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Ligand-Free Pd-Catalyzed Carbonylative Cross-Coupling Reactions under Atmospheric Pressure of Carbon Monoxide: Synthesis of Aryl Ketones and Heteroaromatic Ketones

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The carbonylative Suzuki cross-coupling reactions of boronic acids with aryl iodides catalyzed by $Pd_2(dba)_3$ as a ligand-free catalyst under atmospheric pressure of carbon monoxide has been firstly developed. Under mild reaction conditions, a broad range of aryl/heteroaryl iodides and aryl/heteroaryl boronic acids were selectively coupled to afford the corresponding diaryl ketones in good to excellent yields at low catalyst loadings (0.05 to 2 mol-%). Moreover, the catalyst can also be recycled.

Introduction

Diaryl ketones are important building blocks in the synthesis of natural products and biologically active small molecules, and a number of approaches for their preparation have been introduced.[1] One traditional approach is the Friedel–Crafts acylation of substituted aromatic rings, which requires excess amounts of Lewis acid.[2] Another alternative strategy is the acylation of aryl metal species with functional carboxylic acid derivatives.[3] An efficient and direct route to diaryl ketones is the Pd-catalyzed three-component coupling of aryl halides, boronic acids, and carbon monoxide, which forms two carbon–carbon bonds in a single operation, without the stepwise fashion of introducing the ketone functional group.[4] Consequently, many efficient palladium-based catalytic systems for the reactions have been described.[5] Generally, to suppress unwanted competitive direct Suzuki cross-coupling, a high pressure of CO is employed to achieve good chemoselectivity of the reaction,[5d–5g,5m,5n] and ligands are usually necessary to increase reactivity and stability of the palladium catalysts. Up to now, significant advances have been achieved by palladium-based catalytic systems containing N/P ligands.[5b,5d–5h,5j–5n] For example, Martin and co-workers have successfully developed a PEPPSI-IPr catalyst for the carbonylative cross-coupling of sterically hindered di-*ortho*-substituted aryl iodides and *ortho*-substituted aryl boronic acids under balloon pressure of CO.[5m]

However, ligand-free palladium catalyst would be more desirable from an economical and ecological point of view. Recently, Bhanage and co-workers firstly reported the ligand-free Pd complex catalyzed Suzuki carbonylative reactions of aromatic substrates and a few heteroaryl substrates, but an autoclave (100–200 psi of carbon monoxide) was necessary to drive the reactions.[6] To the best of our knowledge, there is no general study on the Suzuki carbonylative reaction catalyzed by a ligand-free palladium catalyst under atmospheric pressure of carbon monoxide. In continuation of our program on phosphane-free Pd-catalyzed C–C bond-formation reactions,[7] herein we demonstrate for the first time that, without any additional ligand, the commercially available simple Pd source $Pd_2(dba)_3$ (dba = dibenzylideneacetone) is an active catalyst for the Suzuki carbonylative reactions of aryl/heteroaryl iodide under atmospheric pressure of CO. This method allows the preparation of a variety of diaryl ketones/aryl heteroaryl ketones in good to excellent yields at low catalyst loadings under mild reaction conditions.

Results and Discussion

The Suzuki carbonylative reaction of 4-iodoanisole (**1a**) with phenylboronic acid (**2a**) was chosen as the model reaction and influences of different parameters were examined to optimize the reaction conditions (Table 1). Several solvents including THF, anisole, and toluene were evaluated in the presence of $Pd(OAc)_2$ (1 mol-%) and K_2CO_3 (3 equiv.) under balloon pressure of CO and the highest yield and selectivity were observed in anisole (Table 1, Entry 3 vs. Entries 1 and 2). Among the palladium catalysts

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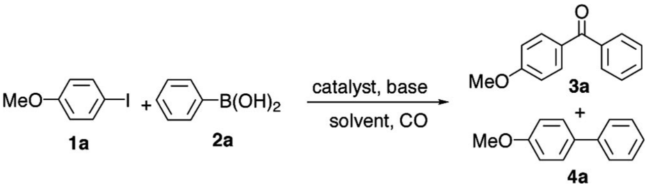
examined, $Pd_2(dba)_3$ gave the best result: 99% yield of **3a** (Table 1, Entry 5 vs. Entries 3 and 4). It is well known that π-acid olefins can not only affect the rate of oxidative addition through formation of an active palladium species, but they might also play a role in stabilization of the catalyst.[8] Thus, we speculated that $Pd_2(dba)_3$ as an olefin-containing catalyst would facilitate the catalytic reaction. The effect of temperature was not obvious and almost quantitative yield was obtained at either 80 or 100 °C (Table 1, Entries 5 and 6). Finally, two other bases were evaluated (Table 1, Entries 7 and 8). A slightly lower yield was observed using Cs_2CO_3 as the base, but a very poor yield of **3a** was found when the organic base Et_3N was used. Therefore, the optimized conditions for Suzuki carbonylative reaction were $Pd_2(dba)_3$ (1 mol-%) as the catalyst, anisole as the solvent, and K_2CO_3 as the base at 100 °C under balloon pressure of CO.

Table 1. Effects of reaction parameters on the Suzuki carbonylative reaction of 4-iodoanisole (**1a**) with phenylboronic acid (**2a**).[a]

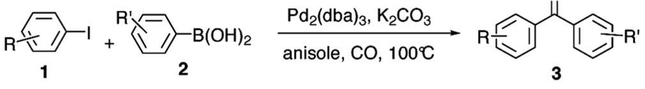


Entry	Catalyst	Conv. [%]	Yield of **3a** [%][b]	Selectivity of **3a** [%]
1[c]	$Pd(OAc)_2$	42	<1	<1
2[d]	$Pd(OAc)_2$	76	60	79
3[e]	$Pd(OAc)_2$	100	82	>99
4[e]	$Pd(CH_3CN)_2Cl_2$	100	89	100
5[e]	$Pd_2(dba)_3$	100	99	100
6	$Pd_2(dba)_3$	100	100	100
7[f]	$Pd_2(dba)_3$	99	96	97
8[g]	$Pd_2(dba)_3$	82	32	85

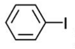
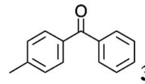
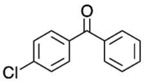
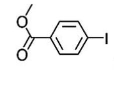
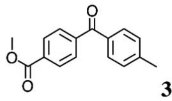
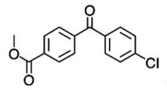
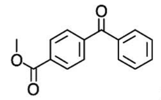
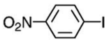
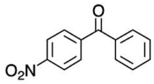
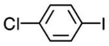
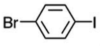
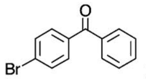
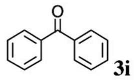
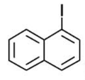
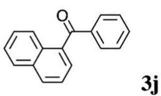
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), catalyst (1.0 mol-%), K_2CO_3 (3 equiv.), CO (balloon pressure), and anisole (2 mL) at 100 °C for 20 h. [b] Determined by GC using biphenyl as an internal standard. [c] THF (2 mL) as the solvent at 60 °C. [d] Toluene (2 mL) as the solvent at 80 °C. [e] At 80 °C. [f] Cs_2CO_3 (3 equiv.) as base. [g] Et_3N (3 equiv.) as base.

Further investigation of the substrate scope was carried out under the optimized reaction conditions. In Table 2, various arylboronic acids as well as aryl iodides were examined and good functional group tolerance of the $Pd_2(dba)_3$ catalytic system was observed. For example, both 4-methylbenzeneboronic acid (**2b**) and 4-chlorophenylboronic acid (**2c**) reacted smoothly with aryl iodides to give unsymmetrical biaryl ketones in high yields (Table 2, Entries 1–4). In addition, aryl iodides containing electron-withdrawing groups including CH_3OCO, Br, and Cl produced desired ketones **3f**, **3c**, and **3h** in good to excellent yields (Table 2, Entries 5, 7, 8). It is noteworthy that up to 85% yield of **3g** was obtained for **1d** with the strong electron-withdrawing substituent NO_2, known to promote the direct coupling reaction, to provide a mixture of biaryl and aryl ketone (Table 2, Entry 6). This selectivity is much better than that reported for $PdCl_2(MeCN)_2$-catalyzed carbonylative coupling reaction of triphenylalane with 4-iodonitrobenzene, affording 41% yield of 4-nitrobenzophenone and 55% yield of 4-nitrobiphenyl.[5a,5d] The carbonylation of 4-bromoiodobenzene (**1f**) selectively occurred at the C–I bond, which gives an opportunity for further functionalization at the intact bromide group in the product ketone (Table 2, Entry 8). To our delight, when the $Pd_2(dba)_3$ catalyst was employed, the reaction also worked well with electron-neutral iodobenzene (**1b**) and sterically hindered 1-iodonaphthalene (**1g**), providing corresponding ketones **3i** and **3j** in 84 and 82% yield, respectively (Table 2, Entries 9 and 10).

Table 2. Suzuki carbonylative reaction of aryl iodides with arylboronic acids.[a]



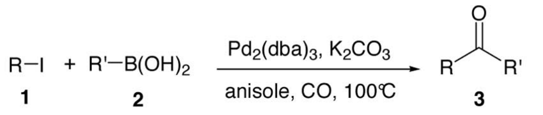
2a : R' = H; **2b** : R' = 4-CH_3; **2c** : R' = 4-Cl

Entry	1	2	3	Yield [%][b]
1	 **1b**	**2b**	 **3b**	98
2	**1b**	**2c**	 **3c**	90
3	 **1c**	**2b**	 **3d**	92
4	**1c**	**2c**	 **3e**	91
5	**1c**	**2a**	 **3f**	94
6	 **1d**	**2a**	 **3g**	85
7	 **1e**	**2a**	**3c**	81
8	 **1f**	**2a**	 **3h**	67
9	**1b**	**2a**	 **3i**	84
10	 **1g**	**2a**	 **3j**	82

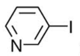
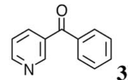
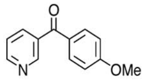
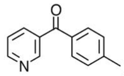
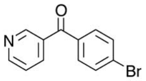
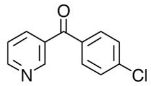
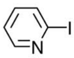
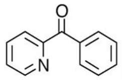
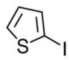
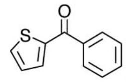
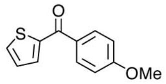
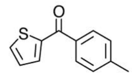
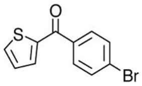
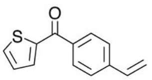
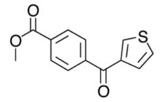
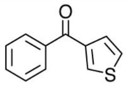
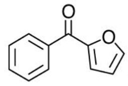
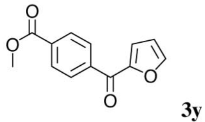
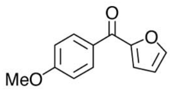
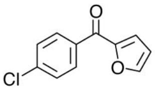
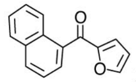
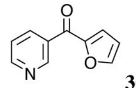
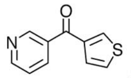
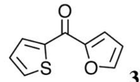
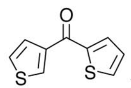
[a] Reaction conditions: **1** (0.2 mmol), **2** (0.2 mmol), $Pd_2(dba)_3$ (1 mol-%), K_2CO_3 (3 equiv.), CO (balloon pressure), anisole (2 mL) at 100 °C for 20 h. [b] Isolated yield.

Heteroaryl-substituted pyridine derivatives that can be formed through Suzuki carbonylative reactions are a very important family of compounds in diverse areas of chemistry such as metal-coordination complexes,[9] pharmaceutical agents,[10] and molecular electronic device materials.[11] However, based on the detrimental electron-withdrawing effect of the nitrogen atom of the pyridine ring that disfavors CO insertion into the pyridyl–palladium intermediate, the use of a higher pressure of carbon monoxide has been a general method for suppressing such a side reaction.[5g,12] To demonstrate the generality of our catalyst system, iodopyridines were treated with various aryl boronic acids under atmospheric pressure of CO to provide pyridyl aryl ketones in good to excellent yields (Table 3, Entries 1–6). Catalyzed

Table 3. Suzuki carbonylative reactions of heteroaryl iodides or heteroaryl boronic acids.[a]



2d : R' = 4-$CH_3OC_6H_4$; **2e** : R' = 4-BrC_6H_4; **2f** : R' = 4-CH_2=CHC_6H_4;
2g : R' = thiophen-3; **2h** : R' = furan-2

Entry	1	2	3	Yield [%][b]
1	 **1h**	**2a**	 **3k**	97
2	**1h**	**2d**	 **3l**	88
3	**1h**	**2b**	 **3m**	84
4	**1h**	**2e**	 **3n**	94
5	**1h**	**2c**	 **3o**	81
6	 **1i**	**2a**	 **3p**	69
7	 **1j**	**2a**	 **3q**	91
8	**1j**	**2d**	 **3r**	92
9	**1j**	**2b**	 **3s**	87
10	**1j**	**2e**	 **3t**	78
11	**1j**	**2f**	 **3u**	66
12	**1c**	**2g**	 **3v**	87
13	**1f**	**2g**	 **3w**	75
14	**1f**	**2h**	 **3x**	85
15	**1c**	**2h**	 **3y**	63
16	**1a**	**2h**	 **3z**	65
17	**1d**	**2h**	 **3A**	72
18	**1g**	**2h**	 **3B**	67
19	**1h**	**2h**	 **3C**	82
20	**1h**	**2g**	 **3D**	87
21	**1j**	**2h**	 **3E**	83
22	**1j**	**2g**	 **3F**	68

[a] Reaction conditions: **1** (0.2 mmol), **2** (0.2 mmol), $Pd_2(dba)_3$ (1 mol-%), K_2CO_3 (3 equiv.), CO (balloon pressure), anisole (2 mL) at 100 °C for 20 h. [b] Isolated yield.

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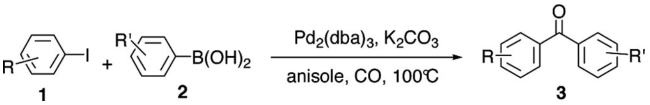
by ligand-free $Pd_2(dba)_3$ (1 mol-%), 2-iodopyridine (**1i**) was found to be less reactive than 3-iodopyridine, providing 69% yield of corresponding ketone **3p** (Table 3, Entry 6 vs. 1), which is comparable to that reported by Miyaura and co-workers using $PdCl_2(PPh_3)_2$ (3 mol-%, 66% yield).[5d] On the other hand, there are few reports on the Pd-catalyzed carbonylative Suzuki cross-coupling reactions of S-heteroaryl/O-heteroaryl substrates due to the formation of stable, catalytically inert compounds.[13] To expand the generality of our catalyst system, carbonylative Suzuki cross-coupling reactions of O- and S-heteroaryl substrates were investigated (Table 3, Entries 7–18). The reactions of 2-iodothiophene (**1j**) proceeded smoothly to give good to excellent yields of the corresponding ketones (Table 3, Entries 7–10). Notably, despite the possibility of competitive Heck, Suzuki, and carbonylative Heck reactions, the Suzuki carbonylative reaction of 4-vinylphenylboronic acid (**2f**) with 2-iodothiophene (**1j**) proceeded selectively to afford a moderate yield (66%) of 4-vinylphenyl 2-thienyl ketone (**3u**; Table 3, Entry 11), an important intermediate that could be easily hydroxycarbonylated to Suprofen, a commercial nonsteroidal anti-inflammatory drug.[14] To the best of our knowledge, this is the first time that ketone **3u** was synthesized by ligand-free catalysis under atmospheric pressure of carbon monoxide, which demonstrates the high selectivity and catalytic activity of our catalyst system.[5n] Furthermore, thiophen-3-ylboronic acid (**2g**) and furan-2-ylboronic acid (**2h**) worked well with a variety of aryl iodides, providing good yield of the expected heteroaryl ketones (63–87%; Table 3, Entries 12–17). Even sterically hindered 1-iodonaphthalene (**1g**) was found to proceed smoothly with furan-2-ylboronic acid (**2h**), affording 67% yield of **3B** (Table 3, Entry 18). From a synthetic viewpoint, it was significant to note that various combinations of heteroaryl iodides with heteroaryl boronic acids could be coupled efficiently by our catalyst system. The carbonylative Suzuki reaction of 3-iodopyridine (**1h**) with furan-2-ylboronic acid (**2h**) and thiophen-3-ylboronic acid (**2g**) resulted in 82 and 87% yield of the corresponding heteroaryl ketones, respectively (Table 3, Entries 19 and 20). Moreover, 2-iodothiophene (**1j**) reacted smoothly with furan-2-ylboronic acid (**2h**) and thiophen-3-ylboronic acid (**2g**), providing 83 and 68% yield of the desired heteroaryl ketones, respectively (Table 3, Entries 21 and 22).

To investigate the efficiency of this simple catalyst, we further decreased the catalyst loading to 0.05 mol-% under the optimized reaction conditions (Table 4). It is noteworthy that this ligand-free catalytic system exhibited high activity for the Suzuki carbonylative reaction of 4-iodoanisole (**1a**) with phenylboronic acid (**2a**) without any further prolonged reaction time (0.1 mol-% of Pd, 99% yield, TON = 990; Table 4, Entry 2), whereas the same reaction affording **3a** in 90% yield needed to be carried out under 2 mol-% of $Pd(tmhd)_2$ (tmhd = 2,2,6,6-tetramethyl-3,5-heptanedionate).[6] By further decreasing the Pd loading to 0.05 mol-% a desirable yield could still be obtained (85% yield, TON = 1700; Table 4, Entry 3). Meanwhile, lowering the palladium amount to 0.1 mol-% in the Suzuki carbonylative reaction of electrically neutral iodobenzene (**1b**) with 4-methoxyphenylboronic acid (**2d**) led to a slight decrease in the yield of the corresponding ketone (i.e., **3a**), whereas the TON grew from 184 (0.5 mol-%) to 910 (Table 4, Entries 4 and 5).

Table 4. Catalytic efficiency of the palladium-catalyzed Suzuki carbonylative reaction.[a]

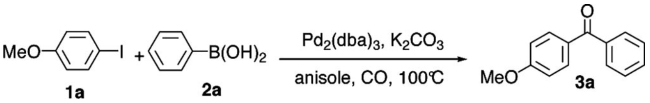


Entry	1	2	Pd loading [mol-%]	Yield [%][b]	TON[c]
1	**1a**	**2a**	0.5	100	200
2	**1a**	**2a**	0.1	99	990
3	**1a**	**2a**	0.05	85	1700
4	**1b**	**2d**	0.5	92	184
5	**1b**	**2d**	0.1	91	910

[a] Reaction conditions: **1** (0.5 mmol), **2** (0.5 mmol), $Pd_2(dba)_3$, K_2CO_3 (3 equiv.), CO (balloon pressure), anisole (2 mL) at 100 °C for 20 h. [b] GC yield with the use of biphenyl as an internal standard. [c] TON: turnover number, defined as mmol (product)/mmol (Pd).

Encouraged by the high efficiency of our catalyst, we then examined the reusability of $Pd_2(dba)_3$ (Table 5). The catalyst was recovered simply by filtration, washing with ethyl acetate and drying under vacuum, and then reused. It was found that the activity of the catalyst remained after four consecutive runs. This result might indicate that the active species was only slightly leached during these experiments, which is significant from a practical point of view.

Table 5. Recycling study of the catalyst.[a]



Run	1	2	3	4
Yield [%][b]	100	90	81	71

[a] Reaction conditions: **1a** (1 mmol), **2a** (1 mmol), $Pd_2(dba)_3$ (1 mol-%), K_2CO_3 (3 equiv.), CO (balloon pressure), anisole (10 mL) at 100 °C for 20 h. [b] GC yield with the use of biphenyl as an internal standard.

Conclusions

In summary, we have described the first efficient and convenient alternative for the preparation of a variety of biaryl ketones by using ligand-free $Pd_2(dba)_3$ as a catalyst under atmospheric pressure of carbon monoxide. Compared with previous reports, several features of the present results were established: (1) The catalytic system is efficient and general not only for a broad range of aryl iodides and aryl boronic acids but also for various combinations of heteroaryl iodides with heteroaryl boronic acids. (2) A variety of functional groups, such as electron-donating groups, including CH_3 and CH_3O, electron-withdrawing groups, including CH_3OCO, Br, and Cl, and even the strongly electron-withdrawing substituent NO_2, are tolerated. (3) The reactions demonstrated high selectivity (up to 100 % for the carbonylative Suzuki reaction of 4-iodoanisole with phenylboronic acid) for the catalytic system, and the important pharmaceutical intermediate 4-vinylphenyl 2-thienyl ketone could be prepared selectively in good yield. (4) This ligand-free $Pd_2(dba)_3$-catalyzed carbonylative Suzuki coupling reaction provided high TONs up to 1700. (5) The catalyst can also be recycled. Further efforts to extend the application of this system in other coupling transformations are underway in our laboratory.

Experimental Section

Typical Experimental Procedure for the Carbonylative Suzuki Coupling Reaction: Aryl iodide **1a** (47.8 mg, 0.2 mmol), aryl boronic acid **2a** (24.9 mg, 0.2 mmol), $Pd_2(dba)_3$ (1.9 mg, 1 mol-%), and K_2CO_3 (83.8 mg, 3 equiv.) were mixed in anhydrous anisole (2 mL) under balloon pressure of CO, and the reaction mixture was stirred at 100 °C for 20 h. The reaction mixture was then filtered through Celite, which was washed three times with ethyl acetate and analyzed by gas chromatography (GC) with biphenyl as the internal standard. The crude product was purified by column chromatography on silica gel (hexanes/EtOAc) to give desired product **3a**. ^1H NMR (400 MHz, $CDCl_3$):[15] δ = 7.82–7.80 (d, $^3J_{H,H}$ = 7.2 Hz, 2 H, H_{phenyl}), 7.75–7.73 (d, $^3J_{H,H}$ = 4.2 Hz, 2 H, 4-MeOC_6H_4), 7.56–7.52 (t, $^3J_{H,H}$ = 7.2 Hz, 1 H, H_{phenyl}), 7.46–7.43 (t, $^3J_{H,H}$ = 7.4 Hz, 2 H, H_{phenyl}), 6.95–6.93 (d, $^3J_{H,H}$ = 7.6 Hz, 2 H, 4-MeOC_6H_4), 3.85 (s, 3 H, OCH_3) ppm.

Typical Experimental Procedure for the Recycling Study of the Catalyst: Aryl iodide **1a** (238.8 mg, 1 mmol), aryl boronic acid **2a** (124.4 mg, 1 mmol), $Pd_2(dba)_3$ (9.5 mg, 1 mol-%), and K_2CO_3 (418.8 mg, 3 equiv.) were mixed in anhydrous anisole (10 mL) under balloon pressure of CO, and the reaction mixture was stirred at 100 °C for 20 h. After each run, the catalyst was recovered by filtration through Celite. The catalyst was then washed with ethyl acetate (3 × 10 mL) and then dried under vacuum. The obtained catalyst was used for the next run.

Supporting Information (see footnote on the first page of this article): Experimental procedures and characterization for all products.

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