

Electronic Supplementary Information for:

A catalytic and mechanistic investigation of a PCP pincer palladium complex in the Stille reaction

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ESI Table 1. Reaction conditions and observed pseudo-first-order rate constants for Reaction (1) at 160 °C in benzene-*d*₆ solvent when Me₃SnPh was used in excess and varied. Both constant for the reactant decay and product formation are displayed.^a

10 ³ /M		10 ⁵ k ₁ /s ⁻¹	
[2]	[Me ₃ SnPh]	4-bromoanisole	4-phenylanisole
0.16	108	16.4±1.2	20.0±2.2
0.16	216	17.8±1.3	35±4
0.16	216	20±6	7.1±1.2
0.16	432	15.2±2.4	14.±1.9
0.16	432	18±3	8.6±1.3
0.16	648	3.6±1.0	4.9±0.9
0.16	648	1.94±0.37	2.1±0.4
0.15	648	55±7	25±4
0.17	864	36.6±2.5	31±10
0.10	864	52±12	41±7
0.15	864	39±6	37±10
0.30	864	82±15	24±6
0.52	864	120±12	93±14

^a[Ferrocene]=3.66 mM and [4-bromoanisole]=9.62 mM in all measurements.

ESI Table 2. Results of the Stille reaction mediated by catalyst precursor **2** under various reaction conditions.

Entry	ArX ^{a†}	[Pd] ^b (%)	T/°C	TON ^d	TOF ^e /h ⁻¹	Yield ^{f,§} (%)
1	PhCl	0.01	110	-	-	-
2	PhCl	0.01	160	590	33	6
3	PhCl	0.0001	160	-	-	Trace
4	PhBr	0.0001	110	-	-	Trace
5	PhI	0.01	110	1300	74	13
6	PhI	0.01	160	8100	450	81
7	PhI	0.0001	110	-	-	Trace
8	4-BrC ₆ H ₄ CHO	0.01	110	700	39	7
9	4-BrC ₆ H ₄ CHO	0.0001	160	-	-	-
10	4-BrC ₆ H ₄ Me	0.01	110	-	-	-
11	4-BrC ₆ H ₄ Me	0.0001	110	-	-	-
12	4-BrC ₆ H ₄ Me	0.0001	160	320000	18000	32
13	4-BrC ₆ H ₄ OMe	0.01	110	1300	71	13
14	4-BrC ₆ H ₄ OMe	0.0001	110	-	-	-
15	4-BrC ₆ H ₄ OMe	0.0001	160	210000	11000	21
16	2-BrC ₆ H ₄ OMe	0.01	110	1200	68	12
17	2-BrC ₆ H ₄ OMe	0.0001	110	-	-	-
18	2-BrC ₆ H ₄ OMe	0.0001	160	270000	15000	27

^a1.0×10⁻³ mol. ^b[Pd]/ArX × 100. ^cRefers to the time after which no improvement of the yield was detected. ^dmol product/mol catalyst, based on GC yield. ^emol product/(mol catalyst × time), based on GC yield. ^fYield determined by GC based on the product. [§]No improvement in yield was detected after 18 h reaction time in all entries.

[†] In all the reactions with phenyl chloride as substrate a white precipitate was obtained after a few hours, which turned the reaction mixture to a yellow-brown suspension during the rest of the reaction time; this was never observed in the aryl bromide or the phenyl iodide reactions.

Crystallography

Slow crystallisation of **1**·THF from THF at room temperature gave yellow, octahedral crystals suitable for single crystal X-ray diffraction. Intensity data was collected at 293 K with a Bruker SMART CCD system using ω -scans and a rotating anode with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$).¹ The completeness of the data set was 95.9% out to $\Theta = 31.67^\circ$. The intensity was corrected for Lorentz, polarisation and absorption effects using SADABS.² All reflections were integrated using SAINT.³ The structure was solved by direct methods and refined by full-matrix least-squares calculations on F^2 using SHELXTL 5.1.⁴ Non-H atoms were refined with anisotropic displacement parameters. Hydrogen atoms were constrained to parent sites, using a riding model.

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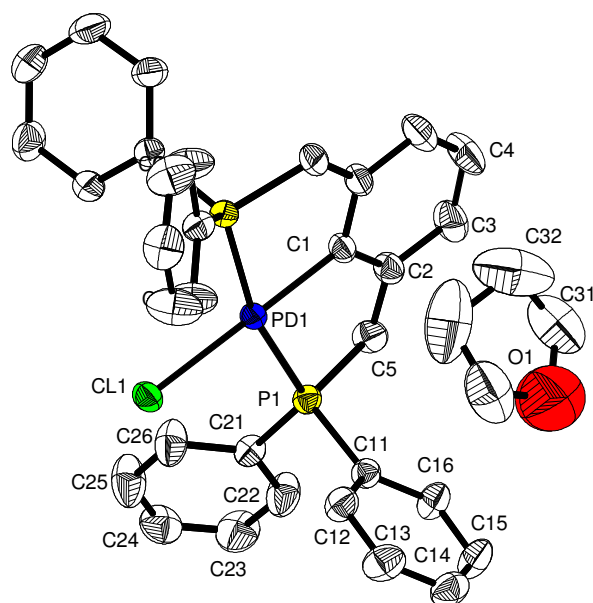


Figure 1. A DIAMOND plot with atomic numbering of the molecular structure of complex **1**. The ellipsoids denote 30% probability. Bond distances (\AA) and angles ($^\circ$) with estimated standard deviations: Pd–C1 = 2.038(3); Pd–Cl = 2.4123(8); Pd–P1 = 2.2938 (6); P1–Pd–P1* = 165.73(3); P1–Pd–C1 = 82.867(16); P1–Pd–Cl = 97.133(16).

Derivation of rate laws

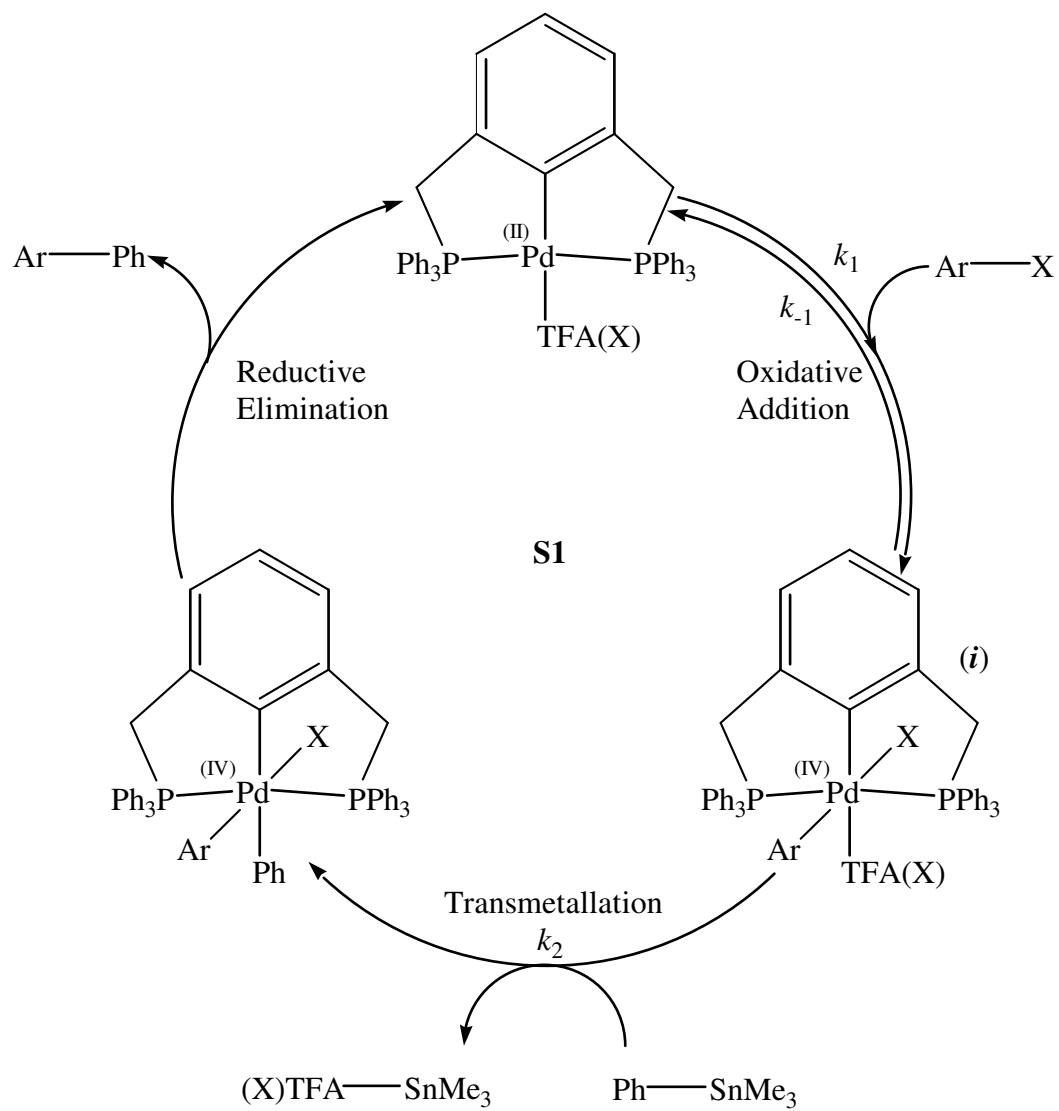
The two most obvious homogeneous possibilities are a Pd(II)-Pd(IV) cycle, as proposed by Jensen, Milstein and others for the Heck reaction, and a classical Pd(0)-Pd(II) cycle. These two cycles are depicted in Scheme S1 and S2.

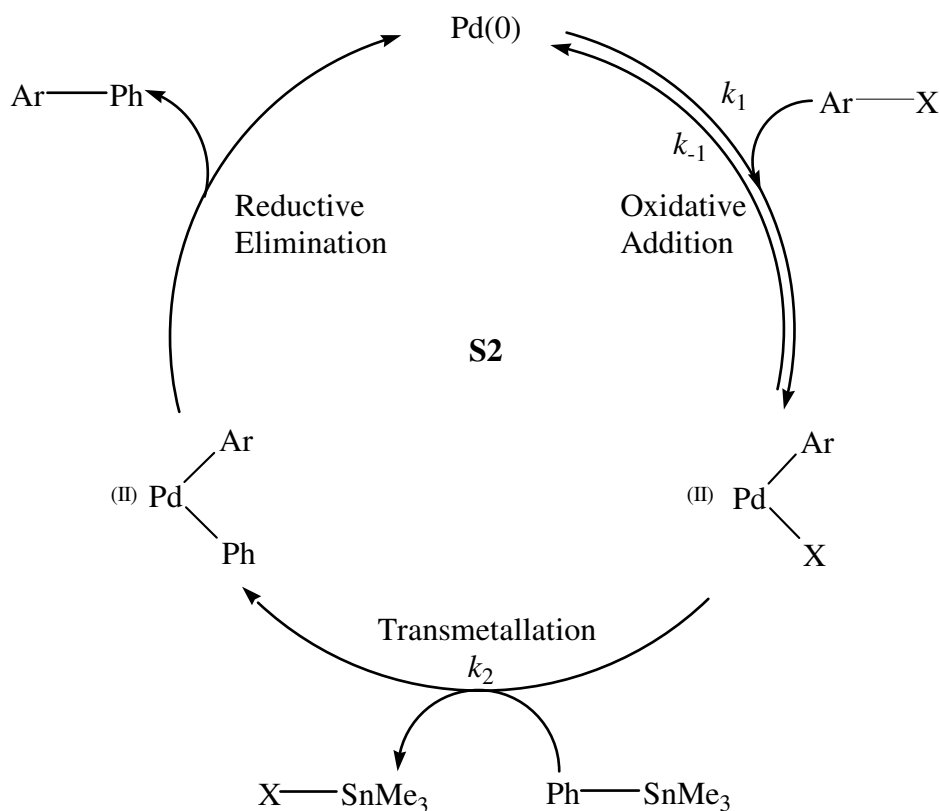
If the reaction is described by Scheme S1 this would, with rate limiting transmetallation and steady state conditions assumed for the intermediate (*i*), give a rate law of the following form:

$$\text{Rate} = \frac{k_1 k_2 [\text{Sn}][\text{ArX}][\text{Pd}]}{k_{-1}[\text{ArX}] + k_2[\text{Sn}]}$$

Obviously the first step needs to be reversible and pushed to the left (to explain the lack of reactivity of both substrates in the preliminary investigation). Thus, $k_{-1} \gg k_2[\text{Sn}]$ and this will simplify the equation to give the observed rate law. Also a reversed order of substrate entry (*i.e.* reversible transmetallation followed by rate determining oxidative addition) would after simplification give the observed rate law. Hence, in principle, a Pd(II)-Pd(IV) cycle is compatible with the observed rate law but it fails to explain the erratic kinetics as well as the COT and mercury test.

A classical cycle (Scheme S2) would also give a rate law of the same form as above if the oxidative addition is reversible and shifted to the left. Earlier investigations of Pd(0)-Pd(II) systems almost always show a zero order dependence on the electrophile, since oxidative addition is irreversible and transmetallation rate determining.





- 1 BrukerAXS, SMART, Area Detector Control Software, Bruker Analytical X-ray System, Madison, Wisconsin, USA, 1995.
- 2 G. M. Sheldrick, SADABS, Program for absorption correction, University of Göttingen, Germany, 1996.
- 3 BrukerAXS, SAINT Integration Software, Bruker Analytical X-ray System, Madison, Wisconsin, USA, 1995.
- 4 G. M. Sheldrick, SHELXTL5.1, Program for Structure solution and least square refinement, University of Göttingen, Germany, 1996.