



A highly efficient Schiff-base derived palladium catalyst for the Suzuki–Miyaura reactions of aryl chlorides

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ABSTRACT

A new palladium complex derived from a bidentate Schiff-base ligand showed excellent activity as catalyst for the Suzuki–Miyaura cross-coupling reactions of less reactive aryl chlorides with arylboronic acids. Under an optimized condition, moderate-to-excellent yields of biaryls were obtained with a wide range of substrates at a relatively low loading of catalyst (0.2 mol %).

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Over the past few years, there has been an exponential rise in the number of publications in palladium-catalyzed Suzuki–Miyaura cross-coupling reactions of aryl halides with arylboronic acids as this method is one of the most powerful and simplest methods for carbon–carbon bond formation in organic synthesis.¹ Today, literally thousands of palladium catalysts are known that effectively promote this reaction under a variety of conditions. Despite considerable advancements, a major challenge which still remains in the Suzuki reaction is to develop catalysts that can activate aryl chlorides as substrates as these chlorides are highly accessible and less expensive compared to corresponding bromides or iodides. Although a sizable number of catalysts are known that can activate aryl chlorides in Suzuki reaction, in most of the cases phosphines such as P^tBu₃,² PCy₃,³ biphenyl-based phosphines,⁴ phosphapalladacycles,⁵ hemilabile phosphines,⁶ indole-based phosphines,⁷ and ferrocenyl phosphines⁸ are employed as ligands. Despite considerable success, the major drawbacks associated with such phosphines are their handling problems, synthetic difficulties, high costs, inherent toxicity, air and moisture sensitivity, etc. In this respect, nitrogen-based ligands are generally advantageous as they are easy-to-handle, less expensive than their phosphine counterparts, usually stable to air/moisture, etc. As a result, a plethora of nitrogen-based ligands such as amines,⁹ N-heterocyclic carbenes (NHC),¹⁰ oximes,¹¹ hydrazones,¹² and

others¹³ have been tested as possible alternatives to phosphines in Suzuki reactions. However, barring a few NHC^{10a–d,f} or oxime-based palladacycles,^{11a,b} a majority of such protocols are incompatible with aryl chlorides. It is worth to note that irrespective of the ligand being either phosphine-based or phosphine-free, aryl chloride activation usually required a high catalyst loading. For instance, recently Sarkar and co-workers reported a highly efficient phosphine-based catalytic system that required 4 mol % catalyst loading.^{7a} Similarly, a few years back, Mino's group had developed a phosphine-free catalytic system that required 10 mol% catalyst loading to activate a simple substrate like 4-chloroacetophenone.¹² However, from the economic point of view, such high loading of catalyst is unacceptable, as the advantage associated with the use of less expensive aryl chlorides is often negated by the high cost of palladium. Thus, efforts are being continued to design alternative catalytic systems that can activate aryl chlorides smoothly with low catalyst loading.

For decades, Schiff-bases have played a key role as chelating multidentate ligands, used in coordination chemistry and catalysis, because of their easy synthesis and high stability.¹⁴ In fact, there have been a number of reports about employment of Schiff-base ligands in palladium-catalyzed Suzuki reactions,¹⁵ but in a majority of the cases good results were usually obtained with aryl bromides or iodides as substrates. Nevertheless, there exist a very few exceptions where Schiff-base derived catalysts showed good results with aryl chlorides also. For example, a few years back, Cui et al.^{15e} developed an amino-salicylaldehyde based Pd catalyst that could

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activate aryl chlorides elegantly at a low catalyst loading (0.5 mol %). Excellent conversions were seen with substrates comprising electron-withdrawing groups (viz. aldehyde, acetyl, and nitro), but electron-rich substrates such as 4-chlorotoluene and 4-chlorophenol gave only low yields. Recently, Hanhan et al.^{13b} designed a ferrocene-based palladium Schiff-base catalyst that showed remarkable activities with aryl chlorides bearing both electron-rich and electron-poor substituents. The higher activities of this catalyst were attributed to the sterically demanding nature and electron-rich property of the ligand caused by the presence of two ferrocene moieties. Very recently, we have reported a binuclear palladium complex (Fig. 1) with a N4-type Schiff-base ligand that showed excellent activity as catalyst for the Suzuki reactions of aryl bromides and iodides in water at room temperature at a low loading of catalyst (0.2 mol %).¹⁶ However, despite fivefold increasing the catalyst loading, changing the solvent systems, and raising the temperature to 80 °C, we were able to get only moderate yields with aryl chlorides. In continuation with our efforts, herein we have developed a new palladium Schiff-base catalyst that shows excellent activity for the Suzuki reactions of aryl chlorides with a low catalyst loading (0.2 mol %). The Schiff-base ligand, *N,N'*-bis(benzylidene)-*o*-phenylenediamine (**L**) was previously reported,¹⁷ however its coordination chemistry with palladium is unknown. In this work, we have prepared a new palladium complex (**2**) by reacting PdCl₂ with the ligand **L** in acetonitrile (Scheme 1). The complex **2** was isolated as brown solid and its identity was confirmed by elemental analyses, ESI-mass, FTIR, ¹H and ¹³C NMR spectroscopy.¹⁸ In the FTIR spectra of the complex **2**, the νC=N band appears at 1609 cm⁻¹ which is marginally higher than the νC=N stretching of the free ligand (1604 cm⁻¹). The imine signal in the ¹H NMR spectra appears at δ 8.83 ppm and compared to free ligand a downfield shift of 0.21 ppm was observed. A similar downfield shift was also observed for the corresponding carbons of the ¹³C NMR spectra of the complex. However, no prominent shifts were observed in the other aromatic protons or carbon resonances.

To evaluate the efficiency of our complex as catalyst for the Suzuki–Miyaura reaction,¹⁹ we have chosen 4-chloronitrobenzene and phenylboronic acid as model substrates. Initial reaction was conducted at room temperature using DMF as solvent and K₂CO₃ as base with 1.0 mol % of the catalyst. We are quite satisfied to see that our reaction proceeded at room temperature, although only 30% product was isolated after a reaction time of 24 h (Table 1, entry 1). However, the product yield could be improved significantly by increasing the reaction temperature. The best result was obtained at 100 °C as quantitative product formation was achieved within 1 h of reaction time (Table 1, entry 4). It is well established that in the Suzuki reaction the choice of solvent often plays a crucial role in the overall performance of a catalyst, and to investigate this effect we have screened different solvents with our model reaction (Table 2). Our study reveals DMF is the best solvent for our catalyst (Table 2, entry 2). The other solvents including water (entry 4) and mixed-aqueous solvents (entries 7–9) gave only poor yields. We have also screened the effects of different bases (Table 3) on our model reaction and noticed that the reaction can tolerate

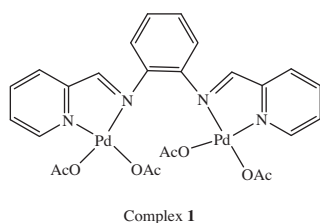
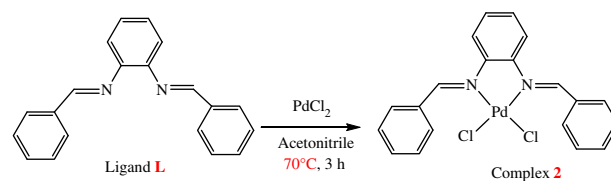


Figure 1. Schematic representation of the previously reported complex.¹⁶



Scheme 1. Synthesis of complex 2.

Table 1

Effects of temperatures in the Suzuki–Miyaura reactions^a of 4-chloronitrobenzene with phenylboronic acid using complex **2** as catalyst

Entry	Temperature (°C)	Time (h)	Yield ^{b,c} (%)
1	26 (rt)	24	30
2	60	5	70
3	80	3	85
4	100	1	98
5	120	1	98

^a Reaction conditions: 0.5 mmol 4-chloronitrobenzene, 0.75 mmol phenylboronic acid, 1.5 mmol K₂CO₃ DMF (6 mL).

^b Isolated yield.

^c Yields are of average of two runs.

Table 2

Effects of solvents in the Suzuki–Miyaura reactions^a of 4-chloronitrobenzene with phenylboronic acid using complex **2** as catalyst

Entry	Solvent	Time (h)	Yield ^{b,c} (%)
1	<i>i</i> PrOH	5	50
2	DMF	1	98
3	Toluene	4	16
4	H ₂ O	6	12
5	Glycerol	4	26
6	THF	4	12
7	<i>i</i> PrOH:H ₂ O	5	23
8	Toluene:H ₂ O	6	10
9	DMF:H ₂ O	5	34

^a Reaction conditions: 0.5 mmol 4-chloronitrobenzene, 0.75 mmol phenylboronic acid, 1.5 mmol K₂CO₃ 6 mL solvent.

^b Isolated yield.

^c Yields are of average of two runs.

common inorganic bases. K₂CO₃ and Cs₂CO₃ are found to be the two most effective bases that can complete the reactions in quick time (Table 3, entries 2 and 5). Other bases usually require extended reaction time to produce good results. Among the bases screened, MgCO₃ was found to be the least effective and gave only 52% yield in 6 h (Table 3, entry 4). Studies on optimization of catalyst quantities (Table 4) reveal that 0.2 mol % palladium loading is essential for completion of the reaction (entry 3). On decreasing the catalyst loading to 0.1 mol %, 56% biphenyl formation was achieved after 4 h (entry 4). A further decrease in catalyst loading resulted in poor conversion even after increasing the reaction time up to 24 h.

Under the optimized condition (DMF, K₂CO₃, 100 °C, 0.2 mol % complex **2**), we have examined the cross-coupling reactions of a wide range of electronically and sterically diverse aryl chlorides with arylboronic acids. As illustrated in Table 5, the results showed that Suzuki-coupling of aryl chlorides with arylboronic acids took place smoothly to get moderate-to-excellent yields of coupling products. However, the steric and electronic natures of substituents have a significant influence on the overall catalytic

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