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In situ generated nickel nanoparticle-catalyzed carbonylative Suzuki reactions of aryl iodides with arylboronic acids at ambient CO pressure in poly(ethylene glycol)[†]

Yanzhen Zhong,^a Xinxing Gong,^a Xiaoshu Zhu,^b Zhuchao Ni,^a Haoyang Wang,^a Jinglin Fu^a and Wei Han^{*a}

A general *in situ* generated nickel nanoparticle-catalyzed carbonylative Suzuki reactions of aryl iodides with arylboronic acids at atmospheric CO pressure in poly(ethylene glycol) has been demonstrated. A wide range of aryl iodides and arylboronic acids can be coupled to the corresponding biarylketones with high yields even in the absence of an added ligand and at low catalyst loading. The nature of the active catalytic species is discussed.

Carbonylative Suzuki coupling remains an indispensable tool for the construction of biaryl ketone scaffolds that are found in a myriad of pharmaceuticals, advanced organic materials, and photosensitizers.¹ This transformation offers unique advantages, such as ease of handling, high stability, low toxicity, and good functional-group compatibility, over other organometallic-based² cross-coupling processes owing to its utilization of organoboron compounds. The catalyst that has been reported to be effective for carbonylative Suzuki coupling is invariably based on a palladium system, although only one example of iron catalysis has also been developed.³ However, the palladium-based methods often require high pressure (often ≥ 5 bar) of carbon monoxide, the cost of ligands (often phosphine ligands) and the use of eco-unfriendly organic solvents.⁴ Consequently, efforts to explore other metal alternatives that can achieve mild, practical, economical, eco-friendly, and efficient catalysis for the carbonylative Suzuki coupling are of great significance.

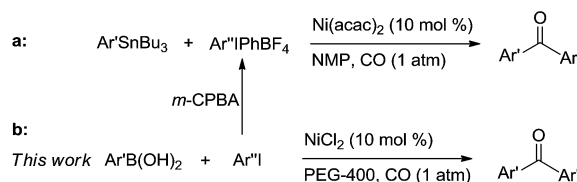
Recently, nickel-catalyzed cross-coupling reactions, including Suzuki coupling, have been attracting considerable

interest, because nickel are more earth abundant, less expensive and less toxic than palladium metal.^{5,6} Nickel and palladium belong to the same group in the periodic table, and can have oxidation numbers of 0 and +2. These characteristics indicate that they should comply with general cross-coupling reactions, because these reactions undergo through sequences of oxidative addition (oxidation state from 0 to +2), transmetalation, and reductive elimination (oxidation state from +2 to 0).⁵ In 1999, Kang and co-workers reported Ni(acac)₂-catalyzed carbonylative cross-coupling of organostannanes with hypervalent iodonium salts (Scheme 1a).⁷ Although this protocol give good yields for the synthesis of biarylketones, the organostannanes are quite toxic, the hypervalent iodonium salts are pre-prepared by the oxidation of corresponding aryl iodides and are expensive, and the substrate scope is rather limited. Therefore, it is imperative to exploit the catalytic potential of nickel for carbonylative Suzuki reactions (Scheme 1b). In addition, the ability to efficiently perform organic reactions in more environmentally benign solvents⁸ remains an important goal of green chemistry development.⁹ We disclose herein our results on the first nickel-catalyzed carbonylative Suzuki reactions of arylboronic acids with aryl iodides under ambient pressure of carbon monoxide and in a solvent that is attractive for industrial applications. Notably, this transformation possesses excellent selectivity even in the absence of a ligand. In addition, the active catalyst is *in situ* generation of nickel nanoparticles, which circumvents cumbersome processes for the preparation of metal nanoparticles (Scheme 2).

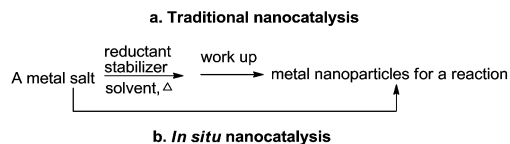
^aJiangsu Collaborative Innovation Center of Biomedical Functional Materials, Jiangsu Key Laboratory of Biofunctional Materials, Key Laboratory of Applied Photochemistry, School of Chemistry and Materials Science, Nanjing Normal University, Wenyuan Road NO. 1, 210023 Nanjing, China. E-mail: whhanwei@gmail.com; Fax: +86-025-8589-1455

^bCenter for Analysis and Testing, Nanjing Normal University, Wenyuan Road NO. 1, 210023 Nanjing, China

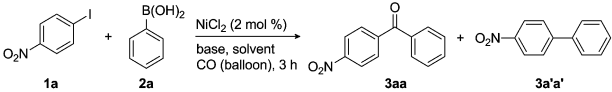
[†] Electronic supplementary information (ESI) available. See DOI: 10.1039/c4ra10739j



Scheme 1 Ni-catalyzed carbonylative cross coupling for the synthesis of biarylketones.

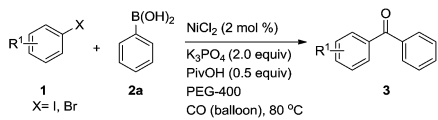
Scheme 2 Traditional nanocatalysis and *in situ* nanocatalysis.

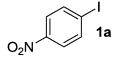
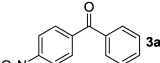
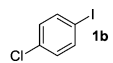
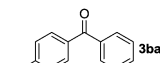
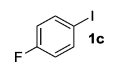
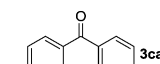

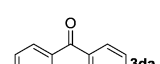

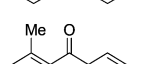

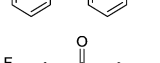
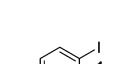
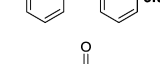
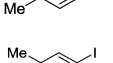
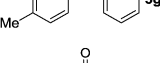
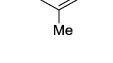
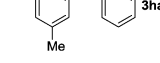
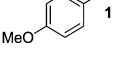
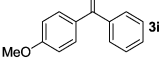
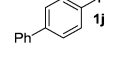
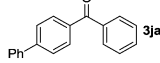

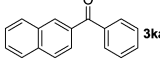

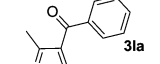
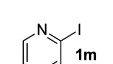
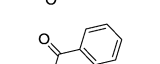
Poly(ethylene glycol) (PEG) is an inexpensive, readily available, and essentially nontoxic solvent and has attracted considerable interest for catalytic processes.¹⁰ Recently, we accomplished carbonylative Suzuki reactions that proceeded in the absence of an extra ligand in PEG-400 under atmospheric pressure of carbon monoxide.^{3,11} On the basis of the work, we initiated our efforts by testing the carbonylative Suzuki reaction of 4-nitroiodobenzene (**1a**) and phenylboronic acid (**2a**) with commercially available and inexpensive NiCl₂ as a catalyst in PEG-400 under 1 atm of CO (Table 1). When K₃PO₄ was chosen as a base, the reaction can provide desired product **3aa** in 76%, along with side product **3a'a'** in 20% yield (entry 1). Our previous work reported that pivalic acid effectively suppressed Suzuki reactions during palladium-catalyzed carbonylative Suzuki reactions.¹¹ As the report notes, the addition of pivalic acid achieved an excellent yield of **3aa** with a sharp decrease in the yield of **3a'a'** (7%) (entry 2). Moreover, when the catalyst loading was decreased to 1 mol%, the **3aa** product was obtained

Table 1 Nickel-catalyzed carbonylative Suzuki reaction of **1a** with **2a**^a


Entry	Acid	Base	Solvent	Yield of 3aa (%)	Yield of 3a'a' (%)
1	—	K ₃ PO ₄	PEG-400	76	20
2	PivOH	K ₃ PO ₄	PEG-400	91	7
				89 ^b	7 ^b
3	AcOH	K ₃ PO ₄	PEG-400	87	10
4	TFA	K ₃ PO ₄	PEG-400	69	11
5	TsOH	K ₃ PO ₄	PEG-400	81	18
6	PivOH	Na ₂ CO ₃	PEG-400	84	11
7	PivOH	K ₂ CO ₃	PEG-400	79	18
8	PivOH	CS ₂ CO ₃	PEG-400	7	90
9	PivOH	NaF	PEG-400	—	—
10	PivOH	KF	PEG-400	40	Trace
11	PivOH	AcOK	PEG-400	57	11
12	PivOH	K ₃ PO ₄	PEG-200	90	10
13	PivOH	K ₃ PO ₄	PEG-600	75	20
14	PivOH	K ₃ PO ₄	PEG-2000	10	—
15	PivOH	K ₃ PO ₄	Ethylene glycol	65	21
16	PivOH	K ₃ PO ₄	PEGDM-190	30	5
17 ^c	PivOH	K ₃ PO ₄	PEG-400	77	18
18 ^d	PivOH	K ₃ PO ₄	PEG-400	75	15

^a Reaction conditions (unless otherwise stated): **1a** (0.5 mmol), **2a** (0.75 mmol), CO (balloon), acid (0.25 mmol), base (1.0 mmol), NiCl₂ (2 mol%), solvent (2.0 mL), 80 °C. ^b Catalyst loading is 1 mol% and reaction time is 13 h. ^c Ni powder (2 mol%). ^d NiBr₂ (2 mol%).

Table 2 Nickel-catalyzed carbonylative Suzuki reaction of **1** with **2a**^a


Entry	Aryl iodide	Product	Time (h)	Yield ^b (%)
1			3	91
2			4	85
3			2	87
4			2	91
5			18	90
6			11	93
7			2	90
8			4	87
9			6	83
10			23	70
11			4	80
12			6	90
13			12	5
14			3	29

^a Reaction conditions (unless otherwise stated): **1** (0.5 mmol), **2a** (0.75 mmol), CO (balloon), PivOH (0.25 mmol), K₃PO₄ (1.0 mmol), NiCl₂ (2 mol%), solvent (2.0 mL), 80 °C. ^b Yield of isolated product after column chromatography.

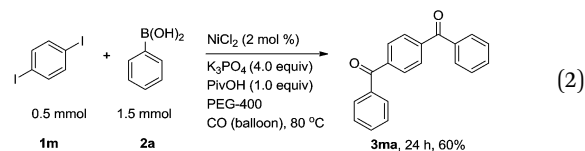
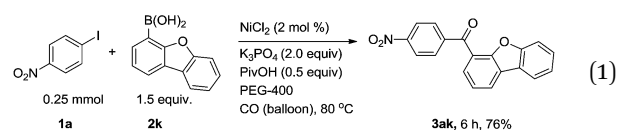
in 89% with a high selectivity in 13 h. Other acids such as AcOH, TFA, and TsOH were examined and found to be less effective than the pivalic acid in suppressing the formation of **3a'a'** (entries 3, 4, and 5). Subsequently, various bases were evaluated and led to significantly lower yields of **3aa** than K_3PO_4 (entries 6–11). The use of PEG-200 as a solvent gave a comparable result with the PEG-400, albeit with a slight higher yield of side product **3a'a'** (entry 12). However, the use of poly(ethylene glycol) dimethyl ether-190 (PEGDM-190) proved ineffective (entry 16). In addition, the use of ethylene glycol increase the side product **3a'a'** yield considerably (entry 15). Other solvents with polyether chains of different lengths, such as PEG-600 and PEG-2000 were found to be less effective than PEG-400 (entries 13–14). These results suggest that having both hydroxyl groups and an appropriate polyether chain length of PEG-400 plays a critical role in this reaction. Ni powder and $NiBr_2$ can give moderate results and are inferior to $NiCl_2$ (entries 17–18).

With this newly established conditions in hand, the scope of the aryl iodide coupling partner was explored. As illustrated in Table 2, electron-poor and -rich aryl iodides bearing *o*/*m*/*p* substituents readily undergo carbonylative Suzuki reactions with phenylboronic acid to afford unsymmetrical biaryl ketones in 70–91% yields. In addition, the reaction conditions are compatible with Cl, which is a convenient handle for further transformations (entry 2). The reaction also worked well with 1-iodo-naphthalene (**1k**) (entry 11). Moreover, 4-iodo-3,5-dimethylisoxazole (**1l**) as an example of a heterocyclic iodide gave 90% of the expected carbonylative product (entry 12). Unfortunately, 2-iodopyrazine (**1m**) and a bromide **1n** were inefficient substrates (low conversions) in the catalytic system (entries 13 and 14).

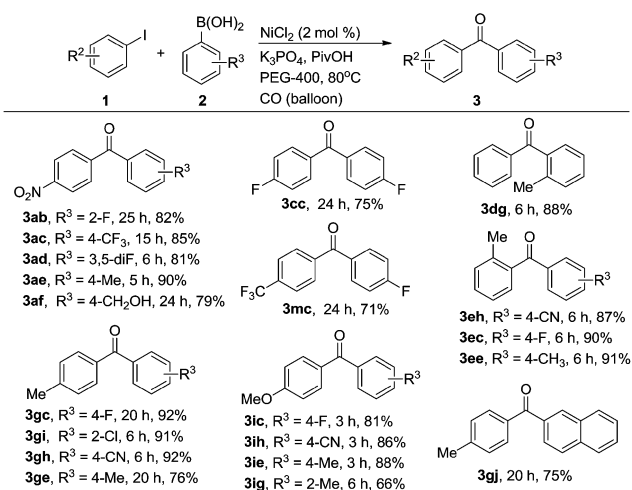
Further, the scope of the arylboronic acid coupling partner was investigated (Scheme 3). Arylboronic acids having electron-donating and electron-withdrawing substituents, such as

CH_3 , OH, F, CF_3 , CN, and Cl provided desired products in good to excellent yields. And the electronic and steric nature of the aryl boronic acids was observed to have little influence on the efficiency of the reactions. In addition 4,4'-difluorobenzophenone (**3cc**), a key intermediate for the synthesis of denagliptin¹² used for the treatment of type II diabetes and aggregation-induced emission (AIE) compounds,¹³ was obtained in a good yield. Furthermore, 2-naphthylboronic acid also underwent facile coupling, thus affording **3gj** in 75% yield.

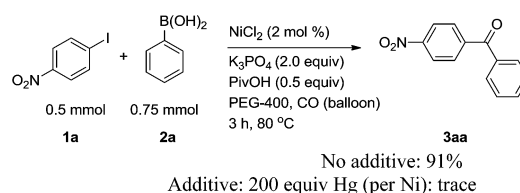
Notably, a heteroarylboronic acid, dibenzofuran-4-ylboronic acid (**2k**) served as a suitable carbonylative Suzuki cross-coupling partner, as indicated in [eqn (1)]. To our delight, double carbonylation of a diiodobenzene, 1,4-diiodobenzene (**1m**) also worked well and delivered the desired product that serves as an important precursor of advanced functional materials,^{14,d} in a synthetically useful yield [eqn (2)].



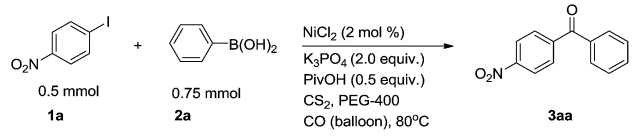
On the basis of our previous work,^{3,11,14} colloidal metal can readily generate in PEG. The mixture of the model reaction was analysed by transmission electron microscopy (TEM) to confirm that nickel nanoparticles was *in situ* generated (see Scheme S1 in ESI†). Moreover, the second reutilized nickel nanoparticles dispersed well (see Scheme S2 in ESI†). To know whether the catalysis occurred on the cluster surface or by leached Ni species,¹⁵ control experiments were carried out to test the homo/heterogeneous nature of the active nanocatalyst by using a mercury and a CS_2 additives.¹⁶ In the absence of a mercury additive, the reaction can provide the expected product **3aa** in 91% yield, whereas in the presence of a mercury additive (200 equiv.) the reaction was completely inhibited (Scheme 4). Furthermore, when 0.65 equiv. of CS_2 (relative to nickel) was added to the model reaction under the standard conditions, the reaction became inefficient to give **3aa** in 19% yield (Table 3, entry 2). Whereas the amount of CS_2 was



Scheme 3 Nickel-catalyzed carbonylative Suzuki reactions of aryl iodides with arylboronic acids. Reaction conditions (unless otherwise stated): **1** (0.5 mmol), **2** (0.75 mmol), CO (balloon), K_3PO_4 (1.0 mmol), PivOH (0.25 mmol), $NiCl_2$ (2 mol%), PEG-400 (2.0 mL), 80 °C. Yield of isolated product after column chromatography was given.



Scheme 4 The effect of the presence of Hg additive.

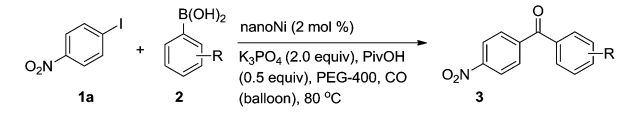
Table 3 Quantitative CS₂ poisoning experiments


Entry	CS ₂ (equiv.)	Time/h	Yield/%
1	0	3	91
2	0.65	3	19
3	1.0	3	Trace

increased to 1.0 equiv., the reactions were completely inhibited (Table 3, entry 3). These poisoning experiments suggest that the active catalyst is very likely to be heterogeneous in nature.¹⁶

To the best of our knowledge, *in situ* generation of nickel nanoparticles as catalyst for carbon-carbon coupling reactions has never been reported.¹⁷ To get an insight into the catalytic activity of both the *in situ* generated nickel nanoparticles and preformed nickel nanoparticles for carbonylative Suzuki reactions, control experiments were performed under the normal conditions (Table 4). According to the Table 4, the novel *in situ* generated nickel nanoparticles exhibit higher catalytic activity than the conventional preformed nickel nanoparticles.¹⁸ This is because *in situ* generated nickel nanoparticles avoid cumbersome processes for the preparation of metal nanoparticles and reduce the probability of aggregation.^{14c}

For practical applications, we employed the carbonylative coupling reaction of 4-iodotoluene (**1g**) and 4-fluorophenyl boronic acid (**2c**) to examine the reusability efficiency of the catalytic system. The catalytic system can be recycled up to five times to give the desired product in 92%, 92%, 92%, 87%, and 85% yield, respectively. This is because *in situ* generated nanoparticles can be stabilized to maintain small particle sizes through catalysis for a reaction.^{14c}

Table 4 Control experiments of *in situ* generated nickel nanoparticles and preformed nickel nanoparticles for carbonylative Suzuki reactions


Entry	R	Catalyst type	Time (h)	Yield (%)
1	H	<i>In situ</i>	3	91
2	H	Preformed	3	65
3	4-Me	<i>In situ</i>	5	90
4	4-Me	Preformed	5	3
5	3,5-DiF	<i>In situ</i>	6	81
6	3,5-DiF	Preformed	6	50

Conclusions

In conclusion, an efficient and ligandless Ni-catalyzed carbonylative reactions of aryl iodides and aryl boronic acids that proceed under ambient pressure of CO in PEG-400 has been developed. This protocol features the first time use of an inexpensive and air-stable Ni salt as a catalyst, is efficient and recyclable, and provides a new approach for carbonylative Suzuki coupling. Notably, compared with a conventional nanocatalysis (pre-prepared nanoparticles), the *in situ* generated nanocatalysis shows a shortcut for nanocatalysis as well as higher catalytic activity. Additional studies directed at evaluating the scope of this transformation and enhancing our understanding of the mechanism are underway.

Acknowledgements

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