Supporting Information for:
Mechanistic Inferences Derived from Competitive Catalytic Reactions:
Pd(binap)-Catalyzed Amination of Aryl Halides

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**Instrumentation**

Reactions were carried out in an Omnical Insight CPR 220 reaction calorimeter, in which the instantaneous enthalpy balance around the vessel was continuously monitored. The sample vessel was a 15 ml septum-cap vial, and the volume of the reactive solution was approximately 5 ml. The data was then manipulated using the ‘Reaction progress kinetic analysis’ technique as described in Ref. 6.

**Materials**

Anhydrous toluene was purchased from Aldrich and stored over molecular sieves. The sodium-tert-butoxide (Aldrich) was stored in a glove box and vacuum dried prior to use; the Benzophenone Hydrazone (Acros) was stored in a fridge and used without further purification. Tridecane (Aldrich), Palladium Acetate (Sigma-Aldrich) and BINAP (Aldrich) were used as received.

**Standard conditions**

In the competitive reaction the Palladium acetate (10.1 mg, 0.045 mmol), Binap (38.4 mg, 0.06 mmol), Sodium-tert-butoxide (269 mg, 2.8 mmol), Benzophenone Hydrazone (244.9 mg, 1.25 mmol), Hexylamine (129.7 mg, 1.28 mmol), Tridecane (149.6 mg, 0.811 mmol) as the internal standard, were added together to the reaction vessel, which was then placed in the calorimeter and heated to 90°C. A thermically equilibrated 3-Bromobenzotrifluoride (524.6 mg, 2.33 mmol) was injected to the thermically equilibrated reaction mixture after 60 minutes. The final conversion was measured by GC on a quenched sample.

**Sampling experiment**

A sampling experiment was performed to verify that the conversion calculated from the calorimetric data was equal to the conversion calculated from GC. Samples were taken at regular intervals, quenched in water/toluene mixture at ambient temperature and analyzed by GC.

For the Benzophenone reaction the conversion was calculated from the equation: $X_{Benz} = \frac{n_{Benz} - n_{Halide}}{n_{0}^{Halide}}$; for the Hexylamine reaction the equation was:
The conversion of the Halide was the sum of these two conversions:

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X^\text{Hexyl} = \frac{H^\text{Hexyl product}}{H_0^\text{Halide}}. 
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X^\text{Halide} = X^\text{Benz} + X^\text{Hexyl}. 
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**Preliminary NMR experiments**

The \(^{31}\text{P}\) and \(^{19}\text{F}\) NMR spectra were recorded on a Bruker 400MHz Avance spectrometer at 278 K (\(^{31}\text{P}, 161.98 \text{ MHz} / ^{19}\text{F}, 376.50 \text{ MHz}\)). In all the measurements toluene was used as the solvent.

The \(^{19}\text{F}\) NMR spectrum of pure samples of the 3-Bromobenzotrifluoride and of the Benzophenone Hydrazone and Hexylamine’s products showed peaks at \(\delta 63.17, \delta 62.85, \delta 62.87\) respectively. The \(^{31}\text{P}\) NMR of pure BINAP and Pd(BINAP)\(_2\) showed signals at \(\delta -13.8\) and \(\delta 27.4\) respectively.

The competitive experiment was done according to the procedure described for reaction calorimetry, under a continuous flow of nitrogen. Samples were taken during the reaction and cooled down before recording the NMR spectra. Air was excluded from the NMR tubes.

**Mass electrospray measurements**

Mass spectrometry measurements were performed with a TOF (time of flight) electrospray method, using a Micromass Q-TOF global tandem mass spectrometer.

In order to prepare the complex, a solution containing the catalyst [Pd(BINAP)\(_2\)], benzophenone hydrazone, 3-bromobenzotrifluoride and sodium-tert-butoxide was heated up to 60°C. At this temperature the amination reaction does not occur, but the complexes involved in the reaction still form.

A NMR spectrum of the solution was taken before the mass measurement.
Four species were identified. Two of these species are already known: pure BINAP and Pd(BINAP)$_2$ 4'.

The two doublets refer to the Pd(BINAP)$_2$ complex 6b we are trying to identify.

The fourth peak might refer to a methanol related complex (methanol is involved in the synthesis of Pd(BINAP)$_2$; there usually are traces of methanol in the toluene as well).

The (BINAP)Pd(amine)Ar which we proposed as the catalyst resting state (6b) has a mass of 1068.

The spectrum is shown in the following figure:
The spectrum shows many peaks; we can see, however, that the sought mass of 1068 (+1 of added charge) is clearly visible.

We can also see an other Pd/BINAP complex, having a mass of 873. This complex could be formed from the decomposition of benzophenone hydrazone and the (BINAP)Pd(Ar)amine complex. Traces of the benzophenone hydrazone are also present in the spectrum.

Another Pd complex was identified at 1054; this complex, which will be further discussed in this section, could also decompose in the Pd/BINAP complex at 873 and the other fragment at 182.

We can make other considerations based on the theoretical isotope distribution and the nitrogen rule.

**Theoretical isotope distribution**

![Image of the spectrum showing a mass electrospray measurement of a toluene solution prepared as described.](image-url)
A theoretical isotope distribution was calculated for this (BINAP)Pd(amine)Ar complex, using an in-house isoform software program (Exalibur 2.0 spectrum simulation software). The distribution mainly represents the isotope distribution of Pd ($^{102}$Pd (1.02%), $^{104}$Pd (11.14%), $^{105}$Pd (22.33%), $^{106}$Pd (27.33%), $^{108}$Pd (26.46% and $^{110}$Pd (11.72%)). The compounds which present similar patterns in the mass spectrum most likely contain a palladium atom.

In the following figure we show, side by side, the theoretical isotope distribution, calculated for the sought complex, and the isotope distribution obtained from the mass measurement referred to the 1069 pea.

The other amine complex at 1054 has most likely been formed during the mass spectrometry procedure, as it is not visible in the NMR spectrum.

The isotope distribution of the 1054 complex confirms it contains palladium; moreover, by superimposing the two isotope distributions of the 1054 and 1069 peaks, as in the following figure, it is evident how these two distributions are very similar, and consequently refer to complexes having a very similar structure.

![Figure 3: comparison of the measured isotope distributions for two peaks found at 1054 and 1069 m/z.](image)

Nitrogen rule
Let us consider now the nitrogen rule. This rule states that if the analyzed molecule contains an even number of nitrogen atoms, the peak on the spectrum will show an odd number; on the contrary, if the molecule contains an odd number of nitrogen atoms, the peak on the spectrum will be an even number. This is because nitrogen is the only common atom where the most common isotope has an odd valence and an even mass.

Our peaks are consistent with the nitrogen rule; the (BINAP)Pd(Ar)amine complex, which contains an even number of nitrogen atoms (2), has an odd peak value; on the contrary, the other benzophenone complex found at 1054 has an even peak and an odd number of nitrogens (1).