



# Carbonylative Suzuki–Miyaura coupling catalyzed by palladium supported on aminopropyl polymethylsiloxane microspheres under atmospheric pressure of CO



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## ABSTRACT

Carbonylative Suzuki–Miyaura cross-coupling reactions of various aryl iodides with phenylboronic acids were catalyzed by palladium supported on amino-modified silica microspheres. Reactions performed with a very low concentration of Pd, under the atmospheric pressure of CO, led to high/moderate yields of multiple benzophenones.

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## 1. Introduction

Palladium-catalyzed cross-coupling reactions have become one of the most popular tools for the synthesis of novel bio-active compounds and advanced materials. Among the different C–C cross-coupling reactions, three substrate-type carbonylations have also been developed [1].

While the carbonylations of aryl halides are well established, the carbonylative coupling reactions of such compounds have been investigated much less. Benzophenones, which are usually formed in these reactions, are important building blocks for a large number of pharmaceuticals and natural products. Hence, there is still a need to develop convenient and more general methodologies for the synthesis of products of this class.

Carbonylative Suzuki reactions generally proceed in the presence of typical homogeneous palladium precursors such as PdCl<sub>2</sub>, Pd(OAc)<sub>2</sub>, [Pd(acac)<sub>2</sub>], [Pd(tmhd)<sub>2</sub>], [Pd<sub>2</sub>(dba)<sub>3</sub>] [2–5], palladium complexes containing phosphine ligands [6–18], or *N*-heterocyclic carbenes (NHC) [19,20], which makes the recovery of the metal from the reaction mixture almost impossible and may result in

the unacceptable contamination of the product with palladium. The high cost combined with the toxic effects of Pd have led to an increased interest in immobilizing the catalysts on supports. There are a few examples of carbonylative S–M coupling with silica-supported phosphine complexes [21], Pd nanoparticles immobilized on supported ionic liquid-like phases [22], *in situ* generated Pd nanoparticles [23], Pd on carbon [24], or even Pd supported on hollow magnetic mesoporous spheres [25]. This class of supported precursors facilitate both the isolation and the recycling of the catalysts by simple filtration, leading to an environmentally cleaner process.

Microspheric-supported palladium catalysts reported in this article have previously been successfully used in the Suzuki–Miyaura coupling [26]. The main goal of the studies was to switch the catalytic activity from the standard Suzuki–Miyaura coupling to the carbonylative Suzuki–Miyaura reaction by a simple change of the reaction conditions [25].

## 2. Results and discussion

### 2.1. Catalyst

The preparation of the catalyst and its structural studies shown in Fig. 1 have been reported previously [26].

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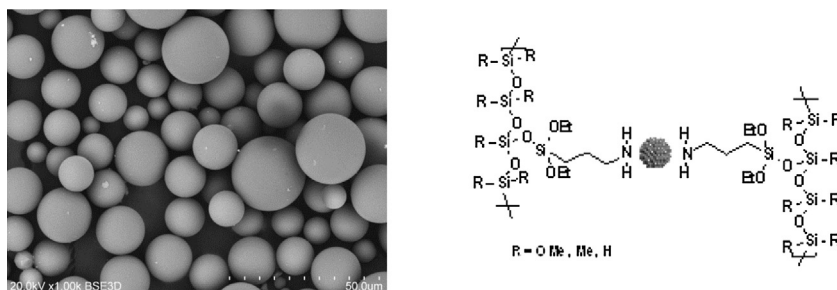


Fig. 1. Catalyst [Pd] surface SEM (left) and proposed molecular structure (right).

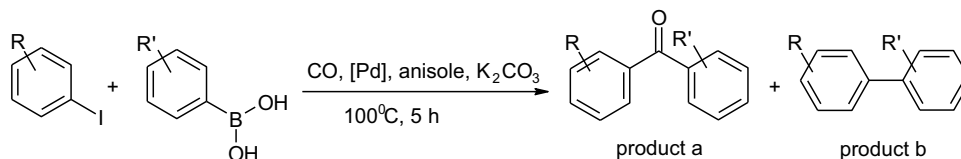


Fig. 2. Carbonylative Suzuki–Miyaura coupling.

## 2.2. Carbonylative Suzuki–Miyaura cross-coupling reactions

The carbonylative Suzuki–Miyaura reaction of aryl iodides with substituted phenylboronic acids was selected as a model reaction for investigations (Fig. 2).

The general reaction conditions were adapted with small changes from previous similar studies [24]. Anisole was chosen as a solvent, because a base  $K_2CO_3$  was the best choice. CO proceeded from a balloon equipped with a capillary under continuous flow atmospheric pressure. Due to the heterogeneous nature of the catalyst, the reaction was performed for 5 h to reach max. 96% conversion of iodide. A longer reaction time only resulted in the increase of the amount of the secondary product (biphenyl). Since there are two competitive reactions, the palladium concentration had to be lowered from the initial 2 mol% to 0.05 mol% to reduce the homocoupling reaction speed, and to increase the saturation of the solution with CO due to its low solubility under these conditions.

The obtained results are presented in Table 1.

Reactions of different aryl iodides with phenylboronic acid show conversions from 0% for 4-iodophenol to over 90%. The highest conversions, up to 91%, were obtained for 4-iodoanisole. There is a strong correlation between the activity and the position of the substituent in the aryl ring. For a substrate with a methoxy group in position 4, the conversion is the highest, reaching 91%. The substituents in positions 3 and 2 decrease the activity of the substrate, allowing for conversion at the level of 80% and 46%. Good results were also obtained for 1-iodonaphthalene, 82%. 4-Nitro- and 4-methyl-substituted iodides showed a moderate and a low activity of 40% and 24%. 2-Iodothiophene was almost not active in this reaction and gave only a trace of the product. Attempts 1a and 4a were carried out with the catalyst reduced before the reaction. No significant change in activity was observed. The differences were in the range from 1% to 2% of the total substrate conversion.

For further study, 4-iodoanisole was selected as a representative halide. Reactions with substituted boronic acids showed conversions from 51% for 1-naphthylboronic acid to 0% for 4-formylboronic acid, phenylboronic acid pinacol ester, and 4-carboxyphenylboronic acid. 4-Methyl-1-naphthyl and 3,5-dimethoxyboronic acid show moderate reactivity with conversions from 50% to 47%. 4-Vinyl, 4-tertbutyl, and 4-acetylboronic acids showed low or very low activity in these reactions, with conversions from 30% to 2%. It should also be noted that, during all the performed reactions, the product of the homo-coupling of boronic

acid was formed in small to moderate quantities as a result competing reactions. This can be prevented by raising the pressure of CO or reducing the concentration of the catalyst. Interestingly, lowering the concentration of the catalyst does not influence the carbonylative S–M reaction rate, but it reduces the amount of the unwanted product. Thus, in our opinion, the reaction rate limiting factor is the concentration of CO in the reaction solution.

In order to prove this theory, two model reactions were carried out in a steel autoclave with a CO pressure of 5 bar. Both showed a significant increase in conversion to the carbonyl product, with a slight increase of the total substrate conversion (Table 2). In most cases the amount of byproduct (product b) was reduced by half or even more. It was therefore clearly shown that the selectivity of the carbonylative S–M reaction was significantly improved already at CO pressure of 5 bar. For example, excellent selectivity was achieved for 4-iodoanisole and dimethoxyboronic acid (Table 2). In this case the yield of product a increased from 44% to 60% after increase of CO pressure from 1 bar to 5 bar. Similarly, in carbonylative coupling of 4-iodoanisole with 1-naphthylboronic acid increase of the yield of product a from 15% to 38% was noted (Table 2). Thus, in our system the suppression of S–M coupling reaction was achieved just by small increase of the CO pressure. Such modification of the reaction conditions is in our opinion simpler than application of pivalic acid as an agent inhibiting S–M reaction [23].

## 2.3. Carbonylative Suzuki–Miyaura coupling of di-halogenated benzenes

In the course of studies, carbonylation reactions with di-halogenated benzenes have also been conducted. The expected products, diketones, may be of interest for the synthesis of functional materials [27].

Two substrates, 1,4-diiodobenzene, and 1-bromo-4-iodobenzene were used and difference in their activity has been observed (Table 3).

The conversion of 1-bromo-4-iodobenzene was 60% and increased to 75% when amount of phenylboronic acid increased from 1.2 to 2.4 equivalents. The mono-carbonylation product, 4-bromo-benzophenone (c) was formed as the main one (50%) together with 4-bromo-biphenyl (e) (10%), which is a normal product of the Suzuki–Miyaura coupling reaction. When 1,4-diiodobenzene was used as a substrate, the main products were 1,4-dibenzoylbenzene (d) (30%), and 4-iodobiphenyl (e), approxi-

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