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Efficient, recyclable and phosphine-free carbonylative Suzuki coupling reaction using immobilized palladium ion-containing ionic liquid: synthesis of aryl ketones and heteroaryl ketones[†]

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The carbonylative Suzuki coupling reaction of aryl and heteroaryl iodides was studied by using immobilized palladium ion-containing ionic liquid (ImmPd-IL). The protocol was optimized with respect to various reaction parameters, applied to a wide variety of substituted aryl/heteroaryl iodides and various aryl/heteroaryl boronic acids with different steric and electronic properties, and afforded the corresponding products in good to excellent yield. This is an efficient, heterogeneous catalyst which avoids the use of phosphine ligands, and its reusability was tested in up to four consecutive cycles. The recycled catalyst was characterized by using XPS analysis.

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Introduction

Biaryl and hetero aryl carbonyls are important moieties present in numerous natural products, biologically active compounds, agrochemicals and pharmaceutical compounds.¹ Owing to their increasing biological and industrial importance researchers have emphasized the development of many economical and efficient synthetic strategies for these biaryl carbonyl compounds.

The most common synthetic route to biaryl ketones involves Friedel–Crafts acylation of aromatic cycles with acyl halides using an over stoichiometric amount of aluminium trichloride. However, this methodology is incompatible with many functional groups.^{2,3} An alternative method for the synthesis of biaryl ketones is the acylation of aryl metal species with carboxylic acid derivatives.⁴ The most promising method for the synthesis of unsymmetrical biaryl ketones is the transition metal-catalyzed three-component cross-coupling reaction of aryl metal reagents, carbon monoxide (CO) and aryl electrophiles.⁵ This process is one of the most efficient and direct routes to several aryl ketones, as it introduces a carbonyl group in a single step, which is now considered to be a useful tool for the synthesis of a wide variety of carbonyl compounds. Since then, a range of aryl metal reagents, such as copper,⁶ zinc,⁷ magnesium,⁸ silicon,⁹ aluminium¹⁰ and tin¹¹ have been reported for carbonylative coupling reactions. However, these carbonylative cross-coupling reactions have several drawbacks due to the formation of biaryl side products ensuing from direct coupling of the aryl groups without carbon monoxide insertion. In 1993, Suzuki and co-workers firstly reported an aryl boron reagent for the carbonylative coupling reaction using a palladium catalyst.¹² This reaction provides a versatile tool for the direct synthesis of biaryl ketones using boronic acids as a reagent, which are generally non-toxic, and stable in air and moisture. After the first report by Suzuki, significant advances have been made for this transformation to date, by using a variety of palladium-based homogeneous catalytic systems.^{13,14}

However, despite their potential utility, all of the above catalysts employed so far for the carbonylative Suzuki coupling reactions were homogeneous and palladium–phosphine based complexes, without any consideration of a recyclability aspect. Furthermore, the use of expensive, toxic and air/moisture sensitive phosphine ligands along with difficulties associated with catalyst–product separation thereby, limited their applications. To resolve this issue, some ligand free protocols for the carbonylative Suzuki coupling reaction have been developed, but problems with the recycling of the precious metal catalysts occurred.¹⁵

Hence, due to the high costs of the transition metal catalysts and their toxicity in pharmaceutical applications, an increased interest in immobilizing catalysts has arisen. Immobilized catalysis avoids the possible metal/ligand contamination of the desired product, and also minimizes waste derived from the reaction workup, appending to the develop-

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ment of green chemical processes.^{16,17} Considering this, various immobilization strategies for metal complexes have been developed, wherein the metal/ion is coordinated by a ligand grafted on to an inorganic or organic solid support.¹⁸ Recently, ionic liquids containing metal ions have been used as catalytic precursors; furthermore, they can be immobilized on solid supports to facilitate the reuse of this immobilized catalyst. These immobilized palladium catalysts have been successfully used for various organic transformations.^{19–21}

In spite of significant advances in this area, there are very few reports that employ immobilized palladium complexes as catalysts for the carbonylation reaction. Moreover, a literature survey reveals that there is a limited number of reports on carbonylative Suzuki coupling reactions using heteroaryl halides and heteroaryl boronic acid derivatives.

In this regard, an immobilized palladium ion-containing ionic liquid [ImmPd-IL] was prepared, characterized and applied in the coupling reactions.²² Recently, we have explored the ImmPd-IL catalyst for alkoxy and amino carbonylation reactions.²³ Inspired by all the prominent preliminary results of ImmPd-IL and continuing interest in developing efficient, phosphine free, recyclable protocols for the carbonylation reactions,²⁴ herein, we have explored the ImmPd-IL catalyst for carbonylative Suzuki coupling reactions (Scheme 1).

Results and discussion

In this study, the ImmPd-IL used was synthesized according to the procedures based on our previous publications,²² The synthesis of the immobilized palladium ion-containing ionic liquid catalyst is as follows (Scheme 2).

1-methyl-3-(3-trimethoxysilylpropyl) imidazolium chloride was synthesized by mixing *N*-methylimidazole (0.690 mol) and 3-trimethoxysilylpropyl chloride (0.690 mol) in a dry 300 mL flask under a nitrogen atmosphere and refluxing for 48 h. After cooling to room temperature, the resultant liquid was washed with dehydrated ethyl acetate five times and dried at room temperature under reduced pressure for 48 h. The obtained compound was stored at 253 K under dry nitrogen.

Silica (Aerosil 300, surface area 300 m² g⁻¹, calcined at 573 K for 1.5 h in air) and 1-methyl-3-(3-trimethoxysilylpropyl) imidazolium chloride (weight ratio 1:1) was dispersed in dehydrated toluene and the mixture was refluxed for 48 h



Scheme 1 The carbonylative Suzuki coupling reaction of aryl and heteroaryl iodides with aryl/heteroaryl boronic acids using the ImmPd-IL catalyst.



Scheme 2 The preparation of the immobilized palladium ion-containing ionic liquid.

under nitrogen. After reflux, the toluene was removed by filtration using a glass filter, and the excess ionic liquid was removed by washing with dichloromethane several times. The resultant solid is denoted as Imm-IL. In the next step, Imm-IL was added to an acetonitrile solution of PdCl₂ and refluxed for 24 h. Acetonitrile and excess metal chloride were removed by washing with acetone using a glass filter several times. The metal loading of ImmPd-IL was 3.4 wt% as determined by XRF measurements.

For testing this prepared ImmPd-IL catalyst, the carbonylative cross coupling reaction of iodobenzene with phenyl boronic acid was chosen as a model system. The influence of various reaction parameters such as solvent, base, temperature, time and CO pressure were examined on the model reaction, and results obtained are summarized in Table 1.

It was observed that the nature of the solvent affects the reaction outcome: when the reaction was conducted in polar solvents such as *N*,*N*-dimethylformamide (55%), water (10%), a lower yield of the desired product was obtained (Table 1, entries 1–2), whereas non polar solvents such as THF (62%), anisole (60%) and toluene (90%) provided good results

 Table 1
 The effect of reaction parameters on the carbonylative Suzuki coupling

 reaction of iodobenzene with phenyl boronic acid^a

Entry	Solvent	Base	Time (h)	Temp. (°C)	Yield $(\%)^b$
The eff	ect of the so	olvent			
1	DMF	K_2CO_3	8	100	55
2	Water	K ₂ CO ₃	8	100	10
3	THF	K ₂ CO ₃	8	100	62
4	Anisole	K ₂ CO ₃	8	100	60
5	Toluene	K ₂ CO ₃	8	100	90
The eff	ect of the ba	ase			
6	Toluene	Cs_2CO_3	8	100	72
7	Toluene	Na ₂ CO ₃	8	100	69
8	Toluene	Et ₃ N	8	100	40
The eff	ect of the te	mperature			
9	Toluene	K_2CO_3	8	90	80
10	Toluene	K_2CO_3	8	80	75
The eff	ect of the ti	me and the	CO pressure	2	
11	Toluene	K_2CO_3	6	100	81
12^c	Toluene	K_2CO_3	8	100	76

^{*a*} Reaction conditions: iodobenzene (1 mmol), phenyl boronic acid (1.2 mmol), ImmPd-IL (2 mol%), Base (3 mmol), solvent (10 mL), CO pressure = 1 MPa. ^{*b*} GC yield. ^{*c*} CO pressure = 0.5 MPa.

(Table 1, entries 3-5). As toluene furnishes the maximum yield of the desired product, it was used for further studies (Table 1, entry 5). Next, we turned our attention to the study of the effect of bases on the reaction outcome; hence, we attempted a reaction using various organic and inorganic bases (Table 1, entries 5-8). Among the inorganic bases screened, K₂CO₃ was found to give the desired product in excellent yield (Table 1, entry 5). The organic base triethylamine was found to be ineffective for the carbonylative Suzuki coupling reaction (Table 1, entry 8). Decreasing reaction temperatures to up to 80 °C decreased the yield of the desired product (Table 1, entries 9-10); hence, 100 °C was chosen as the optimum reaction temperature for further reactions. When the reaction time was decreased, a lower yield of the desired product was observed (Table 1, entry 11). Then, the influence of the CO pressure was also studied (Table 1, entry 12), and the optimum pressure was used for further studies.

Therefore, the optimized reaction conditions for the carbonylative Suzuki coupling reaction were: ImmPd-IL (2 mol%) as a catalyst, K_2CO_3 (3 mmol) as a base in toluene as a solvent (10 mL) under 1 MPa CO pressure at 100 °C for 8 h.

With these optimized reaction conditions in hand, we investigated the scope of the developed protocol for the coupling of a variety of phenyl boronic acids with a range of aryl and heteroaryl iodides. Various electron-donating and electron-withdrawing groups such as -CH₃, -OCH₃, -COCH₃, -NO2 and -Br on aryl iodides and phenyl boronic acids were well tolerated to give the corresponding biaryl ketones in good to excellent yields. Iodobenzene reacts with phenyl boronic acid to give 88% yield of benzophenone (Table 2, entry 1). 4-iodotoluene furnishes an excellent yield of 4-methyl benzophenone (Table 2, entry 2), whereas the reactions of sterically hindered 2-iodoaniline with phenyl boronic acid provided 84% yield of the desired biaryl ketones (Table 2, entry 3). 4-acetyliodobenzene provides a moderate yield of the desired product (Table 2, entry 4). It was observed that the presence of strong electron-withdrawing groups, such as -NO2 on aryl iodide, decreases the yield of the corresponding carbonylated products (Table 2, entry 5). We probed the carbonylative Suzuki coupling reaction of bromobenzene and chlorobenzene, but it only gave traces of the desired products even after a prolonged reaction times.

It is noteworthy that the reaction of various substituted phenyl boronic acids such as (4-methylphenyl)boronic acid, (4methoxyphenyl)boronic acid and (4-bromophenyl)boronic acid with iodobenzene furnishes good to excellent yields of the desired biaryl ketones (Table 2, entries 6–8).

With the aim of developing a more general protocol for the preparation of heterocyclic biaryl ketones, we examined the carbonylative cross coupling reaction of heterocyclic aryl iodides with different aryl boronic acids (Table 3, entries 1–8). Initially, we examined the carbonylative cross-coupling reaction of 3-iodopyridine with phenyl boronic acid, which provides 89% yield of the respective heteroaryl ketone (Table 3, entry 1). Encouraged by this result, we screened substituted aryl boronic acid derivatives, which provided moderate to good

 Table 2
 The carbonylative Suzuki coupling reaction of aryl iodides with various aryl boronic acids^a



^{*a*} Reaction conditions: aryl iodide (1 mmol), aryl boronic acid (1.2 mmol), CO pressure = 1 MPa, ImmPd-IL (2 mol%), K₂CO₃ (3 mmol), toluene (10 mL), 100 °C, 8 h. ^{*b*} Isolated yield.

yields of the expected carbonylated products (Table 3, entries 2–3). 2-iodothiophene reacts with the phenyl boronic acids (4-methylphenyl)boronic acid and (4-methoxyphenyl)boronic acid, which provides 80%, 79% and 77% yield of the corresponding ketones, respectively (Table 3, entries 4–6).

Gratifyingly, heterocyclic boronic acids were also well tolerated in the carbonylative coupling reaction with aryl iodides. Thiophen-3-ylboronic acid reacts with iodobenzene and 4-iodotoluene, which provided 85% and 80% yields of the expected heteroaryl ketones, respectively (Table 3, entries 7–8).

In an effort to make the synthesis more applicable, the reusability of the catalyst was also examined for the standard reaction of iodobenzene with phenyl boronic acid. After completion of the reaction, the mixture was filtered, the catalyst was washed with distilled water and methanol, and

Entry	Aryl/hetero iodide	Aryl/hetero aryl boronic acid	Product	Yield $(\%)^b$
1		B(OH) ₂		89
2		Me B(OH) ₂	O N Me	81
3		MeO B(OH)		80
4	s	B(OH) ₂		80
5	s I	Me B(OH) ₂	S S S S S S S S S S S S S S S S S S S	79
6	K s l	MeO B(OH)	S S S S S S S S S S S S S S S S S S S	77
7		B(OH) ₂		85
8	Me	B(OH) ₂	Me	80

^{*a*} Reaction conditions: aryl/hetero aryl iodide (1 mmol), aryl/hetero aryl boronic acid (1.2 mmol), CO pressure = 1 MPa, ImmPd-IL (2.5 mol%), K₂CO₃ (3 mmol), toluene (10 mL), 100 °C, 10 h. ^{*b*} Isolated yield.

dried under reduced pressure. The ImmPd-IL was found to be effectively reused in up to four consecutive cycles while maintaining high activity and selectivity (Fig. 1).



Fig. 1 ImmPd-IL catalyst reusability.

The slight decrease in yield up to the forth recycle might be due to handling loss of the catalyst. To confirm whether there is any leaching of the Pd catalyst from the immobilized solid support, we carried out the ICP-AES analysis of the 1st and the 4th recycle run, where the Pd content was found to be below the limit of detection (0.01 ppm). Thus, we conclude that the ImmPd-IL catalyst was successfully recycled and the reusability procedure was tested for up to four consecutive cycles.

XPS spectra were measured for the fresh ImmPd-IL for the 1st recycle and the 4th recycle catalysts. The wide scan and the Pd 3d region are shown in Fig. 2. The wide scans show no large difference, indicating that the fresh and retrieved catalysts do not differ much. As for the Pd 3d region, two peaks at 337 eV and 342.4 eV for the fresh ImmPd-IL correspond to $3d_{5/2}$ and $3d_{3/2}$ for the Pd²⁺ species, respectively. For the 1st and 4th recycle catalysts, both peaks tend to shift to lower values, suggesting that the catalysts are slightly reduced after the 1st



Fig. 2 XPS spectra for the fresh and recycled catalysts (a) wide scan, (b) Pd 3d region.

recycle and significantly reduced after the 4th recycle. The decrease of Cl 2p was also observed after the recycles.

Conclusions

In conclusion, the present study reports an efficient and reusable protocol for the carbonylative Suzuki coupling reaction of aryl and heteroaryl iodides with different phenyl boronic acids by using a well-defined heterogeneous ImmPd-IL complex as a versatile catalyst. The reaction system was optimized with respect to various reaction parameters and applied to the carbonylative Suzuki coupling reaction of a range of aryl/heteroaryl boronic acids with a variety of aryl and heteroaryl iodides, furnishing good to excellent yields of the corresponding products. Furthermore, the catalytic system was also recycled up to four consecutive times without any significant loss in catalytic activity.

Experimental section

All chemicals and reagents were procured from commercial suppliers and used without further purification. The products were characterized using ¹H NMR (Varian Mercury 300 NMR Spectrometer) and GC-MS (Shimadzu GC-MS QP 2010). The progress of the reaction was monitored using GC analysis (Perkin-Elmer, Clarus 400). The product was purified by column chromatography on silica gel (100–200 mesh). All the products are well known in the literature.

A typical experimental procedure for the carbonylative Suzuki reaction of aryl iodides

To a 100 ml autoclave, aryl iodide (1.0 mmol), aryl boronic acid (1.2 mmol), ImmPd-IL (2 mol%), toluene (10 mL) and K₂CO₃ (3 mmol) were added. The mixture was first stirred for 10 min and then flushed with CO three times, then 1 MPa of CO was applied, and the reaction mixture was heated at 100 °C for 8 h. After completion of the reaction, the reaction mixture was cooled to room temperature and the remaining CO gas was carefully vented and the reactor was opened. The reactor vessel was thoroughly washed with ethyl acetate $(2 \times 10 \text{ mL})$ to remove any traces of product and catalyst if present. The catalyst was filtered and the residue obtained was purified by column chromatography (silica gel, 100-200 mesh; petrol ether (b. p. 60 °C-70 °C)/ethyl acetate) to afford the desired carbonylated product. The products were confirmed by GC, GC-MS, and ¹H NMR spectroscopic techniques. The purity of the compounds was determined by GC-MS analysis.

A typical experimental procedure for the carbonylative Suzuki reaction of heteroaryl iodides

To a 100 ml autoclave, heteroaryl iodide (1.0 mmol), aryl boronic acid (1.2 mmol), ImmPd-IL (2.5 mol%), toluene (10 mL) and K_2CO_3 (3 mmol) were added. The mixture was first stirred for 10 min and then flushed with CO three times, then 1 MPa of CO was adjusted, and the reaction mixture was heated at 100 °C for 10 h. After the completion of the reaction, the reaction mixture was cooled to room temperature, the remaining CO gas was carefully vented and the reactor was opened. The reactor vessel was thoroughly washed with ethyl acetate (2 \times 10 mL) to remove any traces of the product and the catalyst if present. The catalyst was filtered and the residue obtained was purified by column chromatography (silica gel, 100–200 mesh; petrol ether (b. p. 60 °C–70 °C)/ethyl acetate) to afford the desired carbonylated product. The products were confirmed by GC, GC-MS, and ¹H NMR spectroscopic techniques. The purity of the compounds was determined by GC-MS analysis.

A typical procedure for recycling the ImmPd-IL catalyst

The catalyst obtained after filtration was washed with distilled water (5 mL \times 3) and then with methanol (5 mL \times 3) to remove any organic material present. The resulting catalyst was dried under reduced pressure and used for the next cycle.

Characterization of the products

4-methylbenzophenone (Table 2, entry 2). (172 mg, 88%), ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 7.77–7.75 (d, 2H, *J* = 7.0 Hz),

7.71–7.69 (d, 2H, J = 8.2 Hz), 7.54–7.42 (m, 3H), 7.26–7.24 (d, 2H, J = 7.9 Hz), 2.4 (s, 3H); GC-MS (EI, 70 eV): m/z (%) = 196 [M⁺] (72), 119 (100), 105 (35), 91 (39), 77 (28).

4-Acetylbenzophenone (Table 2, entry 4). (170 mg, 76%), ¹H NMR (300 MHz, CDCl₃): $\delta = 8.07-8.04$ (d, J = 8.8 Hz, 2 H), 7.88–7.87 (d, J = 8.4 Hz, 2 H), 7.82–7.79 (d, J = 8.4 Hz, 2 H), 7.65–7.59 (t, J = 8.8 Hz, 2 H), 7.52–7.47 (t, J = 7.5 Hz, 1 H), 2.66 (s, 3 H); GCMS (EI, 70 eV): m/z (%) = 224 [M⁺] (50), 209 (100), 181 (20), 147 (30), 105 (75), 77 (79), 43 (30).

4-Nitrobenzophenone (Table 2, entry 5). (204 mg, 90%), ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 8.35–8.34 (d, 2H, *J* = 8.8 Hz), 7.95–7.93 (d, 2H, *J* = 8.4 Hz), 7.81–7.79 (d, 2H, *J* = 6.8 Hz), 7.65–7.49 (m, 3H); GC-MS (EI, 70 eV): *m*/*z* (%) = 227 [M⁺] (45), 105 (100), 77 (55).

4-Bromobenzophenone (Table 2, entry 8). (206 mg, 79%), ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 7.78–7.76 (d, 2H, *J* = 7.3 Hz), 7.69–7.67 (d, 2H, *J* = 8.2 Hz), 7.63–7.61(d, 2H, *J* = 8.2 Hz), 7.60–7.47 (m, 3H); GC-MS (EI, 70 eV): *m*/*z* (%) = 260 [M⁺] (45), 181 (40), 105 (100), 77 (55).

3-Benzoylpyridine (Table 3, entry 1). (162 mg, 89%), ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 9.03–9.01 (d, *J* = 1.2 Hz, 1H), 8.86–8.85 (dd, *J* = 4.8 and 1.8 Hz, 1H), 8.18–8.16 (dd, *J* = 7.9 and 1.8 Hz, 1H), 7.78 (d, *J* = 7.9 Hz, 2H), 7.79–7.39 (m, 4H); GC-MS (EI, 70 eV): *m*/*z* (%) = 183 [M⁺] (100), 105 (90) 77 (85), 51 (40).

Pyridin-3-yl-*p***-tolyl-methanone (Table 3, entry 2).** (160 mg, 81%), ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 8.90 (s, 1H), 8.74–8.72 (d, *J* = 4.4 Hz, 1H), 8.09–8.06 (d, *J* = 1.4 Hz, 1H), 7.72–7.70 (d, *J* = 7.8 Hz, 2H), 7.43–7.46 (dd, *J* = 4.87 & 4.87 Hz, 1H), 7.29–7.25 (d, *J* = 7.8 Hz, 2H), 2.45 (s, 3H); GC-MS (EI, 70 eV): *m/z* (%) = 197 [M⁺] (51), 182 (50), 119 (100), 91 (39), 77 (40).

2-Benzoylthiophene (Table 3, entry 4). (151 mg, 80%), ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 7.88–7.85 (d, *J* = 7.6 Hz, 2H), 7.73–7.71 (m, 5H), 7.15–7.17 (m, 1H); GC-MS (EI, 70 eV): *m/z* (%) = 188 [M⁺] (70), 111 (100), 77 (31).

Thiophen-2-yl-*p***-tolyl-methanone (Table 3, entry 5).** (159 mg, 79%) ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 7.75–7.70 (d, *J* = 8.5 Hz, 2H), 7.65–7.73 (m, 1H), 7.60–7.58 (m, 1H), 7.29–7.28 (d, *J* = 7.6 Hz, 2H), 7.14–7.11 (m, 1H), 2.45 (s, 3H); GC-MS (EI, 70 eV): *m*/*z* (%) = 202 [M⁺] (100), 187 (55), 119 (80), 111 (71), 77 (35).

(4-methoxyphenyl)(thiophen-2-yl)methanone (Table 3, entry 6). (168 mg, 77%), ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 7.91–7.89 (d, *J* = 8.5 Hz, 2H), 7.69–7.67 (m, 2H), 7.17–7.15 (m, 1H), 6.95–6.98 (d, *J* = 8.5 Hz, 2H), 3.89 (s, 3H); GC-MS (EI, 70 eV): *m*/*z* (%) = 218 [M⁺] (75), 187 (35), 135 (100), 77 (39).

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