Simple, recyclable, and self-assembled palladium(II)–alkyl Schiff base complex for Suzuki coupling reaction: Chain length dependence and heterogeneous catalysis

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Fig.S1. WDCA images of prepared palladium catalysts and its precursors.



Fig. S2. AFM images of the surface topographies of (a) Cat.1, (b) Cat.2, (c) Cat.4 and (d) Cat.5.



Fig. S3. UV-Vis spectrum of the supported palladium catalysts:(a) Cat.1, (b) Cat.2, (c) Cat.3, (d) Cat.4 and (e) Cat.5.



Fig S4 Anchoring of PBB and immobilization of Pd(II) onto the APTES modified supports.



Fig S5 Three-phase test for the Suzuki reaction in the absence (A) and present (B) of the catalyst.

Three-phase test, which was developed by Rebek and Gavina,¹ is a definitive approach for validating the heterogeneous/homogenous nature of the reaction. Daviees, ² Corma,³ and other scholars⁴ employed the three-phase test in various systems. The test consists of anchoring one of the reactants (aryl halide) on the support surface. The supported reactant and another soluble reagent (in our case, 4ferrocenylphenylboronic acid) are then subjected to reaction in the presence of the catalyst, which is immobilized in the third phase (solid, Cat.3 in our case). If the active palladium species leach into the solution, the anchored reactant can be converted to some degrees. By contrast, if the reactive sites come from the supported metal center, no transformation should be observed for the anchored reagent. For this test, we used 4-bromobenzaldehyde (PBB) covalently anchored on the APTES modified substrate surface to provide PBB-SiO₂/ITO (Scheme 2). For comparison, we also prepared Pd•NH2-SiO2/ITO as catalyst under the reaction conditions (Scheme 2). It is reported that Pd•NH₂-SiO₂ shows a high activity for Suzuki coupling reaction, which is ascribed to the quasi homogeneous catalytic process following the "release and catch" mechanism.⁵ PBB-SiO₂/ITO, 4ferrocenylphenylboronic acid, and catalyst (Cat. 3/Pd•NH2-SiO2/ITO) were then subjected to the reaction

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	H ₃ CBr +	B(OH) ₂ Cat. 3 Base, Solv Temperat	→ H ₃ C{ vent, ture		
Entry	Solvent	Base	Time(h)	Temperature (°C)	Yield (%) ^b
1	DMF	K ₂ CO ₃	12	80	6
2	toluene	K ₂ CO ₃	12	80	35
3	DMSO	K ₂ CO ₃	12	80	10
4	Et ₃ N	K ₂ CO ₃	12	80	8
5	THF	K ₂ CO ₃	12	80	5
6	CH ₃ OH	K ₂ CO ₃	12	80	40
7	CH ₃ OH-H ₂ O(1:1)	K ₂ CO ₃	12	80	45
8	H ₂ O	Na ₂ CO ₃	12	80	80
9	H ₂ O	NaHCO ₃	12	80	60
10	H ₂ O	NaOH	12	80	54
11	H ₂ O	NaOAc	12	80	45
12	H_2O	Na ₂ HPO ₄	12	80	30
13	H_2O	KH ₂ PO ₄	12	80	77
14	H ₂ O	K ₃ PO ₄	12	80	82

Table S1 Effect of solvents, bases and temperature on Suzuki cross-reaction.^a

15	H ₂ O	CsCO ₃	12	80	83
16	H_2O	t-BuNa	12	80	89
17	H_2O	Et ₃ N	12	80	80
18	H_2O	K ₂ CO ₃	12	40	35
19	H_2O	K ₂ CO ₃	12	50	43
20	H_2O	K ₂ CO ₃	12	60	63
21	H_2O	K ₂ CO ₃	12	70	74
22	H ₂ O	K ₂ CO ₃	10	80	85
23	H_2O	K ₂ CO ₃	12	80	98
24°	H_2O	K ₂ CO ₃	12	80	45
25	H_2O	K ₂ CO ₃	15	80	99
25	H ₂ O	K ₂ CO ₃	18	80	99

^a Reaction conditions: 0.125 mmol of 4-bromotoluene, 0.15 mmol of PhB(OH)₂, 0.15 mmol of base and catalyst $(1.27 \times 10^{-8} \text{ mol} \cdot \text{cm}^{-2} \text{ Pd})$ in 5.0 mL of solvent at 80°C, 12h. 0. 15 mmol of TBAB as phase transfer catalyst was added in H₂O as a solvent.

^b HPLC yield.

^c In the absence of TBAB

Table S2 Recyclability of Cat.3- catalyzed (1 cm×1cm) Suzuki coupling reaction.

$H_{3}C \longrightarrow Br + A = B(OH)_{2} \xrightarrow{Cat., K_{2}CO_{3}} H_{3}C \longrightarrow H_{3}C = A = A = A = A = A = A = A = A = A = $							
Cycles	1 st	2 nd	3 rd	4 th	5 th	6 th	7 th
Yields (%)	98	97	97	96	95	93	90

Reaction conditions: 4-bromo toluene (0.125 mmol), PhB(OH)₂ (0.15 mmo), K₂CO₃ (0.15 mmo), TBAB (0.15 mmo), catalyst (1.27×10^{-8} mol·cm⁻² Pd) and H₂O (5.0 mL); temperature = 80°C, 12h. Yield determined by HPLC.

Entry	R	Product	Yield ^b (%)
1	<i>p</i> -CH ₃ O	Н3СО-	93
2	<i>о</i> -СН ₃ О		89
3	<i>p</i> -NH ₂		95
4	<i>m</i> -NH ₂		93
5	<i>p</i> -СНО	онс-	99
6	о-СНО	CHO	90
7	<i>p</i> -NO ₂	0 ₂ N-	98
8	<i>m</i> -NO ₂		97
9	<i>p</i> -CN		99
10	o-CN		88
11	<i>p</i> -CF ₃	F ₃ C	98
12°	naphthalene		93
13 ^d	<i>p</i> -CH ₃ O	H ₃ CO-	trace
14 ^e	p-NO ₂	0 ₂ N-	trace
15 ^f	<i>p</i> -СНО	онс-	trace

Table S3 Cat.**3** catalyzed Suzuki coupling reaction of various aromatic halides and phenylboronic.^a

$$\begin{array}{c} & & \\ R \end{array} \xrightarrow{} X & + \end{array} \xrightarrow{} B(OH)_2 & \xrightarrow{} Cat. \ 3 \ K_2CO_3 \\ \hline H_2O, \ 80^{\circ}C \end{array} \xrightarrow{} R \end{array} \xrightarrow{} \begin{array}{c} \\ R \end{array} \xrightarrow{} \end{array}$$

^a Reaction conditions: aryl bromides (0.125 mmol), PhB(OH)₂ (0.15 mmol), K₂CO₃ (0.15mmol),

TBAB (0.15 mmol), catalyst ($1.27 \times 10^{-8} \text{ mol} \cdot \text{cm}^{-2} \text{ Pd}$) and H₂O (5.0 mL); temperature = 80° C, 12h. ^bYield determined by HPLC. ^c1-bromonaphthalene.

d, e, f X=Cl

Various *p*-substituted aryl bromides and 1-bromonaphthalene, lead to high yields of coupled products (entries 1, 3, 5, 7, 9, 11, and 12). Several-substituted aryl bromides provided products with low yields probably because of the electronic effect (entries 2, 4, 6, and 10). Unfortunately, aryl iodides gave a few yields of biaryls (Entries 13–15).