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Acetanilide palladacycle: an efficient catalyst for room-temperature Suzuki–Miyaura cross-coupling reaction

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The catalytic activity of three acetanilide palladacycles derived from easily accessible and commercially available acetanilide derivatives, viz. *N*-phenylacetamide (L1), *N*-(4-chlorophenyl)acetamide (L2) and *N*-(4-methylphenyl)acetamide (L3) has been examined in Pd-catalyzed Suzuki–Miyaura reaction of arylboronic acid with aryl bromides at room temperature. The complex 1L3 exhibited efficient activity in the Suzuki–Miyaura reaction (up to 99% isolated yield) under mild reaction conditions.

Additional supporting information may be found in the online version of this article at the publisher's web site.

Keywords: palladacycle; acetanilide; Suzuki–Miyaura; isopropanol; biaryl

Introduction

Biaryl compounds served as building block materials for the synthesis of a wide range of vital compounds, such as pharmaceuticals, fine chemicals, agrochemicals, natural products and smart engineering materials, including conducting polymers and molecular wires.[1] Palladium-catalyzed Suzuki–Miyaura cross-coupling reaction is one of the most widely used and versatile methodologies for the synthesis of unsymmetrical biaryls under mild reaction conditions.[2] The Suzuki–Miyaura cross-coupling reaction is efficiently catalyzed by wide variety of Pd-based catalysts, and efficacy of the catalytic system has been achieved by changing the ligand environment around palladium.[3] Consequently, significant efforts have been made in designing novel catalyst systems of Pd(0) or Pd (II) complexes with phosphine-based ligands such as tertiary phosphines, hemilabile-type phosphines, sterically crowded biphenyl-type phosphines, and imidazole- and imidazolium-functionalized phosphines.[4] Although complexes containing such ligands often show excellent activity, moisture sensitivity,[5] and the requirement of high temperature and undesirable solvents such as DMF, *N*-methylpyrrolidine, dimethoxyethane,[6] are some of the major drawbacks in majority of cases. Moreover, in most of cases the ligands are either very expensive or difficult to synthesize. Recently, nitrogen-containing ligands such as *N*-heterocyclic carbenes,[7] amines[8] and oxime[9] have emerged as efficient ligands for Suzuki–Miyaura reaction with the potential to overcome most of the drawbacks of traditional phosphine ligands. Additionally, some common laboratory chemicals and reagents such as sodium sulfate,[10], PEG[11] and EDTA[12] have been successfully utilized as promoters for the reaction. Moreover, some easily accessible Schiff base type[13] and thiosemicarbazone[14] ligands have been used effectively in Pd-catalyzed Suzuki–Miyaura reaction. Very recently, Costa and Nobre utilized bisamides as ligands in Suzuki coupling of aryl bromides at a catalyst loading of 2 mol% $PdCl_2$.[15] This study ascertained that a similar catalytic tendency can be achieved using easily accessible acetanilide (*N*-phenylacetamide) derivatives as a ligand. Acetanilide is a routinely used cheap laboratory chemical with immense potential as a ligand. Moreover, acetanilide derivatives are well-known precursors for palladacycles, which have wide applicability in various organic transformations such as orthoalkylation[16] and Fujiwara–Moritani reaction.[17] The cyclopalladated acetanilide with bulky *N*-heterocyclic carbene (NHC), 1,3-bis(2,6 diisopropylphenyl) imidazol-2-ylidene (IPr), has been found an effective palladium pre-catalyst for the Suzuki–-Miyaura cross-coupling reaction.[18] However, to the best of our knowledge, the potential of simple acetanilide-derived palladacycles has not been utilized in the Suzuki–Miyaura cross-coupling reaction. Herein, we wish to report a facile and efficient room-temperature Suzuki–Miyaura reaction strategy using acetanilide-based palladacycles prepared by well-precedented orthometalation of acetanilide derivatives. For this we have used cheap, easily accessible and commercially available acetanilide derivatives, viz. *N*-phenylacetamide (**L1**), *N*-(4-chlorophenyl)acetamide (**L2**) and *N*-(4-methylphenyl)acetamide (**L3**) as palladacycle precursors (Fig. 1). This type of amide-based palladacycle can easily be synthesized within short reaction times under mild reaction conditions (Fig. 1).[16b]

Experimental

General Information

Melting points were determined using a Buchi B450 melting point apparatus. Elemental analyses were performed using an Elementar Vario EL III Carlo Erba 1108 instrument. IR spectra

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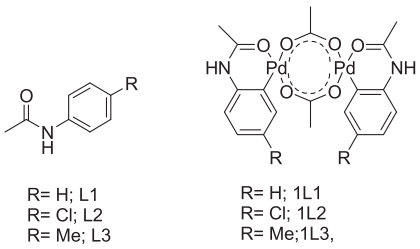


Figure 1. Structure of acetanilide derivatives **L1**, **L2** and **L3**, and their corresponding palladacycles.

(4000–250 cm^{-1}) were recorded in KBr on a Shimadzu Prestige-21 FT-IR spectrophotometer. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions operating at 400.13, and 100.62 MHz, respectively, on a Bruker Advance II 400 NMR spectrometer, and chemical shifts were reported relative to tetramethylsilane. Electrospray ionization (ESI) (+) mass spectra were recorded on a Water ZQ-4000 mass spectrometer.

General Information about Catalytic Experiments

Suzuki–Miyaura cross-coupling reactions were carried out under aerobic condition at room temperature. Progress of the reactions was monitored by TLC using aluminum-coated TLC plates (Merck silica gel $60F_{254}$) under UV light. The products were purified by column chromatographic technique using silica gel (60–120 mesh). The various products separated were characterized by melting point, ^1H and ^{13}C NMR and mass spectral data and compared with the authentic samples.

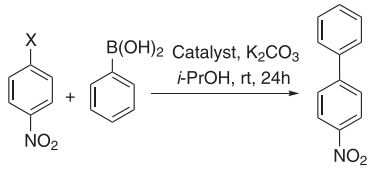
General Procedure for Suzuki–Miyaura Reactions of Aryl Halides Using Palladium Complex

A 50 ml round-bottom flask was charged with a mixture of aryl halide (0.5 mmol), aryl boronic acid (0.55 mmol), base (1.5 mmol) and palladium complex (0.5 mol%), and the mixture was stirred at room temperature for the required time. After completion, the reaction mixture was diluted with water (20 ml) and extracted with ether (3 × 20 ml). The combined extract was washed with brine (2 × 20 ml) and dried over Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue was subjected to chromatography (silica gel, ethyl acetate–hexane, 1:9) to obtain the desired products. The products were confirmed by comparing the melting point, ^1H and ^{13}C NMR and mass spectral data with authentic samples.

Results and Discussion

To examine the efficiency of the different acetanilide derivatives (**L1–L3**) in Suzuki–Miyaura reaction, the reaction of 4-bromonitrobenzene (0.50 mmol) and phenylboronic acid (0.55 mmol) was chosen as a model reaction using isopropanol as solvent and K_2CO_3 as base, and the reaction was performed under aerobic conditions at room temperature in the presence of Pd $(OAc)_2$ (0.5 mol%) and ligands **L1–L3** (0.5 mol%).[19] The results are summarized in Table 1. It may be observed from the table that, even in the absence of any ligand, the coupling reaction of 4-bromonitrobenzene and phenylboronic acid proceeded with 55% isolated yield (Table 1, entry 1), accompanied by a substantial amount of homodiaryl as by-product. However, in the presence of the ligand **L1** the desired product was obtained with improved yield (Table 1, entry 2). Moreover, the use of ligand **L1** significantly reduced the formation of homodiaryl. Similarly, use of ligand *N*-(4-chlorophenyl)acetamide (**L2**) and *N*-(4-methylphenyl)acetamide (**L3**) gave very good yields of isolated cross-coupling product (Table 1, entries 3 and 4). Among the three ligands used, *N*-(4-methylphenyl)acetamide (**L3**) demonstrated the highest catalytic activity (Table 1, entry 4), whereas 4-chloroacetanilide (**L2**) showed the lowest activity (Table 1, entry 3). In the Suzuki–Miyaura reaction, the *in situ* generated catalytic species and the pre-formed catalyst often exhibit different catalytic activities.[20] Therefore, to compare the catalytic activities of these *in situ* formed catalysts with that of pre-formed catalyst, we synthesized acetanilide-based palladacycles using acetanilide derivatives (**L1–L3**) as ligand.[16b] Acetanilide derivatives are well-known precursors for CN-palladacycle, and it is worth mentioning here that the acetanilide-derived palladacycle complexes **1L1–1L3**, which can be prepared vary easily, were previously reported in the literature.[16b] It is observed that the use of 0.5 mol% pre-formed palladacycle complexes **1L1–1L3** as catalyst under the above-mentioned conditions provides excellent yields compared to that of the *in situ* formed catalyst (Table 1, entries 2 vs. 5, 3 vs. 6, 4 vs. 7). Although the reason for different catalytic activities is not clear, one possible reason could be the slow rate of formation of the *in situ* complex at room temperature, as synthesis of the complexes (**1L1–1L3**) requires refluxing conditions. The best result was obtained with the palladacycle derived from *N*-(4-methylphenyl)acetamide, **1L3** (Table 1, entry 7). We have also examined the effectiveness of the current catalytic system in the cross-coupling chemistry of aryl chlorides using 4-chloronitrobenzene as coupling partner. Under the given set of reaction conditions, 4-chloronitrobenzene

Table 1. Effect of acetanilide derivatives in Suzuki–Miyaura coupling



Entry	X	Catalyst (0.5 mol%)	Yield (%)[a]
1	Br	$Pd(OAc)_2$	55
2	Br	$Pd(OAc)_2$/**L1**	78
3	Br	$Pd(OAc)_2$/**L2**	70
4	Br	$Pd(OAc)_2$/**L3**	85
5	Br	[$Pd(OAc)_2$/**L1**](**1L1**)	90
6	Br	[$Pd(OAc)_2$/**L2**](**1L2**)	85
7	Br	[$Pd(OAc)_2$/**L3**](**1L3**)	99
8	Cl	[$Pd(OAc)_2$/**L1**](**1L1**)	25
9	Cl	[$Pd(OAc)_2$/**L2**](**1L2**)	28
10	Cl	[$Pd(OAc)_2$/**L3**](**1L3**)	40
11	Br	[$Pd(OAc)_2$/**L3**](**1L3**)	95[b]

Reaction conditions: 4-bromonitrobenzene (0.50 mmol), $PhB(OH)_2$ (0.55 mmol), K_2CO_3 (1.5 mmol), *i*-PrOH (3 ml), *in situ* prepared catalyst was used (entries 2–4): $Pd(OAc)_2$ (0.5 mol%), acetanilide **L1–L3** (0.5 mol%), pre-formed palladacycle **1L1–1L3** was used (entries 5–10).

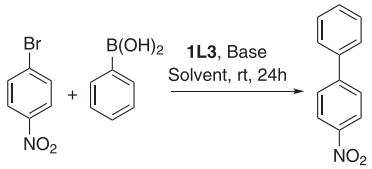
[a]Isolated yield.

[b]Pd complex **1L3** (0.25 mol%) was used.

underwent the cross-coupling reaction with lower yields compared to the aryl bromide counterpart (Table 1, entries 8–10). The cross-coupling reaction also proceeded with 0.25 mol% Pd complex **1L3** (Table 1, entry11).

It is a well-known fact that the choice of solvent and base significantly influences the Suzuki–Miyaura reaction. Thus, to study the effect of different solvents in our system, we performed a series of reactions between 4-bromonitrobenzene and phenylboronic acid in the presence of various solvents using K_2CO_3 as base, and acetanilide-derived palladacycle **1L3** as catalyst. The results are summarized in Table 2. It is seen from the table that the reaction proceeds in both protic (Table 2, entries 1–5) and aprotic (Table 2, entries 6–8) solvents, although significant variations in yields were noted. The reaction seemed to be more facile in polar alcoholic solvent (Table 2, entries 1 and 3) than in other polar solvents like THF, DMF or CH_3CN. However, the reaction did not proceed well in water and gave only 60% isolated yield (Table 2, entry 9). The best result was obtained in isopropanol, which is considered an eco-friendly and desirable solvent for organic synthesis.[21] To study the effect of bases in our system, we carried out the reaction in the presence of various bases using isopropanol as solvent. The study showed that the reaction proceeds smoothly in the presence of K_2CO_3, Na_2CO_3 and Na_3PO_4 with equal ease (Table 2, entries 1, 10 and 14). However, the yield of cross-coupling product significantly diminished in the presence of NaOH and KOH (Table 2, entries 11 and 12). Moreover, an organic base such as Et_3N was not suitable for the current catalyst system (Table 2, entry 13). The coupling reaction did not proceed in the absence of base (Table 2, entry 15). The scope of the described Suzuki–Miyaura coupling was evaluated by investigating the reactions of a wide array of electronically diverse aryl bromides with arylboronic acids. The coupling reactions were conducted at room temperature in isopropanol with 0.5 mol% **1L3** as catalyst and 3 equiv. K_2CO_3 (Table 3). It was observed that the aryl bromides with electron-withdrawing and electron-donating substituent underwent coupling reactions with phenylboronic acid, effectively affording the desired biaryls in excellent yields (90–100%). The catalytic system is equally effective for electronically diverse arylboronic acids under similar reaction conditions. Moreover, it was found that the deactivated aryl bromides possessing MeO and Me groups gave almost the same or higher yields compared to the activated bromides possessing NO_2 and CHO groups. We have also observed a similar trend in reactivity of activated and deactivated aryl halides with phosphinoamine–Pd(II)–imidazole complexes.[4g] However, the actual reason for the equal efficiency of the catalyst for both activating and deactivating substrates is not clear. It is a well-known fact that dissociation of ligand in the reaction medium produces palladium(0) colloids or nanoparticles and the palladium(0) nanoparticle is the active catalytic species for the Suzuki–Miyaura reaction. With these aspects in mind, we investigated the nature of the catalytic species after completion of the reaction. Transmission electron microscopic images of the catalyst after reaction clearly show the formation of Pd(0) nanoparticles (Fig. S1, supporting

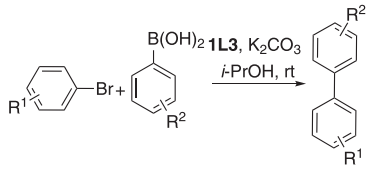
Table 2. Effect of solvent and base in Suzuki–Miyaura coupling



Entry	Solvent	Base	Yield
1	*i*-PrOH	K_2CO_3	99
2	*i*-PrOH–H_2O	K_2CO_3	90
3	EtOH	K_2CO_3	95
4	EtOH–H_2O	K_2CO_3	90
5	DMF–H_2O	K_2CO_3	65
6	DMF	K_2CO_3	70
7	THF	K_2CO_3	80
8	CH_3CN	K_2CO_3	85
9	H_2O	K_2CO_3	60
10	*i*-PrOH	Na_2CO_3	98
11	*i*-PrOH	NaOH	30
12	*i*-PrOH	KOH	30
13	*i*-PrOH	Et_3N	45
14	*i*-PrOH	Na_3PO_4	99
15	*i*-PrOH	—	Nil

Reaction conditions: 4-bromonitrobenzene (0.50 mmol), $PhB(OH)_2$ (0.55 mmol), base (1.5 mmol), solvent (3 ml), 1L3 (0.5 mol%).
[a]Isolated yield.

Table 3. Suzuki–Miyaura reaction of various substrates



Entry	R^1	R^2	Time (h)	Yield (%)[a]
1	4-NO_2	H	20	99
2	4-NO_2	4-OCH_3	20	90
3	4-NO_2	4-$C(CH_3)_3$	22	95
4	4-NO_2	4-Cl	18	90
5	4-NO_2	3-OCH_3	20	97
6	4-OCH_3	H	15	98
7	4-OCH_3	4-OCH_3	15	93
8	4-OCH_3	4-$C(CH_3)_3$	13	90
9	4-OCH_3	4-Cl	15	97
10	4-OCH_3	3-OCH_3	10	95
11	2-CH_3	H	5	94
12	4-CH_3	H	7	96
13	4-CH_3	4-OCH_3	12	97
14	4-CH_3	4-$C(CH_3)_3$	17	98
15	4-CH_3	4-Cl	20	90
16	4-CHO	H	22	88
17	4-$COCH_3$	H	10	90
18	H	H	8	98
19	H	4-OCH_3	14	95
20	2-CH_3	2-OCH_3	20	80

Reaction conditions: arylbromide (0.50 mmol), arylboronic acid (0.55 mmol), K_2CO_3 (1.5 mmol), *i*-PrOH (3 ml), 1L3 (0.5 mol%).
[a]Isolated yield.

information). To investigate this issue further, we next examined the role of possible active palladium(0) nano species by performing the Hg(0) poisoning test,[22,23] in which a reaction catalyzed by metal(0) or nanoparticle species become retarded owing to amalgamation with mercury(0).[24,25] However, metal–ligand complexes bearing metal in higher oxidation states usually remain unchanged in the presence of mercury(0). Therefore an experiment with Hg(0) was performed using 4-bromonitrobenzene (0.5 mmol) and phenylboronic acid (0.55 mmol) as substrate and **1L3** (0.5 mol%) as the palladium source. The palladium complex **1L3** was stirred in isopropanol containing K_2CO_3 and a stoichiometric amount of Hg(0) for 30 min prior to addition of the reacting substrates. Progress was monitored by TLC. Initially, the reaction proceeded smoothly, but subsequently it became retarded, and after 24 h we were able to isolate only 35% of the cross-coupled product. The retarding effect of Hg(0) became prominent as the reaction proceeded, possibly due to the formation of Pd(0) nanoparticles from complex **1L3** during the course of the reaction.

Thus our present result is quite significant as the desired biaryls could be achieved at room temperature using isopropanol as a solvent and with relatively low catalyst loading (0.5 mol% of the Pd complex **1L3**). In comparison with our previous results on the Suzuki–Miyaura cross-coupling reaction involving triphenylphosphine chalcogenides,[4f] triphenylmethylamine[8a] and phosphinoamine–Pd(II)–imidazole complexes,[4g] this method offers a mild and efficient methodology that can promote Suzuki–Miyaura reactions with an easily accessible and cheap ligand system.

Conclusion

We have found that the Suzuki–Miyaura coupling can be carried out in isopropanol with aryl bromides and arylboronic acid in the presence of stable and easily accessible acetanilide-based palladacycles. The reaction advances efficiently at low catalyst loading (0.5 mol% Pd complex) in isopropanol, which is a desirable solvent for organic synthesis. Synthesis of this catalytic complex is very simple and the starting materials used are commercially available and cheap. The formation of Pd(0) nanoparticles was observed during the reaction, which probably acted as the real catalyst. This new protocol is inexpensive and effective for many electronically diverse aryl bromides and arylboronic acids, providing biphenyl derivatives in good to excellent yields (88–99%).

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