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Excellent Suzuki–Miyaura catalytic activity of a new Pd(II) complex with sulfonamide–Schiff base ligand

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A new air-stable Pd(II) complex containing a sulfonamide–Schiff base ligand has been synthesized, characterized and investigated as a catalyst for the Suzuki–Miyaura reactions of aryl halides with arylboronic acids. Theoretical calculations (B3LYP) and spectroscopic evidence suggest that the sulfonamide–Schiff base coordinates to the Pd centre through sulfonamide nitrogen (–SO_2NH_2) rather than imine (–CH=N). The complex shows excellent cross-coupling activity with aryl bromides in water at room temperature and aryl chlorides in isopropanol at 60°C. Copyright © 2016 John Wiley & Sons, Ltd.

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Keywords: Palladium; sulfonamide–Schiff base; Suzuki–Miyaura reaction; water; aryl halides; DFT study

Introduction

Palladium (Pd)-catalysed Suzuki–Miyaura cross-coupling reactions of aryl halides with arylboronic acids have been established as one of the most versatile methods for the construction of C–C bonds in organic synthesis.[1] Like any other homogeneous catalytic reaction, in the Suzuki reaction also the ligand environment around the Pd centre holds the key to controlling the efficacy of a catalytic system. Thus, in the past few years, many attempts have been made to develop novel Pd complexes with accessible ligand systems, which can act as highly active catalysts particularly to deal with inexpensive and readily available aryl chlorides as substrates.[2] Significant advances have been achieved in developing efficient catalytic systems for aryl chlorides with notable ligands such as Buchwald's biaryl phosphines,[3] Kwong's P,N-donor ligands,[4] Fu's tertiary phosphines,[5] Nolan's N-heterocyclic carbenes,[6] Sarkar's indole-based phosphines[7] and others.[8] However, the majority of these systems suffer from limitations like high reaction temperatures (100–130°C),[4,7] use of environmentally undesirable solvents (toluene, dimethylformamide (DMF), dioxane),[3–5] employment of air- and moisture-sensitive phosphines as ligands,[3,5] high palladium loadings (up to 4 mol%), etc.[7] Thus, the advantages associated with excellent activities of such systems are often negated by the high cost and environmental impacts associated with the uses of such phosphines, high metal loadings and undesirable organic solvents. Therefore, from the practical viewpoint, the development of new phosphine-free catalytic systems for Suzuki–Miyaura reactions especially using environmentally benign reaction media under mild conditions is still considered to be a great challenge.

Over the past few decades, Schiff bases have been playing an important role as phosphine-free ligands in catalysis because of their easy synthesis, high stability and air- and moisture-insensitive properties.[9] Like phosphines, the steric and electronic properties of Schiff bases can be easily tuned by properly selecting condensing partners. Hence, Schiff bases have been vigorously explored in Pd-catalysed cross-coupling reactions including Suzuki–Miyaura reactions, and some efficient catalytic systems have been developed so far.[10,11] However, except for a few recent cases,[11] the majority of Schiff base-derived catalytic systems failed to promote aryl chlorides as substrates. Thus, in order to expand the scope of Schiff base ligands further in Suzuki–Miyaura reactions, herein we report the synthesis and catalytic activity of a new Pd(II) complex containing a sulfonamide–Schiff base as ligand. Sulfonamide–Schiff bases are a unique class of compounds that contain both Schiff base (CH=N) and sulfonamide (SO_2NH) fragments in the same ligand framework.[12] Because of the presence of pharmacologically active sulfonamide group, this type of compound continues to occupy an important position in medical chemistry including showing anticancer,[12a] anti-inflammatory[12b] and antimicrobial activities.[12d,12e] The sulfonamide–Schiff base 4-[(benzylidene) amino]benzenesulfonamide (L1) was first reported by Ayad *et al.* in 1991;[13] however, the coordination chemistry and catalytic potentials of sulfonamide–Schiff bases have rarely been studied, despite the fact that these ligands contain at least two potential donor nitrogen sites.[14] Nevertheless, there is one report of the synthesis of a Pd complex with a sulfonamide–Schiff base derivative that showed excellent catalytic activity for alcohol oxidation reaction.[15] However, to the best of our knowledge, there is no report on the use of sulfonamide–Schiff bases in the Suzuki–Miyaura cross-coupling reaction. Thus, as a part of our work on phosphine-free catalytic systems, herein we report a new Pd complex

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containing sulfonamide–Schiff base that shows excellent activity for the Suzuki reactions of aryl halides under mild conditions.

Experimental

Materials and methods

$Pd(OAc)_2$ and the starting material sulfanilamide were purchased from Acros Organics. The substrates used in the Suzuki–Miyaura reactions were purchased from Sigma-Aldrich, Spectrochem and Rankem. All other chemicals and solvents of analytical grade were purchased from various Indian firms. The solvents were distilled and dried prior to use. Elemental analyses (C, H, N) were carried out using a PerkinElmer 2400 Series II analyser. The mass spectrum of the complex was obtained with a Waters ZQ-4000 ESI/MS. Infrared (IR) spectra (250–4000 cm^{-1}) were recorded in KBr using a Shimadzu (Prestige-21) spectrophotometer. ^1H NMR spectra were recorded with a Bruker Avance II 400 MHz spectrometer.

Synthesis of Pd catalyst

The sulfonamide–Schiff base ligand L1 was prepared following a reported procedure.[13] A solution of ligand L1 (0.34 g, 1.33 mmol) in 15 ml of acetonitrile was added dropwise to a solution of $Pd(OAc)_2$ (0.30 g, 1.33 mmol) in 10 ml of acetonitrile. After refluxing the reaction mixture for 4 h, the yellowish precipitate was filtered. The residue was washed with hexane and finally complex **1** was obtained as a light yellow solid. Yield: 82%. Anal. Calcd for $C_{17}H_{18}N_2O_6SPd$ (%): C, 42.11; H, 3.74; N, 5.77. Found (%): C, 42.07; H, 3.72; N, 5.74. MS-ESI (DMSO, *m/z*): 485 $[M + H]^+$, 406 $[M - Ph - H]^+$. Selected IR frequencies (cm^{-1}, KBr): 1622 ($\nu_{C=N}$: imine), 1552 ($\nu_{N\text{–}H(bend)}$: NH_2), 3240 ($\nu_{N\text{–}H(sym)}$: NH_2), 1321 ($\nu_{S=O(asym)}$: SO_2), 1134 ($\nu_{S=O(sym)}$: SO_2) 1589 (ν_{COO}: acetate). ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.12 (s, 3H, CH_3), 2.57 (s, 3H, CH_3), 8.63 (s, 1H, CH=N), 7.34–7.96 (m, 9H, Ph), 6.90 (s, 2H, NH_2).

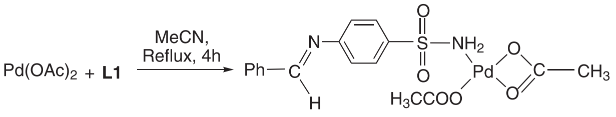
General procedure for Suzuki–Miyaura reaction

A 50 ml round-bottom flask was charged with a mixture of aryl halide (0.5 mmol), arylboronic acid (0.55 mmol), K_2CO_3 (1.5 mmol) and Pd catalyst (0.2 mol% for aryl bromide or 1 mol% for aryl chloride) and the mixture was stirred for required times at room temperature in water (6 ml) for aryl bromides or at 60°C in ^{i}PrOH (6 ml) for aryl chlorides. 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 (3 × 20 ml) and dried over Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue was chromatographed (silica gel, ethyl acetate–hexane, 1:9) to obtain the desired product. The products were confirmed by comparing the ^1H NMR and mass spectral data with those of authentic samples.

Results and discussion

Synthesis and characterization of catalyst

A new Pd complex (**1**) has been prepared by reacting $Pd(OAc)_2$ with ligand L1 in 1:1 molar ratio (Scheme 1). Complex **1** was isolated as a light yellow solid and its identity was confirmed using elemental analyses and ESI mass, IR and ^1H NMR spectroscopies. The complex is insoluble in almost all commonly used solvents except DMSO. The ESI mass spectrum of complex **1** shows a molecular ion peak due to $[M + H]^+$ at *m/z* = 485 with a relative intensity of 10%. For Schiff bases, the analysis of IR spectra clearly indicates whether they are coordinated or not, by observing the changes in the $\nu_{C=N}$ stretching frequency. The $\nu_{C=N}$ stretching in complex **1** appears at 1622 cm^{-1} which is exactly the same as that of the free ligand suggesting that the Schiff base imine is not involved in coordination. On the other hand, upon complexation, a significant shift of ν_{NH2} stretching from 3296 to 3240 cm^{-1} and ν_{NH2} bending from 1579 to 1552 cm^{-1} is observed which substantiates the participation of sulfonamide ($-SO_2NH_2$) nitrogen in coordination with Pd. This fact is further corroborated by ^1H NMR spectra. Most notable is the downfield shift of the sulfonamide proton singlet from 5.70 to 6.90 ppm upon coordination. A similar downfield shift of amine proton signal upon coordination was reported for other Pd complexes with aromatic sulfonamides.[15] The imine proton signal appears almost at the same position as that of the free ligand.



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Scheme 1. Synthesis of Pd complex 1 with sulfonamide–Schiff base ligand.

Density functional study

Due to the insolubility of the complex in commonly used solvents, we are unable to develop diffraction-quality crystals for X-ray study, and hence we have carried out a geometry optimization study for complex **1** using gas-phase density functional theory (DFT) with B3LYP/6-31+G(d) level of theory. Both the theoretically possible imine- and amine-bonded structures were considered for optimization and the optimized structures are shown in Figs. 1(a) and (b),

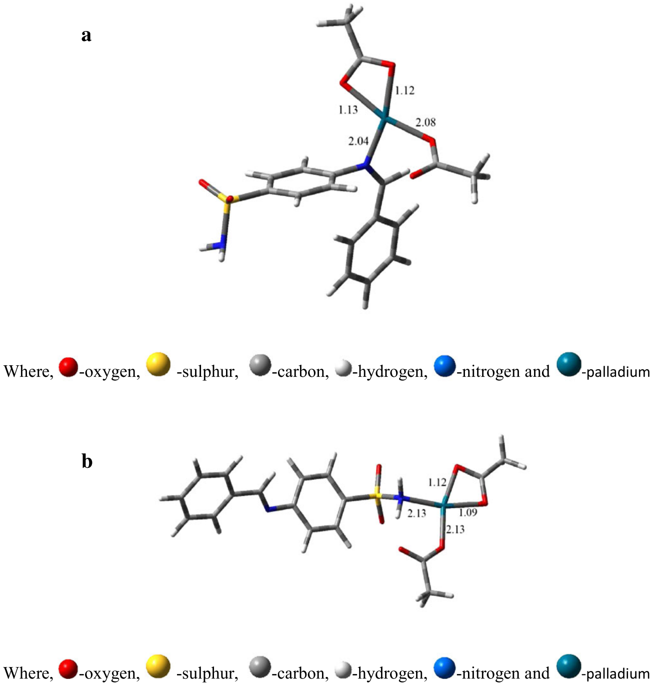

Figure 1. Optimized lowest-energy structure of (a) imine-bonded and (b) amine-bonded Pd complex with sulfonamide–Schiff base with the atom labelling.

respectively. Slightly distorted square planar geometries around Pd centres are observed for both the structures. The optimized structural parameters, bond lengths and angles for the two possible bonding modes of the complex obtained from DFT calculations are listed in the supporting information (Tables S1 and S2). On the basis of total energy calculation, the amine-bonded structure (Fig. 1(b)) is found to be slightly more stable (*ca* 5.34 kcal mol^{-1}) than the imine-bonded structure (Fig. 1(a)). Thus, the computational results further corroborate the spectroscopic findings that amine–Pd is the most likely mode of bonding in complex **1**. The calculated value of Pd–N distance (2.13 Å) is very close to that of some related sulfonamide complexes for which X-ray structures are known (Pd–N distance of 2.04–2.07 Å).[16]

Catalytic Activity

To study the efficacy of our complex as a catalyst for the Suzuki–Miyaura reaction, we chose 4-bromoanisole and phenylboronic acid as model substrates. For solvent optimization study, we considered only protic solvents as these are considered to be environmentally benign from green chemistry perspectives.[17] The reactions were performed using 0.2 mol% of catalyst at room temperature in the absence of additives, as these conditions were found to give the best results with one of our recently reported Schiff base-derived Pd catalysts.[11] The results are summarized in Table 1. We were delighted to observe that water is an excellent solvent for our catalytic system and quantitative formation of 4-methoxybiphenyl is obtained in just 2 h (Table 1, entry 1). It may be noted that during the past few years, water has attracted significant attention as a solvent in Suzuki–Miyaura reactions mainly because of its cost effectiveness and environmentally benign nature.[11,18] Compared with our previously reported catalytic system,[11] the present catalytic system is much superior as it requires much less time to produce similar results. In addition to water, other alcoholic solvents like EtOH and ^{i}PrOH also give comparable results (entries 2 and 4). It is interesting to note that

Table 1. Suzuki–Miyaura cross-coupling reactions of various aryl/heteroaryl bromides with arylboronic acids at room temperature[a]

$$R{-}Br + R'{-}B(OH)_2 \xrightarrow[\text{Base, Solvent, rt} \atop \text{1-24 h}]{\text{Pd Complex } \mathbf{1} \text{ (0.2 mol\%)}} R{-}R'$$

Entry	RBr	R′	Solvent	Base	Time (h)	Yield (%)[b]
1	4-$OCH_3C_6H_4Br$	C_6H_5	H_2O	K_2CO_3	2	99
2	4-$OCH_3C_6H_4Br$	C_6H_5	EtOH	K_2CO_3	3	99
3	4-$OCH_3C_6H_4Br$	C_6H_5	MeOH	K_2CO_3	12	80
4	4-$OCH_3C_6H_4Br$	C_6H_5	^{i}PrOH	K_2CO_3	2	98
5	4-$OCH_3C_6H_4Br$	C_6H_5	*n*-BuOH	K_2CO_3	24	30
6	4-$OCH_3C_6H_4Br$	C_6H_5	^{i}PrOH–H_2O	K_2CO_3	1	99
7	4-$OCH_3C_6H_4Br$	C_6H_5	EtOH–H_2O	K_2CO_3	1	98
8	4-$OCH_3C_6H_4Br$	C_6H_5	H_2O	K_2CO_3	2	99
9	4-$OCH_3C_6H_4Br$	C_6H_5	H_2O	NaOH	3	98
10	4-$OCH_3C_6H_4Br$	C_6H_5	H_2O	KOH	10	95
11	4-$OCH_3C_6H_4Br$	C_6H_5	H_2O	$MgCO_3$	5	96
12	4-$OCH_3C_6H_4Br$	C_6H_5	H_2O	Na_2CO_3	8	99
13	4-$OCH_3C_6H_4Br$	C_6H_5	H_2O	K_2CO_3	2	95
14	4-$CH_3C_6H_4Br$	C_6H_5	H_2O	K_2CO_3	2	97
15	4-$CHOC_6H_4Br$	C_6H_5	H_2O	K_2CO_3	3	98
16	4-$NO_2C_6H_4Br$	C_6H_5	H_2O	K_2CO_3	12/6[c]	45/92[c]
17	C_6H_5Br	C_6H_5	H_2O	K_2CO_3	6	99
18	4-$OCH_3C_6H_4Br$	4-ClC_6H_4	H_2O	K_2CO_3	5	95
19	4-$OCH_3C_6H_4Br$	4-$CH_3C_6H_4$	H_2O	K_2CO_3	3	98
20	4-$OCH_3C_6H_4Br$	3-$NO_2C_6H_4$	H_2O	K_2CO_3	12	20
21	2-$CHOC_6H_4Br$	C_6H_5	H_2O	K_2CO_3	12	64/88[c]
22	2-$CH_3C_6H_4Br$	C_6H_5	H_2O	K_2CO_3	6	62/92[c]
23	2,5-$OCH_3C_6H_3Br$	C_6H_5	H_2O	K_2CO_3	6	85
24	5-Bromopyrimidine	C_6H_5	H_2O	K_2CO_3	12	46/88[d]
25	2-Bromo-3-methylthiophene	C_6H_5	H_2O	K_2CO_3	12	34/91[d]

[a] Reaction conditions: arylbromide (0.5 mmol), arylboronic acid (0.6 mmol), base (1.5 mmol), solvent (6ml).

[b] Isolated yields. Yields are average of two runs.

[c] PrOH–H_2O (1:1) used as solvent.

[d] $T = 50°C$.

product formation becomes slightly faster when neat water, neat ^{i}PrOH or neat EtOH is replaced by mixed aqueous–alcoholic solvents such as H_2O–^{i}PrOH (entry 1 or 4 versus entry 6) or H_2O–EtOH (entry 1 or 2 versus entry 7). On evaluating the effects of bases in our model reaction, we have screened some commonly available bases for our model reaction using water as solvent (Table 1, entries 8–12). Our study reveals that catalyst **1** can tolerate common bases and excellent yields are obtained with almost all the bases screened. However, K_2CO_3 is found to be the most effective base as it requires much less time compared to other bases.

Inspired by the initial reactions, we have explored the scope of our catalyst for several representative coupling reactions with a range of aryl bromides using water as solvent and K_2CO_3 as base (Table 1, entries 13–25). Usually, aryl bromides bearing electron-donating groups (e.g. Me, OMe) and electron-withdrawing groups (NO_2, CHO) at *para*-position couple efficiently with phenylboronic acid to produce corresponding biaryls in excellent yields (Table 1, entries 13–16). High yields are also maintained when phenylboronic acid is replaced by other arylboronic acids such as *p*-chlorophenylboronic acid (entry 18) or *p*-tolylboronic acid (entry 19). However, *m*-nitrophenylboronic acid gives only poor yield. A similar observation for *m*-nitrophenylboronic acid was also noted earlier,[1] although the exact reason for this is not known.

It is worth noting that sterically bulky *ortho*-substituted aryl bromides such as 2-bromotoluene (entry 22) and 2-brombenzaldehyde (entry 21) produce only moderate yields; however, the yields can be significantly improved by using ^{i}PrOH as co-solvent with water in 1:1 proportion. It is important to mention that heteroaryl halides are usually very difficult substrates to activate in Suzuki–Miyaura reactions and often they give low yields. However, in our case, heteroaryl bromides such as 5-bromopyrimidine and 2-bromo-3-methylthiophene under slightly warm conditions give excellent yields when ^{i}PrOH–H_2O is used as solvent (Table 1, entries 24 and 25).

Encouraged by our results with aryl bromides, we have extended the scope of our catalytic system for the cross-coupling reactions of aryl chlorides using water as reaction medium. Initial coupling reactions were performed using *p*-chloronitrobenzene with phenylboronic as model substrates. Unfortunately, only very poor yield is obtained when water is used as solvent at a relatively high temperature of 60°C with 0.2 mol% of catalyst (Table 2, entry 1). As mentioned earlier, aryl chloride activation is one of the most difficult tasks in Suzuki reactions and often requires a drastic reaction condition including very high catalyst loading (up to 10 mol%).[8b] On increasing the catalyst loading to 1 mol%, no significant improvement is observed when water is used as solvent. However, changing the solvent from water to ^{i}PrOH or DMF (Table 2, entries 2 and 4) significantly improves the catalytic efficacy, and almost quantitative conversion of cross-coupling product is obtained. From an environmental perspective, ^{i}PrOH is a superior solvent over DMF[17] and, hence, for remaining aryl chloride screening, ^{i}PrOH was used as solvent (Table 2, entries 8–17). Our study reveals that aryl chlorides bearing electron-withdrawing groups (entries 8 and 9) or electron-donating groups (entries 11 and 12) at *para*-position undergo smooth coupling with phenylboronic acid and afford the desired biaryl in excellent yields. No major differences in yields

Table 2. Suzuki–Miyaura cross-coupling reactions of various aryl/heteroaryl chlorides with aryl boronic acids[a]

$$R{-}Cl + R'{-}B(OH)_2 \xrightarrow[\text{Solvent, } K_2CO_3\text{, 60°C}]{\text{Pd Complex } \mathbf{1} \text{ (1 mol\%)}} R{-}R'$$

Entry	RCl	R′	Solvent	Base	Time (h)	Yield (%)[b]
1	4-$NO_2C_6H_4Cl$	C_6H_5	H_2O	K_2CO_3	12	22/10[c]
2	4-$NO_2C_6H_4Cl$	C_6H_5	^{i}PrOH	K_2CO_3	8	98
3	4-$NO_2C_6H_4Cl$	C_6H_5	^{i}PrOH–H_2O (1:1)	K_2CO_3	12	40
4	4-$NO_2C_6H_4Cl$	C_6H_5	DMF	K_2CO_3	12	98
5	4-$NO_2C_6H_4Cl$	C_6H_5	DMF–H_2O (1:1)	K_2CO_3	12	50
6	4-$NO_2C_6H_4Cl$	C_6H_5	Glycerol–H_2O	K_2CO_3	5	60
7	4-$NO_2C_6H_4Cl$	C_6H_5	Toluene	K_2CO_3	12	20
8	4-$NO_2C_6H_4Cl$	C_6H_5	^{i}PrOH	K_2CO_3	8	96
9	4-$CHOC_6H_4Cl$	C_6H_5	^{i}PrOH	K_2CO_3	12	87
10	C_6H_5Cl	C_6H_5	^{i}PrOH	K_2CO_3	6	96
11	4-$CH_3C_6H_4Cl$	C_6H_5	^{i}PrOH	K_2CO_3	6	98
12	4-$OCH_3C_6H_4Cl$	C_6H_5	^{i}PrOH	K_2CO_3	12	88
13	2-$OCH_3C_6H_4Cl$	4-ClC_6H_4	^{i}PrOH	K_2CO_3	12	68
14	3-Chloropyridine	4-$CH_3C_6H_4$	^{i}PrOH	K_2CO_3	12	88
15	4-$NO_2C_6H_4Cl$	3-$NO_2C_6H_4$	^{i}PrOH	K_2CO_3	12	20
16	4-$NO_2C_6H_4Cl$	4-$CH_3C_6H_4$	^{i}PrOH	K_2CO_3	12	85
17	4-$NO_2C_6H_4Cl$	4-ClC_6H_4	^{i}PrOH	K_2CO_3	6	81

[a] Reaction conditions: aryl chloride (0.5 mmol), arylboronic acid (0.6 mmol), K_2CO_3 (1.5 mmol), solvent (6ml).

[b] Isolated yields. Yields are average of two runs.

[c] Reaction performed with 0.2 mol% catalyst.

are observed when phenylboronic acid is replaced by 4-chloroboronic acid (entry 17) or 4-tolylboronic acid (entry 16). Interestingly, our catalyst can also tolerate other representative substrates that are usually difficult to activate; for instance, sterically bulky substrate (2-chloroanisole; entry 13) or heteroaryl chloride (3-chloropyridine; entry 14).

Conclusions

We have developed a new Pd catalyst containing sulfonamide–Schiff base that showed excellent Suzuki–Miyaura cross-coupling reactivity. Good-to-excellent yields of cross-coupling products were obtained with aryl bromides in water at room temperature and aryl chlorides in ^{i}PrOH under mild conditions (1 mol% catalyst loading, 60°C). A wide range of aryl bromides and chlorides could be conveniently used as substrates.

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Supporting information

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

Table S1: Calculated bond length and bond angles of the imine-bonded isomer

Table S2: Calculated bond length and bond angles of the amine-bonded isomer