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Aqueous Suzuki couplings mediated by a hydrophobic catalyst†

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The catalytic activity of $[(Ph_2P\text{-}o\text{-}C_6H_4)_2N]PdCl$ in aerobic aqueous Suzuki couplings is described. Though hydrophobic, this molecular catalyst is competent in cross-coupling reactions of arylboronic acids with a variety of electronically activated, unactivated, and deactivated aryl iodides, bromides, and chlorides upon heating in aqueous solutions under aerobic conditions to give biphenyl derivatives without the necessity of amphiphiles even in the presence of an excess amount of mercury.

Transition metal-mediated cross-coupling catalysis has evolved over the last decades into one of the most powerful methodologies in organic synthesis, pharmaceutics, and materials chemistry.[1–12] The advance of this catalysis in aqueous media is attractive given the non-toxic, non-flammable, and abundant nature of water.[13–15] Successful examples of aqueous cross-coupling catalysis by well-defined molecular catalysts, however, are rather limited due to the low stability or solubility of catalytically active species in aqueous solutions.[16] To improve aqueous solubility, catalysts are typically designed to contain hydrophilic ligands[17] such as those bearing carboxylate,[18,19] ammonium,[20] sulfonate,[20–22] or polyol[23] functional groups, *etc.* Utilization of amphiphilic additives[24–26] is almost inevitable for hydrophobic catalysts in aqueous cross-coupling reactions. Microwave irradiation[27–29] and heterogeneous catalysis by means of immobilized catalysts[30–33] or metal nanoparticles produced upon decomposition of molecular precatalysts[34–37] represent alternative prevalent approaches.

Metal nanoparticles[38] differ inherently in size and shape, typically rendering rather undesirable multiple active sites comprising different compositions for catalysis. The constitutions and thus activities of these active sites could be very sensitive to their formation procedures and the presence of traces of usually unnoticed components, particularly those prepared *in situ* when molecular precatalysts decompose under catalytic conditions. Reproducibility of catalysis of this type could be troublesome. In this regard, there have been several reports addressing this challenge,[39,40] including concerns of commercially available molecular precatalysts.[41,42] The development of well-defined molecular catalysts where leaching of the metal does not occur during catalysis is therefore of interest and benefit.

Palladium-catalyzed Suzuki couplings are versatile in the development of biaryl derivatives.[6] We have previously reported the catalytic competence of amido phosphine complexes of palladium, *e.g.*, **1** and **2** in Fig. 1, for Suzuki couplings in organic solvents.[43,44] Of note are reactions conducted under aerobic conditions in the presence of exogenous water, an unusual result considering the inherently high basicity of a Pd–amide bond.[45] Note that water in these attempts is not a major solvent. We were therefore interested in aerobic aqueous Suzuki couplings with these promising catalysts. We report herein the catalytic activity of **2a** in this regard without the requirement of any amphiphilic additives despite the hydrophobic nature of this catalyst. Of interest is also its unchanged activity in the presence of mercury,[39,40,46,47] consistent with homogeneous catalysis by a well-defined molecular catalyst that contrasts with the heterogeneous feature of palladium nanoparticles derived *in situ* from the decomposition of other molecular precatalysts such as commercially available $Pd(PPh_3)_4$ and $Pd(OAc)_2$ (*vide infra*).

Complex **2a** is thermally stable at temperatures as high as 200 °C.[48] To survey reaction parameters, we chose to examine the reaction of 4-tolyl bromide with phenylboronic acid catalyzed by 0.1 mol% **2a** in water at 100 °C. Among eight inorganic bases examined (Table 1, entries 1–8), K_2CO_3 outperforms the others to give 4-methylbiphenyl in 67% yield (entry 1). Several organic additives were considered (entries 9–17), among which *n*BuOH effectively improves this catalysis to give 4-methylbiphenyl in 96% yield (entry 15). Tuning the volume ratio of water to *n*BuOH to 2 : 1 led to the desired product in quantitative yield (entry 19). This protocol is also applicable to the transformation of 4′-bromoacetophenone into 4-acetylbiphenyl quantitatively (entry 20). Interestingly, high yield production of 4-acetylbiphenyl from 4′-bromoacetophenone can also be achieved in neat water without exogenous *n*BuOH (entry 21). No palladium black was observed in all these reactions. These

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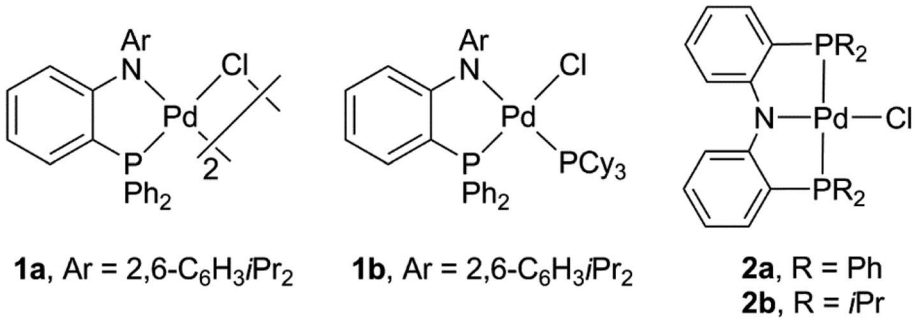
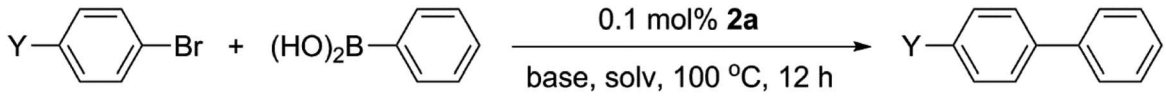


Fig. 1 Representative examples of amido phosphine complexes of palladium.

Table 1 Optimization of reaction parameters[a]



entry	Y	Base	Solvent	Yield[b] (%)
1	Me	K_2CO_3	H_2O	67
2	Me	Na_2CO_3	H_2O	18
3	Me	Cs_2CO_3	H_2O	29
4	Me	$Ba(OH)_2 \cdot 8H_2O$	H_2O	17
5	Me	KOH	H_2O	30
6	Me	NaOH	H_2O	59
7	Me	$K_3PO_4 \cdot H_2O$	H_2O	17
8	Me	KO*t*Bu	H_2O	58
9	Me	K_2CO_3	3/1 (v/v) H_2O/MeCN	0
10	Me	K_2CO_3	3/1 (v/v) H_2O/DMSO	0
11	Me	K_2CO_3	3/1 (v/v) H_2O/acetone	9
12	Me	K_2CO_3	3/1 (v/v) H_2O/MeC(O)OEt	10
13	Me	K_2CO_3	3/1 (v/v) H_2O/Et_2O	3
14	Me	K_2CO_3	3/1 (v/v) H_2O/*n*PrOH	80
15	Me	K_2CO_3	3/1 (v/v) H_2O/*n*BuOH	96
16	Me	K_2CO_3	3/1 (v/v) H_2O/1-pentanol	83
17	Me	K_2CO_3	3/1 (v/v) H_2O/*t*-pentanol	71
18	Me	K_2CO_3	13/1 (v/v) H_2O/*n*BuOH	54
19	Me	K_2CO_3	2/1 (v/v) H_2O/*n*BuOH	100 (100)
20	C(O)Me	K_2CO_3	2/1 (v/v) H_2O/*n*BuOH	100 (99)
21	C(O)Me	K_2CO_3	H_2O	96
22	C(O)Me	—	2/1 (v/v) H_2O/*n*BuOH	1
23[c]	C(O)Me	K_2CO_3	2/1 (v/v) H_2O/*n*BuOH	0
24[d]	C(O)Me	K_2CO_3	2/1 (v/v) H_2O/*n*BuOH	37
25[e]	Me	K_2CO_3	2/1 (v/v) H_2O/*n*BuOH	100
26[e]	C(O)Me	K_2CO_3	2/1 (v/v) H_2O/*n*BuOH	100 (99)
27[f]	Me	K_2CO_3	2/1 (v/v) H_2O/*n*BuOH	34
28[f]	C(O)Me	K_2CO_3	2/1 (v/v) H_2O/*n*BuOH	93
29[g]	Me	K_2CO_3	2/1 (v/v) H_2O/*n*BuOH	100
30[g]	C(O)Me	K_2CO_3	2/1 (v/v) H_2O/*n*BuOH	100
31[h]	Me	K_2CO_3	2/1 (v/v) H_2O/*n*BuOH	100
32[h]	C(O)Me	K_2CO_3	2/1 (v/v) H_2O/*n*BuOH	94
33[e,f]	Me	K_2CO_3	2/1 (v/v) H_2O/*n*BuOH	0
34[e,f]	C(O)Me	K_2CO_3	2/1 (v/v) H_2O/*n*BuOH	16
35[e,g]	Me	K_2CO_3	2/1 (v/v) H_2O/*n*BuOH	13
36[e,g]	C(O)Me	K_2CO_3	2/1 (v/v) H_2O/*n*BuOH	36
37[e,h]	Me	K_2CO_3	2/1 (v/v) H_2O/*n*BuOH	14
38[e,h]	C(O)Me	K_2CO_3	2/1 (v/v) H_2O/*n*BuOH	9

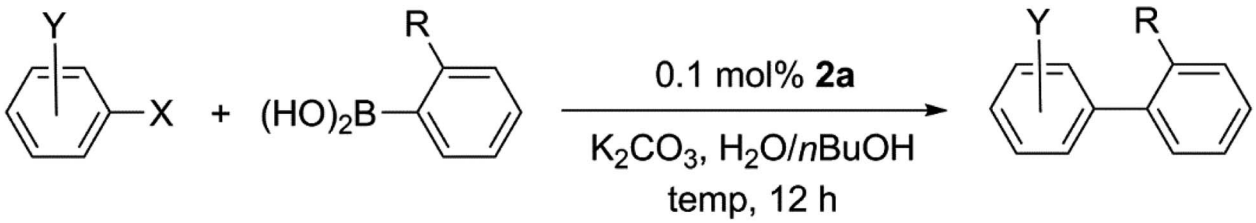
[a] Reaction conditions: 1.0 equiv. of aryl bromide (0.15 mmol), 1.5 equiv. of phenylboronic acid, 2.0 equiv. of base, 2 mL of solvent, run in the air. [b] Determined by GC against dodecane as an internal standard, based on aryl bromide, average of two runs. Yields in parentheses refer to isolated yields; average of two runs. [c] Without **2a**. [d] 0.01 mol% **2a**. [e] 150 equiv. Hg. [f] **2b** in place of **2a**. [g] $Pd(PPh_3)_4$ in place of **2a**. [h] $Pd(OAc)_2$ in place of **2a**.

results are in sharp contrast to those derived from the majority of studies necessitating a hydrophilic catalyst[17–21,23] or an amphiphile[24–26] to assist a hydrophobic catalyst in aqueous catalysis.[13–15] The methodology developed herein thus represents to date a rare example in this regard.

Without a base (entry 22) or **2a** (entry 23), this catalysis hardly proceeds. A turnover number of up to 3.7×10^3 is realized upon lowering **2a** loading to 0.01 mol% (entry 24). In the presence of an excess amount of mercury,[39,40,46,47] the catalytic activities of **2a** remain unchanged (entries 25–26), thereby eliminating the possibility that this catalysis is involved with colloidal, nanoparticle, or bulk Pd(0).[34–37] Though **2b** (ref. 49) (Fig. 1), $Pd(PPh_3)_4$,[50,51] and $Pd(OAc)_2$ (ref. 41,52,53) are catalytically active under otherwise identical conditions (entries 27–32), palladium black was observed in these reactions. Their activities diminish significantly in the presence of mercury (entries 33–38), consistent with, at least in part, heterogeneous catalysis resulting from the decomposition of these pre-catalysts.[39,40,46,47] Evidently, **2a** does not decompose under the conditions employed but undergoes molecular catalysis in aqueous Suzuki couplings. This result is worth noting in view of the complex nature of multiple active sites derived from commercially available $Pd(PPh_3)_4$ or $Pd(OAc)_2$. Of equal interest is the comparison between activities of **2a** (entries 25–26) and **2b** (entries 33–34) in mercury poisoning experiments, highlighting the role that *P*-substituent in the amido PNP ligand plays in this aqueous catalysis.

A number of functional groups are compatible with this aqueous catalysis (Table 2), such as nitro, ketone, aldehyde, fluoride, alkyl, alkoxy, amino, *etc.* Aryl iodides (entries 1–4), bromides (entries 5–12), and chlorides (entries 13–14) are all suitable electrophiles. Building blocks having *ortho* substituents are more challenging (entries 15–24). Increasing the heating bath temperature to 140 °C or the catalyst loading to 0.5 mol% facilitates these reactions. The synthesis of 2,6- or 2,2′-disubstituted biphenyls is straightforward, but the preparation of tri-*ortho*-substituted analogues is less successful. Without

Table 2 Catalytic Suzuki couplings of aryl halides with arylboronic acid[a]



entry	X	Y	R	Temp[b] (°C)	Yield[c] (%)
1	I	4-C(O)Me	H	100	100
2	I	H	H	100	100
3	I	4-Me	H	100	100
4	I	4-OMe	H	100	100
5	Br	4-NO_2	H	100	100 (94)
6	Br	4-C(O)Me	H	100	100 (99)
7	Br	4-CHO	H	100	100 (100)
8	Br	4-F	H	100	100 (99)
9	Br	H	H	100	100
10	Br	4-Me	H	100	100 (100)
11	Br	4-OMe	H	100	100 (95)
12	Br	4-NMe_2	H	100	100 (93)
13	Cl	4-C(O)Me	H	100	62
14	Cl	H	H	100	41
15	Br	H	Me	100	30
16	Br	H	Me	140	100 (97)
17	Br	2-OMe	H	140	95 (94)
18	Br	2-OMe	Me	140	67 (60)
19	Br	2-F	H	140	49
20[d]	Br	2-F	H	140	100 (100)
21[d]	Br	2-F	Me	140	100
22	Br	2,6-Dimethyl	H	140	65 (56)
23[d]	Br	2,6-Dimethyl	H	140	82
24[d]	Br	2,6-Dimethyl	Me	140	14
25	Br	3,5-Dimethyl	H	140	96 (95)

[a] Reaction conditions: 1.0 equiv. of aryl halide (0.15 mmol), 1.5 equiv. of arylboronic acid, 2.0 equiv. of K_2CO_3, 2 mL of solvent (2/1 (v/v) H_2O/*n*BuOH), run in the air. [b] Heating bath temperature. [c] Determined by GC against dodecane as an internal standard, based on aryl halide, average of two runs. Yields in parentheses refer to isolated yields; average of two runs. [d] 0.5 mol% **2a**.

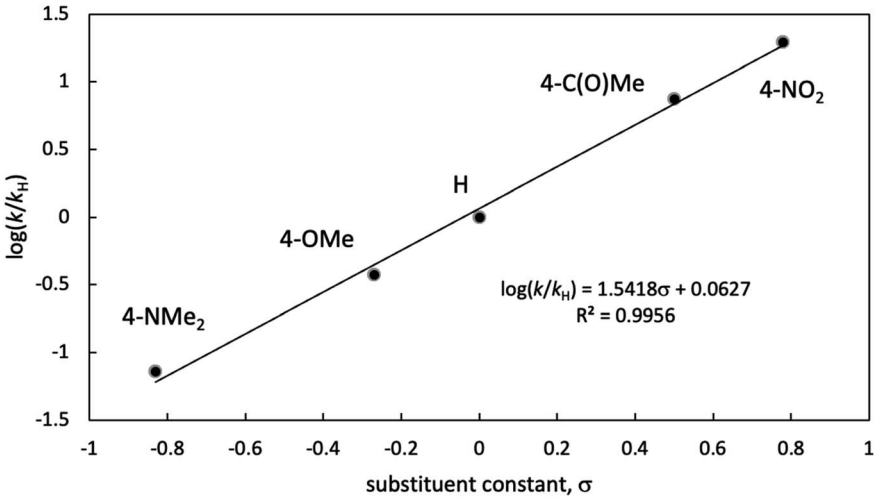


Fig. 2 Hammett plot of competitive reactions of phenylboronic acid with 4-substituted aryl bromides catalyzed by **2a** in H_2O/*n*BuOH at 100 °C.

steric hindrance, the reaction employing 3,5-dimethylphenyl bromide proceeds smoothly (entry 25).

To gain insights into mechanistic possibilities, we examined a series of competitive reactions of phenylboronic acid with electronically activated, unactivated, and deactivated aryl bromides catalyzed by **2a** in H_2O/*n*BuOH at 100 °C, a Hammett plot of which shows a reaction constant ρ of 1.54 ± 0.06 (Fig. 2). This value is relatively small as compared with those found for oxidative addition of aryl iodides to $Pd(PPh_3)_2$ ($\rho = 2$)[54] and aryl chlorides to Pd(XPhos) ($\rho = 2.3$)[55] or Pd(dippp) ($\rho = 5.2$).[56] Oxidative addition of aryl bromides in this study is therefore unlikely the rate-determining step. Relatively smaller reaction constants have also been reported for Suzuki couplings catalyzed by **1a** ($\rho = 0.48$),[43] **1b** ($\rho = 0.66$),[43] or **2a** ($\rho = 0.25$ in dioxane, $\rho = 1.08$ in toluene),[44] Heck olefination by **2a** ($\rho = 0.60$),[48] and Sonogashira couplings by **2a** ($\rho = 0.82$)[49] in organic solvents, where transmetallation is proposed to be the slowest. A similar proposition was also suggested in other Suzuki couplings having a small reaction constant.[57,58] The hypothesis regarding transmetallation as the rate-determining step in this aqueous catalysis is also consistent with the consequence that **2a** outperforms **2b** taking into account that oxidative addition of aryl halides and reductive elimination of biaryl products are more encouraged by the latter given its more electron-releasing and larger *P*-substituents, respectively.

In summary, the amido PNP complex **2a** is a competent catalyst in aqueous Suzuki coupling reactions under aerobic conditions. Of note is the feasibility of this hydrophobic catalyst in aqueous catalysis without the assistance of amphiphiles. A variety of electronically activated, unactivated, and deactivated aryl iodides, bromides, and chlorides are suitable electrophiles, resulting in biaryl products straightforwardly. Mercury poisoning experiments and Hammett reaction constant collectively implicate a molecular mechanism where transmetallation is likely the rate-determining step. All in all, this study demonstrates a facile entry into aerobic aqueous catalysis with a robust hydrophobic catalyst, a rare example contrasting with those requiring amphiphiles[24–26] or those transforming into catalytically active nanoparticles.[34–37] Studies aiming at expanding the territory of **2a** in aqueous catalysis are currently underway.

Author contributions

S.-B. H.: investigation, methodology, formal analysis, validation; L.-C. L.: conceptualization, funding acquisition, project administration, supervision, writing – original draft, writing – review & editing.

Conflicts of interest

There are no conflicts of interest to declare.

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