

Supporting Information

Figure 1s. Block-diagram of synthetic step-routes and resulting experimentally determined products established from initial reaction of $\text{Pd}_{10}(\text{CO})_{12}(\text{PEt}_3)_6$ (**5**) with $\text{Au}(\text{SMe}_2)\text{Cl}$. Reaction conditions for different diagram-labeled steps and identified products are as follows: (a) Reaction under N_2 in acetone/HOAc solution at 50°C for 2 h afforded a black precipitate (BP) along with filtrate A. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of BP in C_6D_6 indicated its compositions to consist of $\text{Pd}_{23}(\text{CO})_{20}(\text{PEt}_3)_{10}$ (**4**) (ca. 60%), $\text{Au}_2\text{Pd}_{21}(\text{CO})_{20}(\text{PEt}_3)_{10}$ (**3**) (ca. 5%), and unidentified products with strong signals at $\delta_1 = 8.1(\text{br})$, $\delta_2 = -1.8$, $\delta_3 = -3.2$, $\delta_4 = -4.2$, $\delta_5 = -4.3$ ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of filtrate A showed the characteristic signal of $\text{Pd}(\text{PEt}_3)_2\text{Cl}_2$ (17.1 ppm), traces of $\text{Pd}_{34}(\text{CO})_{24}(\text{PEt}_3)_{12}$,^{26a,b} and several non-assignable signals (in the range of δ 22.3 – 7.0 ppm) but provided no detectable evidence for the Pd_{10} reactant **5**, $\text{Au}_2\text{Pd}_{21}$ **3**, or $\text{Pd}_{16}(\text{CO})_{13}(\text{PEt}_3)_9$; (b) Room temperature extraction of BP with THF followed by crystallization under CO via vapor diffusion from hexane/acetone mixture (3/2 ratio) gave $\text{Au}_2\text{Pd}_{28}(\text{CO})_{26}(\text{PEt}_3)_{10}$ (**1**) (20% based on Pd) and solution B; (c) Addition of heptane to concentrated solution B gave Pd_{10} **5** (8%). (d) Crystallization from entire filtrate A under CO via vapor diffusion from 95% EtOH gave $\text{Au}_2\text{Pd}_{21}$ **3** (7%) and Pd_{10} **5** (17%). (e) Crystallization from entire filtrate A under CO without additional solvents gave only $\text{Au}_2\text{Pd}_{21}$ **3** (4.7%). (f) Crystallization from entire filtrate A under N_2 via vapor diffusion from 95% EtOH gave $\text{Pd}_{16}(\text{CO})_{13}(\text{PEt}_3)_9$ (11%) and $\text{Pd}_{34}(\text{CO})_{24}(\text{PEt}_3)_{12}$; (<1%). (g) Crystallization from solution A' under CO via vapor diffusion from 75% EtOH gave Pd_{10} **5** (6%). Most reactions also gave rise to Pd black.

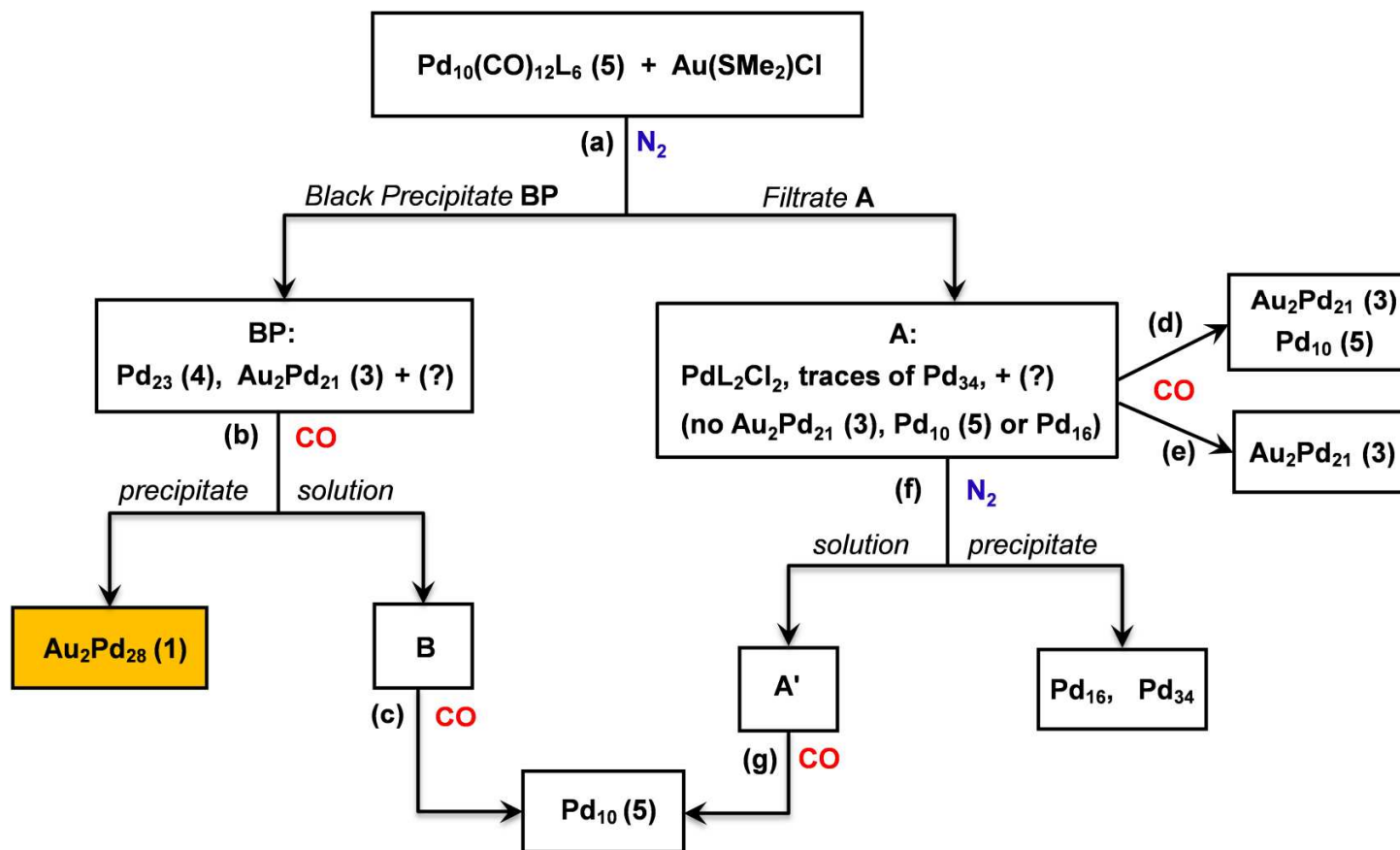


Figure 1s