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Ligand-Free Palladium Catalyzed Oxidative Carbonylative Homocoupling of Arylboron Reagents at Ambient Pressure

Hongyuan Zhao[a] and Wei Han*[a]

Abstract: Arylboronic acids or potassium aryltrifluoroborates were readily oxidatively carbonylated to their corresponding diaryl ketones in high yields with high selectivities by ligand-free palladium-catalyzed homocoupling at atmospheric pressure. This novel method employs molecular oxygen or iodine as the oxidant and offers an attractive alternative to transition-metal based oxidant systems.

Diaryl ketones have attracted continuous attention in many areas serving as important synthetic intermediates and common building blocks for C-C bond formation.[1] As core scaffolds, diaryl ketones also exist in a tremendous range of natural products, pharmaceuticals, advanced materials, and photosensitizers.[2] Due to their siginificant importance, much interest has been paid to the synthesis of diaryl ketones.

Arylboronic acid derivatives have high stability toward air, water, and heat, ready availability, and low toxicity. For these advantageous properties, they have found widely applications in synthetic chemistry.[3] The transformation of these compounds into diaryl ketones is typically accomplished through palladium-catalyzed carbonylatve Suzuki coupling or carbonylative homocoupling using gaseous CO as carbonyl source.[4] CO is a strong π-acidic ligand, decreases the electron density of Pd(0) species, and thus increases the difficulty of the oxidative addition of organic halides towards Pd(0) species.[5] Consequently, the carbonylative Suzuki coupling usually need high CO pressure and high temperature. Moreover, costly ligands are almost always required to achieve efficient catalysis.

Recently, oxidative carbonylative homocoupling of arylboronic acids with CO has emerged as an attractive new alternative to the classic carbonylation strategy. This is because the oxidative carbonylative process is on the basis of high-valent Pd(II) species that circumvents the reluctant oxidative addition step.[5a,6] However, the Pd-catalyzed carbonylative homocoupling of arylboronic reagents has underdeveloped. Frequently, the homocouplings from arylboronic reagents were reported as side reactions with poor selectivity.[7] Recently, Xiao group demonstrated a highly selective $Pd(PPh_3)_4$-catalyzed carbonylative homocoupling of arylboronic acids to give diaryl ketones in the presence of $AgNO_3$ as oxidant.[8] Subsequently, a seminal example of $Pd(PPh_3)_2Cl_2$-catalyzed synthesis of symmetric diaryl ketones from arylboronic acids was reported by Jiao group. Notably, this method employed environmental-friendly oxygen as oxidant, albeit with CuCl as co-oxidant.[9]

Organotrifluoroborate is a valuable alternative to boronic acid and boronate ester. The organotrifluoroborate doesn't undergo undesirable side reactions with commonly used bases, organic acids, and nucleophiles due to their tetracoordinate nature.[10] Thus, organotrifluoroborates, in contrast to most other boron reagents, can be employed to build molecular complexity, while leaving the carbon-boron bond intact.[11] To the best of our knowledge, although organotrifluoroborates present all of the advantages aforementioned, the carbonylative homocoupling of these species into the corresponding diaryl ketones has never been reported.[12]

Therefore, we focused on developing a more practical and inexpensive method for catalytic carbonylative homocoupling of aryltrifluoroborates and arylboronic acids in the absence of a transition-metal oxidant and a phosphine ligand. Herein, we report the oxidative carbonylative homocoupling of aryltrifluoroborates and arylboronic acids using oxygen or iodine as the oxidant at atmopsheric pressure.

On the basis of our previous research where catalytic carbonylations proceeded successfully in PEG-400 solvent,[13] investigations were initiated on the oxidative carbonylation of phenylboronic acid in PEG-400 using Na_3PO_4 as base under ambient pressue (CO/O_2 = 5:1) (Table 1). We found that an iodide additive played a decisive role in the transformation (Table 1, entries 1-4). To our delight, NaI as the iodide additive gave 50 % yield of the desired product **2a**, albeit with the concomitant generation of side product **2a'** in 20% yield (entry 2). Encouraged by this result, various bases were screened (entries 6-15), with the finding that $KHCO_3$ turned out to be the best base and enhanced the carbonylative coupling to give **2a** in 85% yield with high selectivity even at 80 °C (entry 15).[14] Replacing PEG-400 with NHD (polyethylene glycol dimethylether with an average molecular weight of 250 Da) or dioxane as the solvent resulted in failure of the reaction (entries 18-19).

When 4-methoxyphenylboronic acid (**1b**) as substrate was subjected to the reaction conditions, a poor yield of the desired product (**2b**) was obtained. To get better result, the amount of NaI and the ratio of CO to O_2 were optimized: almost no reaction happened without oxygen, whereas with the increase of the proportion of O_2 to CO, homocoupling side product **2b'** readily formed (Table 2, entries 1-4). When the ratio of CO to O_2 was 4:1, an ideal result can be obtained in the presence of NaI (30 mol%) (Table 2, entry 5).

Having identified the optimal conditions, we turned to examine the scope of arylboronic acids (Scheme 1). The model substrate phenylboronic acid (**1a**) gave the carbonylative product **2a** in 85% yield. Arylboronic acids bearing either electron-rich or electron-deficient substituents, regardless of

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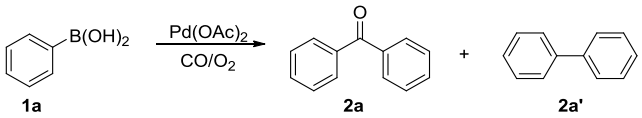
their positions (*o*-, *m*-, *p*-), gave rise to the desired products in good yields. The reaction times were found to be only loosely correlated with the electronic nature of the substituents on the phenyl ring. A variety of functionalities, such as methoxy (**2b**), methyl (**2c-f**), fluoro (**2g** and **2i**), chloro (**2h** and **2j**), trifluoro (**2k**), and trifluoromethoxy (**2l**) were well tolerated under normal conditions. When naphthalene-1-boronic acid was emloyed, a moderate yield of **2m** can be abtained.

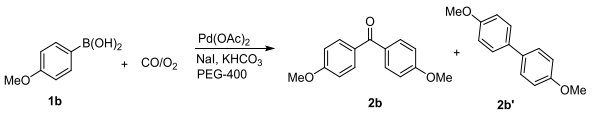
Table 1. Optimization of Reaction Conditions.[a]



Entry	[I]	Base	Tem.	Sol.	Yield of **2a** (%)	Yield of **2a'** (%)
1[b]	TBAI	Na_3PO_4	100 °C	PEG-400	35	30
2[b]	NaI	Na_3PO_4	100 °C	PEG-400	50	20
3[b]	KI	Na_3PO_4	100 °C	PEG-400	10	50
4[b]	-	Na_3PO_4	100 °C	PEG-400	Trace	Trace
5	NaI	Na_3PO_4	100 °C	PEG-400	65	10
6	NaI	NaF	100 °C	PEG-400	10	65
7	NaI	CsF	100 °C	PEG-400	10	70
8	NaI	Na_2CO_3	100 °C	PEG-400	75	5
9	NaI	$NaHCO_3$	100 °C	PEG-400	Trace	5
10	NaI	K_2CO_3	100 °C	PEG-400	15	25
11	NaI	K_3PO_4	100 °C	PEG-400	20	10
12	NaI	$KHCO_3$	100 °C	PEG-400	85	3
13	NaI	Et_3N	100 °C	PEG-400	5	Trace
14	NaI	DBU	100 °C	PEG-400	30	Trace
15	**NaI**	**$KHCO_3$**	**80 °C**	**PEG-400**	**85**	**4**
16	NaI	$KHCO_3$	50 °C	PEG-400	80	Trace
17	NaI	$KHCO_3$	25 °C	PEG-400	Trace	Trace
18	NaI	$KHCO_3$	80 °C	NHD	Trace	Trace
19	NaI	$KHCO_3$	80 °C	dioxane	Trace	Trace
20	I_2	$KHCO_3$	80 °C	PEG-400	5	64

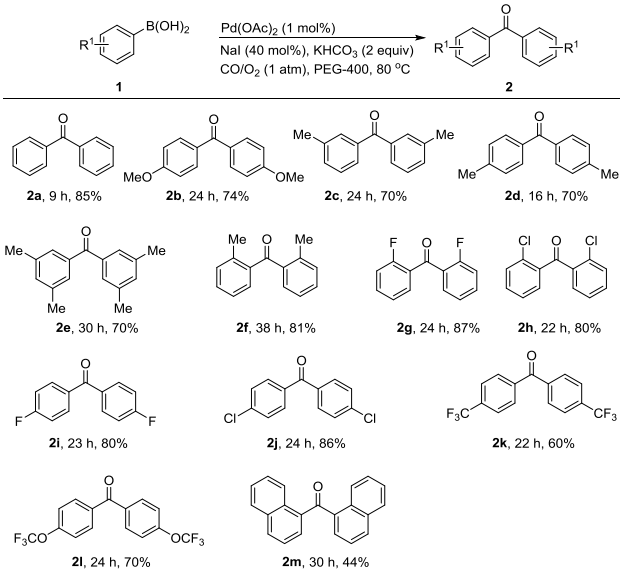
[a] *Reaction conditions* (unless otherwise noted): phenylboronic acid (0.5 mmol), $Pd(OAc)_2$ (1 mmol%), iodide (15 mmol%), base (2 equiv), CO/O_2 (5:1, 1 atm), PEG-400 (2 ml), 100 °C, and 9 h. [b] Base (4 equiv).

Table 2. Further Optimization.[a]



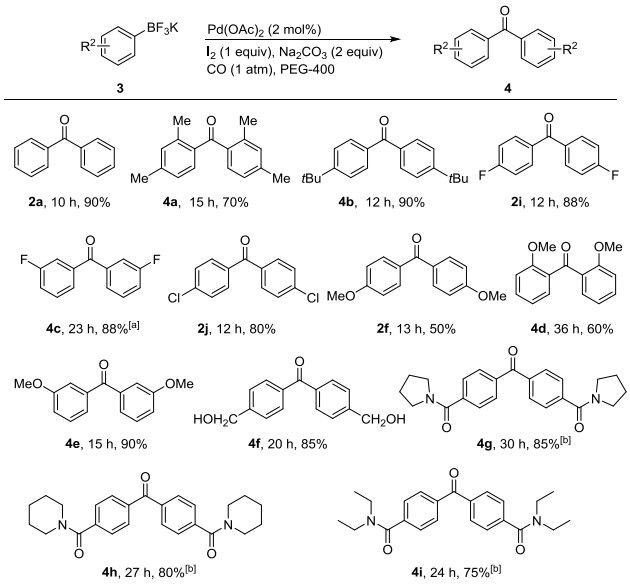
Entry	CO/O_2	NaI (mol %)	Yield of **2b** (%)	Yield of **2b'** (%)
1	2:1	15	29	44
2	2:1	30	45	20
3	4:1	30	55	5
4	5:1	30	48	10
5	**4:1**	**40**	**74**	**5**
6	4:1	100	67	10
7	1:0	40	trace	trace

[a] *Reaction conditions* (unless otherwise noted): Reaction conditions (unless otherwise noted): **1b** (0.5 mmol), $Pd(OAc)_2$ (1 mol%), NaI, $KHCO_3$ (2 equiv), CO/O_2, 80 °C, and 24 h.



Scheme 1. Pd-catalyzed carbonylative homocoupling of arylboronic acids. *Reaction conditions* (unless otherwise stated): **1** (0.5 mmol), $KHCO_3$ (1.0 mmol), NaI (40 mol%), $Pd(OAc)_2$ (1 mol %), PEG-400 (2 mL), CO/O_2 (4:1, 1 atm), and 80 °C.

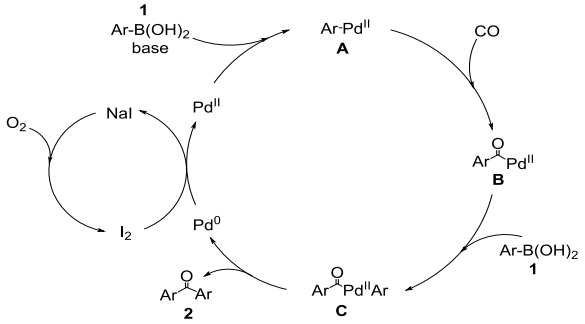
Considering the advantages aforementioned of organot_ rifluoroborates,[10,11] we further extended the protocol to aryltrifluoroborates. Unfortunately, only a trace of carbonylative product was obtained when potassium phenyltrifluoroborate was used under the above standard conditions. After a concise optimization, we found out that using iodine (1.0 equiv) as the oxidant instead of oxygen the carbonylative homocoupling was greatly enhanced to give the desired product **2a** in 80% yield. Additionally, replacing $KHCO_3$ with Na_2CO_3 as the base resulted in a higher yield



Scheme 2. Pd-catalyzed carbonylative homocoupling of potassium aryltrifluoroborates. *Reaction conditions* (unless otherwise stated): **3** (0.5 mmol), Na_2CO_3 (1.0 mmol), I_2 (0.5 mmol), $Pd(OAc)_2$ (2 mol %), deoxygenized PEG-400 (2 mL), CO (1 atm), and 80 °C. [a] $KHCO_3$ (1.0 mmol) replaced Na_2CO_3. [b] 100 °C.

(90%) of **2a** (Scheme 2). When catalytic iodine (50 mol%) was used, the yield of **2a** was decreased to 71%. Under the newly established conditions, we next examined the carbonylative homocoupling reactions of various potassium aryltrifluoroborates (Scheme 2). To our delight, a broad scope of potassium aryltrifluoroborates could be carbonylated in good to excellent yields with high selectivities, including *ortho*-, *para*-, and *meta*-substituted potassium aryltrifluoroborates. Both electron-rich and electron-poor potassium aryltrifluoroborates achieved comparable results. Fluoro-substituted potassium aryltrifluoroborates underwent facile carbonylative homocoupling to provide fluorinated biaryl ketones (**2i** and **4c**) that are potentially important intermediates in the synthesis of drugs and organic materials. Indeed, **4c** is a key intermediate in the preparation of denagliptin employed for the treatment of type II diabetes.[15] Chloro substitute, a reactive group in Pd-catalyzed cross-coupling reactions, could be tolerated by this protocol (**2j**). Notably, considerably reactive hydroxyl group proved to be compatible functional group (**4f**). Potassium aryltrifluoroborates bearing cyclic amide moiety were also effective substrates with this method (**4g-h**).

On the basis of the above results and previous reports,[5-6,16-18] a possible mechanism for the present transformation is outlined in Scheme 3 (anionic ligands omitted for clarity). The intermediate **A** is first generated by the transmetalation of the arylboronic acid with Pd(II) catalyst.[16] Subsequently, the coordination of CO with the intermediate **A** and insertion into the Pd–C bond affords a palladium acyl intermediate **B**, which further reacts with another arylboronic acid to form a palladium intermediate **C**.[17] Finally, reductive elimination of **C** gives the ketone product **2** and Pd(0) which can be reoxidized to the Pd(II) species by NaI/O_2 or iodine.[5-6,18]



Scheme 3. Proposed mechanism for the present transformation.

In summary, we have developed the first phosphine-free palladium-catalyzed aerobic oxidative carbonylative homocoupling of potassium aryltrifluoroborates and arylboronic acids. This protocol allows for highly selective transformation of the organoborons into the corresponding symmetric diaryl ketones using O_2 or iodine as the ultimate oxidant without the the assistance of a transition-metal oxidant under 1 atm atmosphere. Further elucidation of the mechanism and the extension to other substrates are in progress.

Experimental Section

General Procedure for aerobic oxidation of arylboronic acid to biarylketone with ambient oxygen. A flask was charged with aryl boronic acid **1** (0.5 mmol), $Pd(OAc)_2$ (0.005 mmol, 1.1 mg), NaI (30.4 mg. 0.2 mmol), $KHCO_3$ (101.2 mg, 1.0 mmol), and PEG-400 (2 ml) before standard cycles evacuation and backfilling with mixture of CO and O_2 (4:1, 1 atm). Then, the mixture was stirred at 80 °C for the indicated time. At the end of the reaction, the reaction mixture was extracted with diethyl ether (3 × 15 mL). The organic phases were combined, and the volatile components were evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether / diethyl ether).

Acknowledgements

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Keywords: Biaryketones • Carbonylation • Oxidation• Palladium • Synthetic methods

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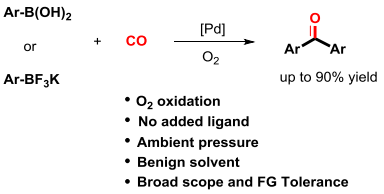
Entry for the Table of Contents (Please choose one layout)

Layout 1:

COMMUNICATION

Palladium-catalyzed oxidation of arylboronic acids or potassium aryltrifluoroborates to biarylketones with oxygen or iodine as the sole oxidant at ambient pressure is reported. This protocol features a good substrate scope of arylborons bearing a wide range of functional groups and gives desired products in high yields with high selectivities.



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