP. To the resulting solution was added enough toluene to bring the volume to 5 mL mark. The final concentrations were then 3.40×10^{-5} M [Pd(BINAP)$_2$], 5.7×10^{-3} M PhBr, 0.50 M *N*-methylpiperazine and 1.2×10^{-4} M – 8.2×10^{-3} M BINAP.

For experiments to determine the order of the reaction of [Pd(BINAP)$_2$] with PhBr (5.7 mM) in the concentration of amine, separate stock solutions of 1.7×10^{-4} M [Pd(BINAP)$_2$] and 0.041 M BINAP were prepared and 1 μL of the solution of [Pd(BINAP)$_2$] (1.7×10^{-7} mol), 3 ml of the solution of BINAP (1.2×10^{-4} mol) and 3 μL of [PhBr] (2.8×10^{-5} mol) were added to a 5 ml volumetric flask. To these solutions were added 0-825 μL samples of octylamine or 0-555 μL of *N*-methylpiperazine. To the resulting solution was added enough toluene to bring the volume to the 5 mL mark. The final concentrations were then 3.4×10^{-5} M [Pd(BINAP)$_2$], 5.7×10^{-3} M PhBr, 0.025 M BINAP and 0 M – 1.0 M amine.

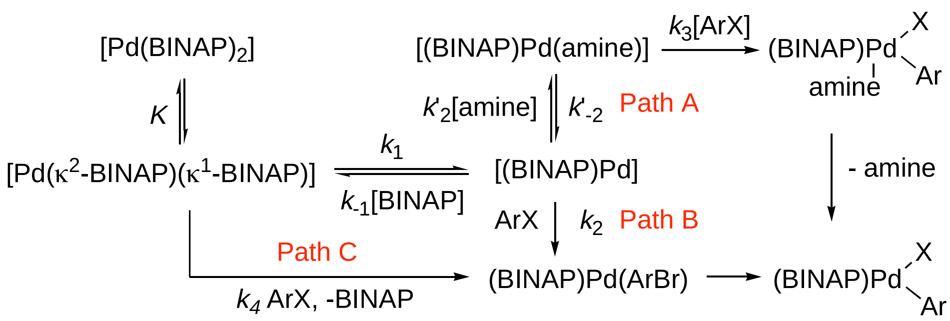
For experiments to determine the order of the reaction of [Pd(BINAP)$_2$] with PhBr (0.50 M) in the concentration of amine, separate stock solutions of 1.7×10^{-4} M [Pd(BINAP)$_2$] and 0.021 M BINAP were prepared and 1 μL of the solution of [Pd(BINAP)$_2$] (1.7×10^{-7} mol), 100 μl of the solution of BINAP (2.1×10^{-6} mol) and 274 μL of [PhBr] (2.6×10^{-3} mol) were added to a 5 ml volumetric flask. To these solutions were added 0-555 μL samples of *N*-methylpiperazine. To the resulting solution was added enough toluene to bring the volume to the 5 mL mark. The final concentrations were then 3.4×10^{-5} M [Pd(BINAP)$_2$], 0.50 M PhBr, 4.11×10^{-4} M BINAP and 0 M – 1.0 M amine.

The resulting solutions were shaken and transferred to quartz cuvettes attached to airtight Teflon valves. The cell block of the UV-visible spectrometer was heated at 60 °C or 70 °C. The absorbance of [Pd(BINAP)$_2$] was monitored at λ = 519 nm, with a 1 s signal averaging time and 60, 120 or 300 s between acquisitions over at least four five half-lives. Kinetic data were fit to the expression $A_{519} = Be^{kt} + c$, in which k is the pseudo-first-order rate constant k_{obs}.

Determination of k_{obs} for Reaction of [Pd(BINAP)$_2$] with *tol*-BINAP in the absence of amine and in the presence of octylamine and N-methylpiperazine. Samples were prepared by weighing 4.3 mg of Pd(BINAP)$_2$ and 17 mg of *tol*-BINAP directly into NMR sample tubes equipped with air-tight Teflon valves. For experiments to determine k_{obs} in the *presence* of amine, octylamine (50 μL) or *N*-methylpiperazine (33 μL) was added to the NMR tube. The appropriate amount of THF was added with an air-tight syringe to create a total volume of 0.60 mL in each NMR sample tube. The final concentrations of Pd(BINAP)$_2$ and *tol*-BINAP were 5.3 and 43 mM respectively in all experiments, and the final concentrations of octylamine and N-methylpiperazine were 0.50 M. The decay of [Pd(BINAP)$_2$] and accumulation of [Pd(*tol*-BINAP)$_2$] and [Pd(*tol*-BINAP)(BINAP)] was monitored by ^{31}P NMR spectroscopy at 45 °C.

Derivation of rate equations for Scheme 1

Scheme 1



For Path B and Path C

$$k_{obs} = \frac{Kk_1k_2[\text{ArX}]}{k_2[\text{ArX}] + k_{-1}[\text{BINAP}]} + Kk_4[\text{ArX}] \quad \text{(S1)}$$

under conditions in which k_{-1}[BINAP] >> k_2[ArX] (phosphine dissociation is reversible), then

$$k_{obs} = \frac{Kk_1k_2[\text{ArX}]}{k_{-1}[\text{BINAP}]} + Kk_4[\text{ArX}] \quad \text{(S2)}$$

For Path A

$$k_{obs} = \frac{Kk_1k'_2k_3[\text{ArX}][\text{amine}]}{k_{-1}k'_{-2}[\text{BINAP}] + k_3k_{-1}[\text{ArX}][\text{BINAP}] + k'_2k_3[\text{amine}][\text{ArX}]} \quad \text{(S3)}$$

under conditions in which k_{-1}[BINAP] >> k'_2[amine] and k'_{-2} >> k_3[ArX] (phosphine dissociation and amine coordination are reversible), then

$$k_{\text{obs}} = \frac{k_1k'_2k_3[\text{amine}][\text{ArX}]}{k_{-1}k'_{-2}[\text{BINAP}]} \quad \text{(S4)}$$

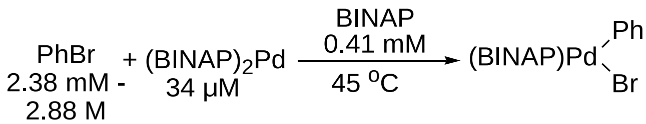
For the combination of Path A, B and C

$$k_{obs} = \frac{Kk_1k_2[\text{ArX}](k'_{-2} + k_3[\text{ArX}])}{(k_{-1}[\text{L}] + k_2[\text{ArX}] + k'_2[\text{amine}])(k'_{-2} + k_3[\text{ArX}]) - k'_{-2}k'_2[\text{amine}]} + Kk_4[\text{ArX}]$$

$$+ \frac{Kk_1k_2k_3[\text{ArX}][\text{amine}]}{(k_{-1}[\text{L}] + k_2[\text{ArX}] + k'_2[\text{amine}])(k'_{-2} + k_3[\text{ArX}]) - k'_{-2}k'_2[\text{amine}]} \quad \text{(S5)}$$

under conditions in which k_{-1}[BINAP] >> k'_2[amine] and k'_{-2} >> k_3[ArX] (phosphine dissociation and amine coordination are reversible), then

$$k_{obs} = \frac{Kk_1k_2[\mathrm{ArX}]}{k_{-1}[\mathrm{BINAP}]} + Kk_4[\mathrm{ArX}] + \frac{Kk_1k'_2k_3\,[\mathrm{ArX}][\mathrm{amine}]}{k_{-1}k'_{-2}[\mathrm{BINAP}]} \qquad \text{(S6)}$$



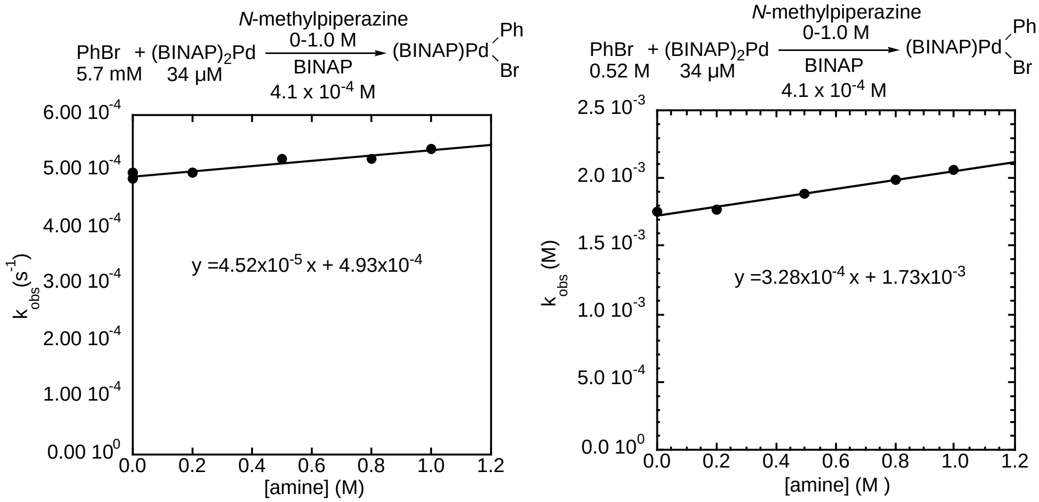


Figure S1. Plots that compare the effect of *N*-methylpiperazine on the observed rate constant of reactions conducted with low and high concentrations of PhBr. Left: k_{obs} vs [*N*-methylpiperazine] for the reaction of PhBr (5.7 x 10^{-3} M) with $Pd(BINAP)_2$ (3.4 x 10^{-5} M) in the presence of BINAP (4.1 x 10^{-4} M) at 60 °C. Right: k_{obs} vs [*N*-methylpiperazine] for the reaction of PhBr (0.50 M) with $Pd(BINAP)_2$ (3.4 x 10^{-5} M) in the presence of BINAP (4.1 x 10^{-4} M) at 60 °C.

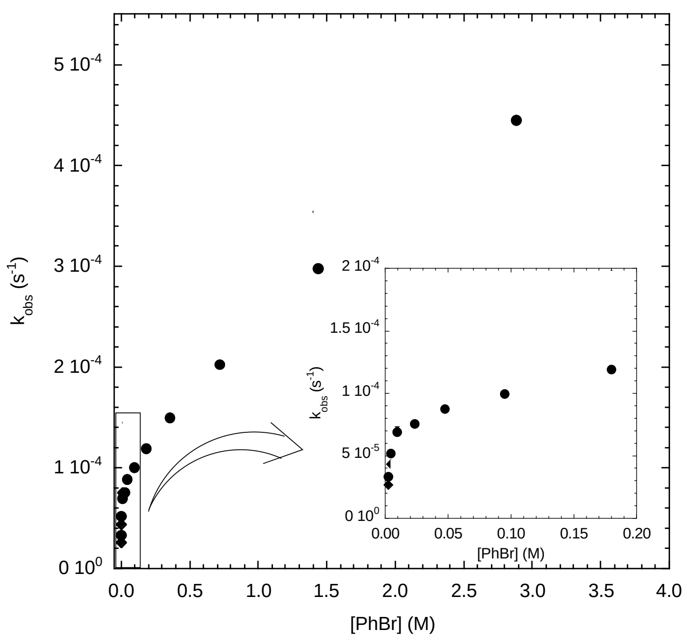


Figure S2. Plot of k_{obs} vs [PhBr] for the reaction of $[Pd(BINAP)_2]$ (3.40 x 10^{-5} M) with PhBr (2.88 x10^{-3}-2.88 M) in the presence of added BINAP (4.11 x 10^{-4} M) at 45° C. The inset provides an expanded view of the data obtained from reactions conducted with concentrations of PhBr below 0.20 M.

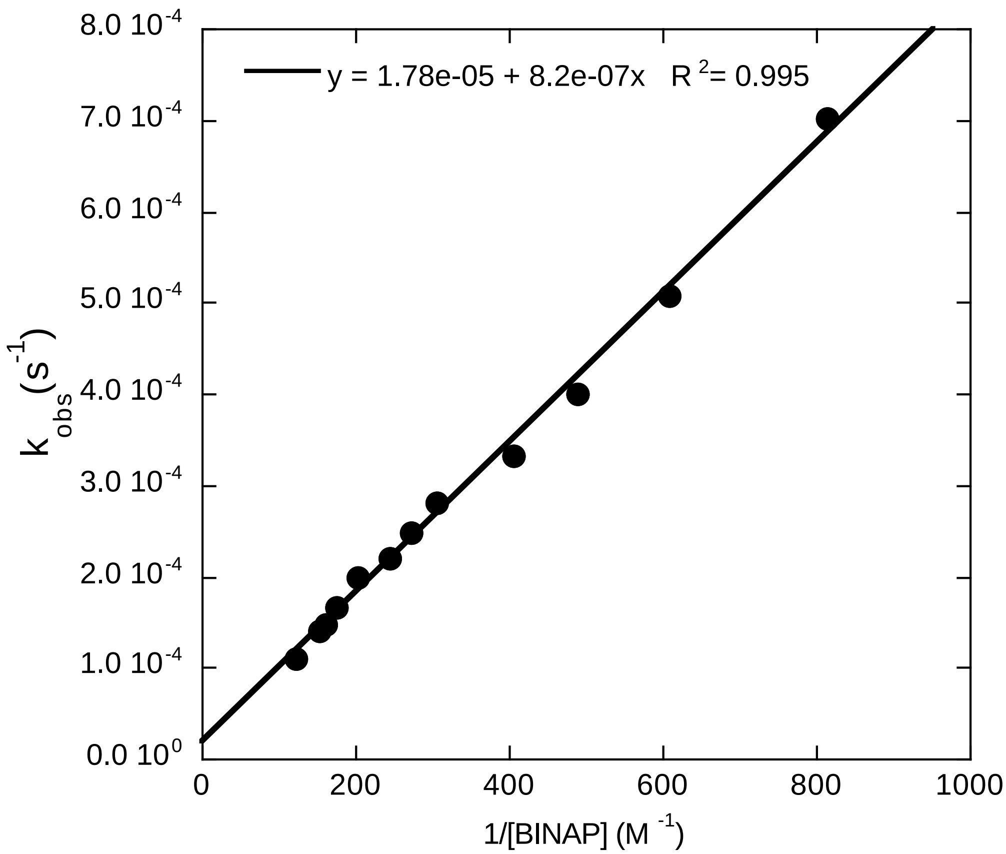


Figure S3. Plots of k_{obs} vs 1/[BINAP] for the reaction of $Pd(BINAP)_2$ (3.4 x 10^{-5} M) with 3-bromoanisole (4.7 x 10^{-3} M) in the presence BINAP (1.2 x 10^{-3}–8.2 x 10^{-3} M) at 70 ^{o}C.