Asian Journal of Chemistry; Vol. 34, No. 11 (2022), 2922-2928

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2022.23979

Synthesis, Spectral and Catalytic Properties of Palladium(II) Complexes Containing Hydrazone Schiff Base Ligands

M. SATHYA and G. VENKATACHALAM*

P.G. & Research Department of Chemistry, Government Arts College, Dharmapuri-636705, India

*Corresponding author: E-mail: gvchem@gmail.com

Received: 23 June 2022; *Accepted*: 20 August 2022; *Published online*: 19 October 2022; AJC-21007

Palladium(II) complexes of bidentate hydrazone Schiff bases were synthesized and characterized by means of physico-chemical and spectroscopic (FT-IR, UV-vis and NMR) techniques. All the palladium(II) complexes were tested as catalyst for Suzuki-Miyaura and Sonogashira coupling reactions and exhibits moderate to good catalytic activity.

Keywords: Palladium(II) complexes, Schiff base ligands, Catalyst, Suzuki-Miyaura coupling reaction, Sonogashira coupling

INTRODUCTION

A number of reports published in the last few decades have proved the importance of the palladium(II) catalysis in variety of reactions [1-3]. The importance was recognized by awarding the 2010 Chemistry Nobel Prize for "palladium-catalyzed cross couplings in organic synthesis" [4,5]. Over the past decades, significant progress has been achieved using a variety of homogeneous catalysts. Generally, homogeneous palladium catalysts are popular for their high selectivity, activity and resistance towards poisons, but are difficult to recover and reuse [6]. Among them, great attention has been paid to palladium catalyzed carbon-carbon bond forming reactions such as Suzuki-Miyaura [7] and Sonogashira [8,9] coupling reactions, that are widely employed for the preparation of a great variety of organic molecules. The palladium-catalyzed couplings of aryl halides with aryl boronic acids represent the most successful methods for the preparation of biaryls [10-17].

In past few decades, there has been an exponential rise in the number of publications in the Suzuki-Miyaura coupling reactions. In recent years, efforts are being given to develop alternative systems comprised of non-toxic and air stable ligands like *N*-heterocyclic carbenes (NHCs) [18,19], Schiff base [20-22], thiosemicarbazones [23], *etc.* for cross-coupling reaction. Among these systems, from the cost and synthetic accessibility point of views, Schiff bases are found to be the most effective ligand system [24,25] like phosphines, the stereo-electronic property in Schiff bases can easily be tuned by choosing the right condensing partners [26]. Manipulating the ligand environment around the palladium center leads to the change of efficiency of the catalytic system composed of Pd(0) or Pd(II) derivatives associated with suitable ligands [27-30]. Recently, various nitrogen containing ligands involved in the Suzuki-Miyaura reaction have attracted a great deal of attention [31-39].

Schiff bases are well recognized as multidentate ligands in catalytic systems among different *N*-based ligands, because they are formed by a simple synthetic path with the commercially available materials. They also exhibit high a tolerance under a broad range of redox conditions [40-42]. Also, the ability to easily change the electronic and steric properties of Schiff bases is one of their most important advantages [43-48]. Schiff bases have been considered as versatile ligands, especially in terms of their donor atoms and substituents, thereby providing the possibility for designing metal complexes with useful chemical properties [49]. They possess a wide variety of applications in biological, inorganic, analytical and catalytic processes [50]. Phosphine based ligands have widespread pharmacological applications including antiviral, antioxidant, antifungal, anticancerogenic, antibacterial and antitumor activities [51]. Particularly, phosphine based palladium(II) complexes have been reported to possess significant bioactivities [52]. These metals play vital roles in controlling gene expression, inhibiting cell division and hence are used as valuable anticancer drugs.

However, problem associated with such complexes is their ready dissociation in solution leading to reactive species that are unable to reach their pharmacological targets such as DNA. This rapid aquation and formation of reactive species could be overcome if palladium(II) complexes are stabilized by bulky ligands such as triphenylphosphine [53].

Transition metal complexes incorporating Schiff base ligands have displayed several interesting properties in which organic transformations *viz*. C-C bond formation is the prime interest among the researchers. The synthesis and reactivity of new N,O-donor ligands and their coordination to palladium metal continues to attract interest owing to the possibility of tailoring the steric and electronic properties of the different groups. Schiff base ligands are particularly attractive because of their ease of synthesis, ability to stabilize metal with varying oxidation states and ease of fine-tuning their electronic and steric properties [54]. Herein, we report the synthesis, characterization and catalytic properties of the newly synthesized palladium(II) complexes containing hydrazone Schiff base ligands and their towards the coupling reaction of aryl halides.

EXPERIMENTAL

$PdCl_2(PPh_3)_2$ was purchased from Arrora Matthey India Ltd., whereas 2-hydroxy-1-naphthaldehyde, hydrazine monohydrate, *o*-vanillin, triethylamine and all other solvents were purchased from Sigma-Aldrich, USA. The substrates for Suzuki-Miyaura reaction were also procured from Sigma-Aldrich, USA. The aldehydes with hydrazine monohydrate ligands were synthesized according to the literature methods [55].

Characterization: The analysis of carbon, hydrogen and nitrogen contents were performed on elementary system model vario EL 111 at Sophisticated Test and Instrumentation Center (STIC) Cochin University, Kochi, India. The Infrared spectra of the complexes were recorded in an Agilent resolution Pro Spectrophotometer. A JASCO V-630 UV-vis Varian spectrophotometer was used to record the electronic spectra. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer in $CDCl_3$ solution. Electronic spectra of the complexes were recorded in $CDCl_3$ solution with a Cary 300 Bio UV-vis Varian spectrophotometer from 800 to 200 nm using cuvettes of 1 cm path length. Melting points are uncorrected and were determined in the capillary tubes on a Boetius micro heating apparatus.

Synthesis of Schiff base ligands: To an ethanolic solution of appropriate aldehyde (0.488 g, 4 mmol) was added of hydrazine monohydrate (0.272 g, 2 mmol) and mixture was heated under reflux for 1 h. The precipitate thus formed was washed with cold ethanol and dried in vacuum.

Synthesis of Pd(II) Schiff base complexes: To an ethanolic solution of $[PdCl_2(PPh_3)_2]$ (0.1 g; 0.1 mmol) was added a Schiff base ligand $[HL_1]$, (0.1 g; 0.1 mmol) followed by triethylamine (0.1 g; 0.1 mmol) and the mixture was stirred at room temperature for 1 h and the resulting dark brown solution was refluxed for 5 h. The formation of product was checked by TLC and solution was evaporated to give a solid mass, which was purified by silica gel column chromatography (eluent: CH_2Cl_2) to afford pure palladium complex (**1**) as an orange solid. Similarly, complexes **2** and **3** were synthesized following the same procedure as described for the complex **1**, using appropriate ligands.

$[PdCl(PPh_3)(HL_1)$ (1): Yield: 60%, Anal. calcd. (found) % for $C_{32}H_{26}N_2O_2PPdCl$: C, 58.24 (59.73), H, 3.73 (4.04), N, 4.01 (4.35); IR (KBr, ν_{max}, cm^{-1}): 1607, 1481, 1433, 1270; UV-vis (nm): 230 (π-π*), 330 (n-π*), 410 (LMCT); ^{1}H NMR ($CDCl_3$) δ (ppm): 6.9-7.7 (m, Ar), 8.7 (HC=N), 11.4 (OH); ^{13}C NMR ($CDCl_3$) δ (ppm): (117-133; m, Ar); 164 (HC=N).

$[PdCl(PPh_3)(HL_2)]$ (2): Yield 52%, Dark brown colour. Anal. calcd. (found) % for $C_{40}H_{30}N_2O_2PPdCl$: C, 64.91 (66.49); H, 3.50 (4.03); N, 3.01 (3.76); IR (KBr, ν_{max}, cm^{-1}); 1599, 1479, 1396, 1299; UV-vis (nm): 210 (π-π*), 350 (n-π*). ^{1}H NMR ($CDCl_3$) δ (ppm): 7.10-8.10 (m, Ar), 9.60 (HC=N); ^{13}C NMR ($CDCl_3$) δ (ppm): (127-133; m, Ar).

$[PdCl(PPh_3)(HL_3)]$ (3): Yield 50% Orange-red colour; Anal. calcd. (found) % for $C_{34}H_{31}N_2O_4PPdCl$: C, 56.61 (57.96); H, 4.01 (4.40); N, 3.43 (3.97); IR (KBr, ν_{max}, cm^{-1}): 1604, 1459, 1313, 1245; UV-vis (nm): 240 (π-π*), 360 (n-π*), 430 (LMCT); ^{1}H NMR ($CDCl_3$) δ (ppm): 6.80-7.80 (m, Ar), 8.70 (HC=N), 11.50 (OH), 3.9 (OCH_3); ^{13}C NMR ($CDCl_3$) δ (ppm): 115-135 (m, Ar), 164 (HC=N), 56.24 (OCH_3).

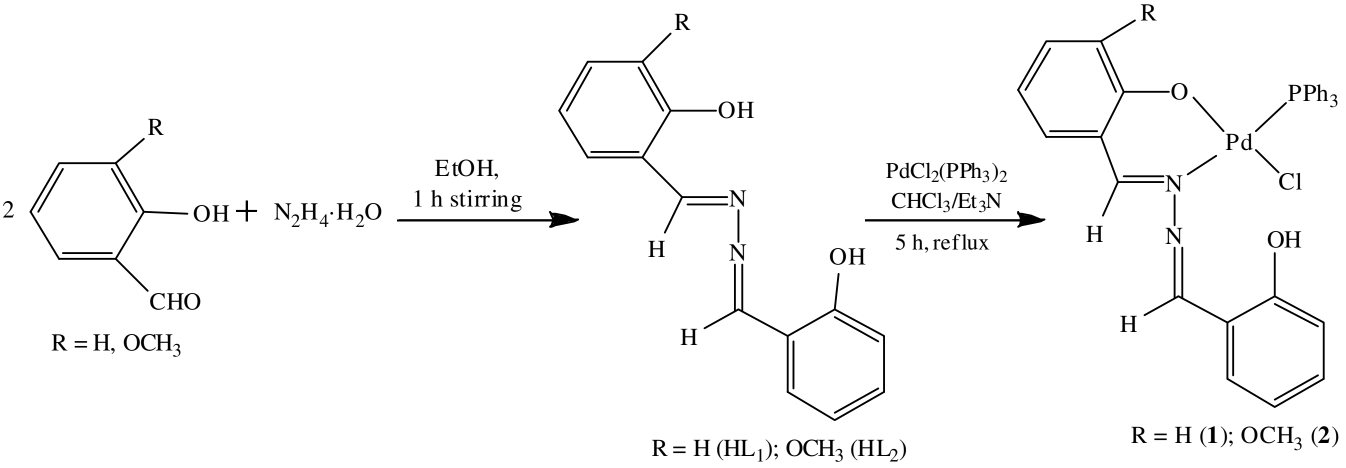
General procedure for Suzuki-Miyaura reactions: A 50 mL round bottom flask was charged with aryl halide (0.5 mmol), aryl boronic acid (0.75 mmol), K_2CO_3 (1 mmol) and the complex catalyst (**1-3**) (1 mol %). The mixture was then refluxed at 80 ºC for 2 h. The progress of the reaction was monitored by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 20 mL water and extracted with diethyl ether (3 × 15 mL) and dried over $MgSO_4$. The crude product was purified by column chromatography by using hexane as eluent.

General procedure for Sonogashira coupling reactions: To a slurry of aryl halide (0.5 mmol), palladium catalyst (0.3 mol%) in an appropriate solvent (5 mL), phenyl acetylene (0.75 mmol) and K_2CO_3 (1.25 mmol) were added and heated at required temperature. After completion of the reaction (monitored by TLC), the flask was removed from the oil bath and 20 mL of water was added, followed by extraction with ether (4 × 10 mL). The combined organic layers were washed with water (3 × 10 mL), dried over anhydrous $MgSO_4$ and filtered, solvent was removed under vacuum. The residue was dissolved in hexane and analyzed by the GC-MS analysis.

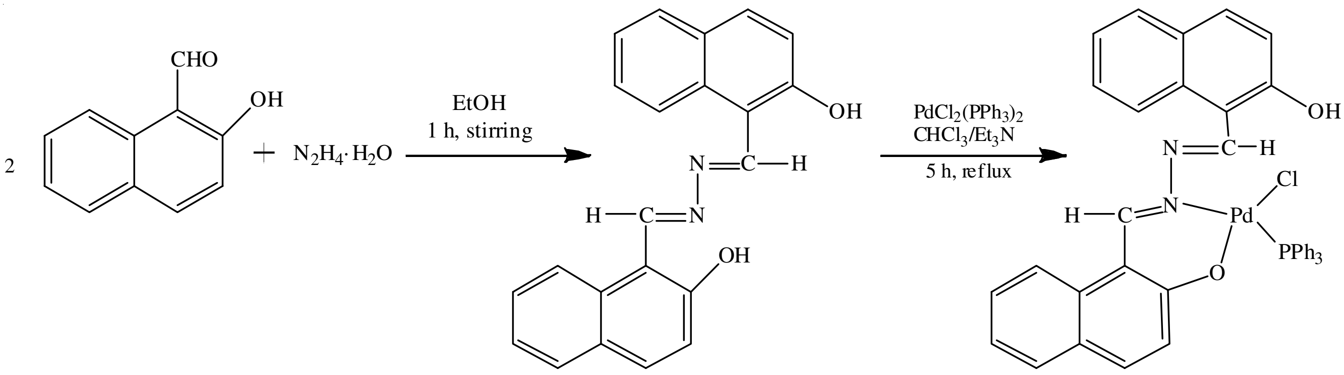
RESULTS AND DISCUSSION

Complexes of the types $[PdCl(PPh_3)L_{1-3}]$ (L_{1-3} = Schiff base ligands) were synthesized by the reaction compounds H_2L_1, H_2L_2 and H_3L_3 with $[PdCl_2(PPh_3)_2]$ afforded the corresponding bidentate palladium complexes (**1-3**) in the modulate yields (**Schemes I** and **II**).

Palladium(II) complexes are air and moisture stable in the solid state and even in solution. The complexes were characterized by elemental analysis, UV-vis, FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopies. Attempts made to grow single crystals suitable for SC-XRD analysis were unsuccessful. The present ligand system was choosen to study the binding mode of O, N-donor set with palladium metal center. Since hydrazine forms Schiff base ligands with one and two molecules of aldehyde



Scheme-I: Synthesis of palladium(II) complexes **1** and **2**



Scheme-II: Synthesis of palladium(II) complex (**3**)

leading to different binding sites. To our surprise, mononuclear palladium complexes were obtained with a bidentate fashion of O,N-donor set and remaining coordinate sites were uncoordinated to the metal center. A change in solvent molar composition (or) temperature did not lead to the formation of dipalladium complexes.

Infrared spectra: The Schiff base ligands (H_2L_1-H_2L_3) showed a strong band at 1620-1601 cm^{-1} and they are assigned to the CH=N stretching frequency. The C=N stretching frequencies displayed by the palladium(II) Schiff base complexes (**1-3**) are lower than those for the uncomplexed ligands. This lowering of the C=N stretching frequency, observed at 1607-1599 cm^{-1} for those palladium complexes, is attributed to coordination of the C=N bond in the chelate ring to the metal center [56].

UV spectra: Complexes (**1-3**) in chloroform solutions exhibit characteristic absorptions in the region 200-800 nm and are given in Fig. 1. Strong absorption bands observed at 210-260 nm are assigned to the π–π^* transitions in the Schiff base ligands, wheres the medium absorption bands, appearing at 290-360 nm, are assigned to the n–π^* transition. The π–π^* and n–π^* transitions for the free ligands were shifted to higher wavelength as a consequence of the coordination to the metal ions, indicating the formation of palladium Schiff base complexes. In addition, these spectra showed a band around 350-410 nm, assigned to an MLCT transition, which strongly

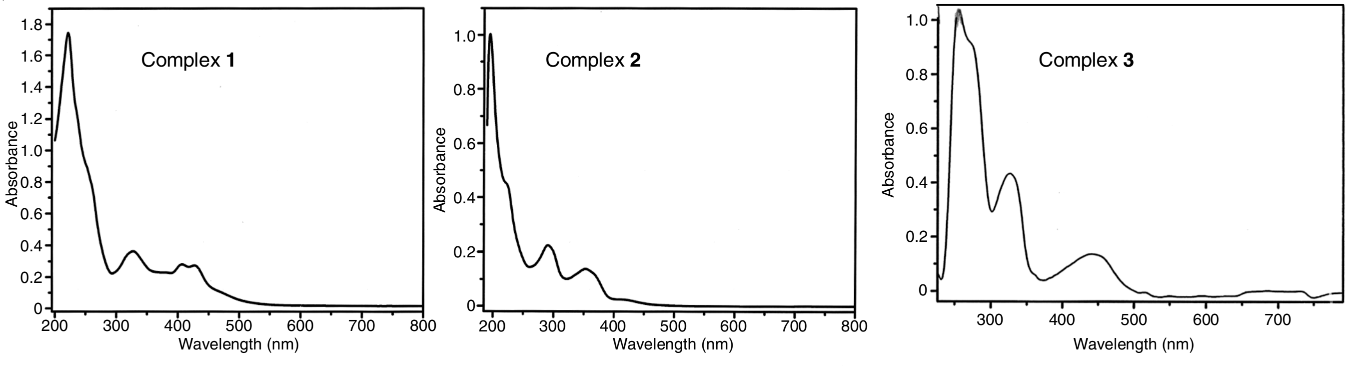


Fig. 1. UV-vis spectra of complexes **1-3**

favours the square-planar geometry around the central metal ion [57-59].

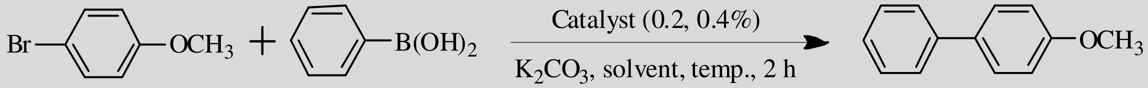
^{1}H NMR spectra: Complexes (**1-3**) show that aromatic one of the OH peaks in these palladium(II) complexes, expected to appear in the downfield region around 11.57-11.40 ppm for H_2L_1-H_2L_3 are not observed and it this due to the coordination of the phenolic oxygen atom to the metal atom by deprotonation and the other OH groups is uncoordinated. The presence of the azomethine proton (CH=N) attached to the phenyl ring was confirmed by the singlet 9.6-7.8 ppm. Further, the aromatic protons of all these complexes are observed as multiplets around 6.8-8.7 ppm. The methoxy proton in the complex **3** appeared as a singlet at 3.9 ppm. The ^{13}C NMR spectra of complexes **1** and **3** were recorded and showed peaks around 164 ppm for the azomethine carbon (CH=N) atom. The methoxy carbon signal (OCH_3) was observed for complex **3** at 56.24 ppm.

Catalytic application in Suzuki-Miyaura coupling reactions: In order to evaluate the catalytic activity of the complexes for Suzuki-Miyaura coupling reaction 4-bromoanisole and phenylboronic acid are chosen as model substrates. Irrespective of solvent systems under similar experimental conditions, complex **1** has shown superior results over complex **2** (Table-1). An initial solvent optimization study with both the complexes (Table-1) reveals that EtOH (entry 5) and DMF (entry 8) are the two best solvents systems, however, considering greener prespective; EtOH is chosen as the reaction media for further study.

Various bases, catalyst loading and temperature were screened (Table-2). Different organic and inorganic bases were studied, the yield of the cross-coupling products was reduced when organic bases such as Et_3N or KOH were employed (Table-2, entries 3 & 4). A considerable increase in the product formation was observed in the presence of Cs_2CO_3 and K_2CO_3 at room temperature (Table-2, entries 1 & 2); hence, the economically low-cost K_2CO_3 was chosen as a base for these coupling reactions. A substantial acceleration rate of the reaction (Table-2, entries 5-8) was observed upon increasing the temperature (50, 60, 80 and 100 ºC). Then, different catalyst loadings 0.5 and 0.05 mol% were investigated for the reaction (Table-2, entries 6, 9-11). Among the catalyst was found to be the best (Table-2, entry 10). Therefore, it was decided to use K_2CO_3 as base, EtOH as solvent and 0.1 mol% catalyst as the optimum conditions in further studies.

Effects of different substrates: To investigate the effects of different substrates in present catalyst system, several different

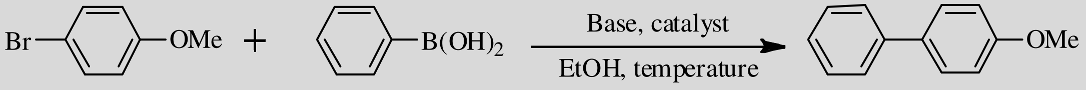
TABLE-1
SCREENING OF THE COMPLEXES AS CATALYSTS FOR THE SUZUKI-MIYAURA REACTION OF 4-BROMOANISOLE WITH PHENYL BORONIC ACID



Entry	Solvents	Temp. (°C)	Catalyst (mol%)	Yield (%)		
				1	2	3
1	CH_2Cl_2	Room temp.	0.4	41	35	38
2	Acetone	Room temp.	0.4	45	39	32
3	EtOH	Room temp.	0.4	49	28	42
4	EtOH	50	0.4	50	30	45
5	EtOH	80	0.4	92	70	81
6	EtOH	80	0.2	52	34	40
7	H_2O	80	0.4	No reaction	No reaction	97
8	CH_2Cl_2	80	0.4	100	96	No reaction

[a] Reaction conditions: 4-Bromoanisole (0.4 mmol), phenylboronic acid (0.75 mmol), K_2CO_3 (1.5 mmol), solvent (4 mL).
[b] Isolated yield after column chromatography.

TABLE-2
EFFECT OF BASES, CATALYST LOADINGS AND TEMPERATURE FOR THE SUZUKI-MIYAURA REACTION



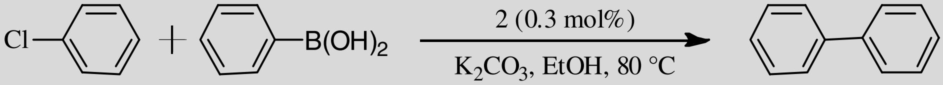
Entry	Base	Temp. (°C)	Catalyst loading (mol%)	Time (h)	Yield (%)[b]
2	K_2CO_3	25	0.50	14.0	95
3	Et_3N	25	0.50	14.0	36
4	KOH	25	0.50	14.0	46
5	K_2CO_3	50	0.50	4.0	98
6	K_2CO_3	60	0.50	2.0	98
7	K_2CO_3	80	0.50	1.0	98
8	K_2CO_3	100	0.50	0.5	98
9	K_2CO_3	60	0.25	2.0	96
10	K_2CO_3	60	0.10	2.0	100
11	K_2CO_3	60	0.05	2.0	80

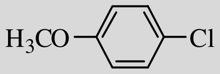
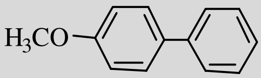
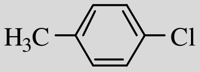
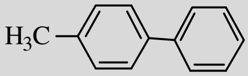
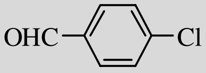
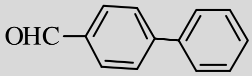
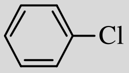
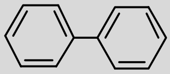
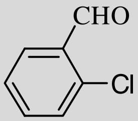
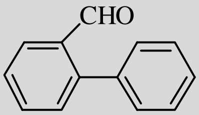
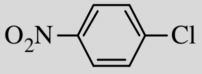
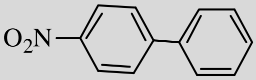
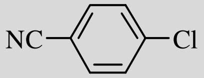
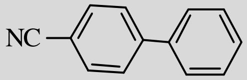
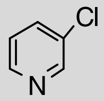
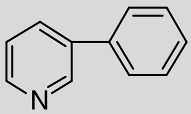
[a] Reaction conditions: 4-Bromoanisole (0.5 mmol), phenylboronicacid (0.75 mmol), K_2CO_3 (1.5 mmol), catalyst in 5 mL of EtOH at various temperatures; [b] Isolated yield after column chromatography.

substrates were used under the optimized conditions. It was observed that complex **1** effectively converts aryl bromides containing electron withdrawing substituent like –CHO (Table-3, entry 3) as well as electron donating substituents like $-CH_3$, OCH_3 (Table-3, entries 1 & 2) at *para*-position into the corresponding biaryls in to moderate-to-excellent yields. It may be noted that the synthesized catalyst is also very effective with more challenging substrates like sterically hindered *ortho*-substituted aryl chlorides. For instance, the reaction of 2-chlorobenzaldehyde (Table-3, entry 5) with phenyl boronic acid gives 58% yield of the desired product.

The yield of the cross-coupled product was not satisfactory when inorganic base such as K_2CO_3 or Cs_2CO_3 were employed (Table-4, entries 5 & 6), the other organic solvents including CH_3CN, THF, DMF and ethanol were also, low palladium concentrations gave decreased yield (Table-4, entries 1 & 2).

TABLE-3
SUZUKI-MIYAURA REACTIONS OF VARIOUS ARYL AND HETEROARYL CHLORIDES AND ARYL BORONIC ACIDS USING COMPLEX **1** AS CATALYST



Entry	Substrate	Product	Time (h)	Catalyst yield (%)		
				1	2	3
1			4	82	88	85
2			5	73	71	76
3			5	70	68	74
4			5	74	79	71
5			5	58	52	56
6			7	76	71	74
7			7	80	83	79
8			7	82	80	83

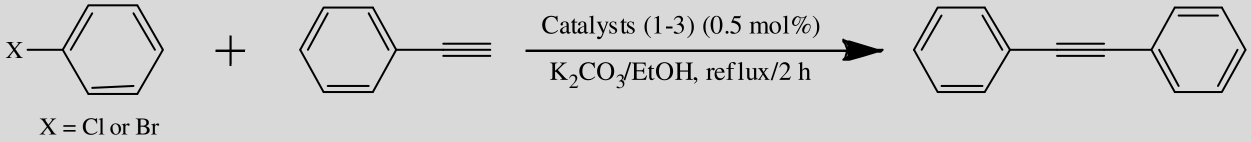
[a] Reaction conditions: Substrate (0.5 mmol), aryl boronic acid (0.75 mmol), K_2CO_3 (1.5 mmol), EtOH (4 mL).
[b] Isolated yield after column chromatography.

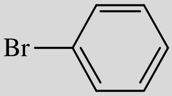
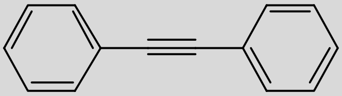
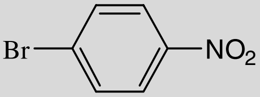
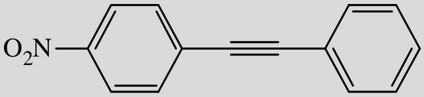
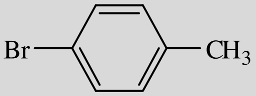
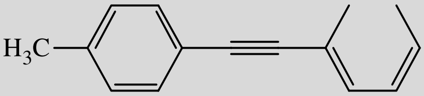
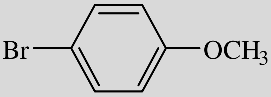
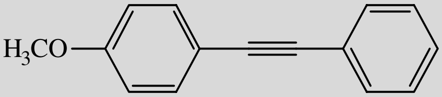
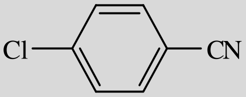
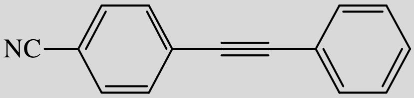
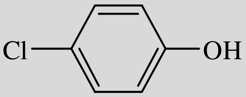
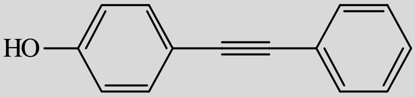
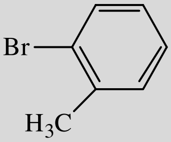
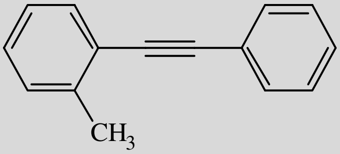
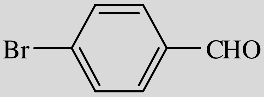
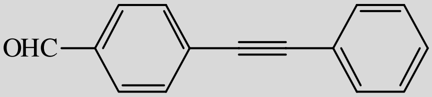
TABLE-4
OPTIMIZATION OF THE CONDITIONS FOR THE SONOGASHIRA REACTION OF IODOBENZENE WITH PHENYLACETYLENE[a]

Entry	Catalyst (mol% of Pd)	Base	Solvent	Time (h)	Temp. (°C)	Yield (%)[b]
1	0.2	Et_3N	–	24	30	37
2	0.3	Et_3N	–	24	30	45
3	0.6	Et_3N	–	24	30	86
4	0.7	Et_3N	–	24	30	53
5	0.6	K_2CO_3	–	24	30	61
6	0.6	Cs_2Cl_2	–	24	30	43
7	0.6	KOH	–	24	30	70
8	0.6	Et_3N	CH_3CN	24	30	68
9	0.6	Et_3N	THF	24	30	49
10	0.6	Et_3N	DMF	24	30	43
11	0.6	Et_3N	_	1	80	93
12	0.6	Et_3N	EtOH	1	80	64

[a] Reaction conditions: Iodobenzene (0.5 mmol), phenylacetylene (0.75 mmol), base (1,25 mmol), solvent (2 mL), catalyst (0.3 mol%), temperature (80 °C); [b] Isolated yield after column chromatography.

TABLE-5
SONOGASHIRA COUPLING OF PHENYL ACETYLENE WITH ARYL HALIDES CATALYZED BY COMPLEXES



Entry	Substrate	Product	Catalyst yield (%)		
			1	2	3
1			71	76	63
2			70	62	58
3			82	61	53
4			66	60	56
5			73	65	61
6			87	89	93
7			76	62	53
8			81	73	64

[a]Reaction conditions: Substrate (1 mmol), phenyl acetylene (1,2 mmol), K_2CO_3 (1 mmol), catalyst (0.5 mol%), solvent (5 mL), temperature 80 °C; [b]Isolated yield after column chromatography.

An increase in the catalytic loading (0.7 mol%) gave poorer result (Table-4, entry4). It was concluded that the reaction was more favourable using Et_3N as base and environmentally neat conditions at 80 ºC in the presence of (0.6 mol%) of the catalyst (Table-4, entries 3 and 11).

Aryl halides react with phenylacetylene, producing the corresponding product with moderate to excellent conversion (Table-5, entry 3, 82%). Good conversion was observed for all the substrates in 2 h, as expected, satisfactory results was obtained for all the electron-deficient substrate in the phenyl acetylene (Table-5, entry 6), having conversions of 87, 89 and 93%. 2-Bromotoluene (Table-5, entry 7) gave the corresponding product in a slightly lower yield (53-76%), which may be due to steric effects compare with *p*-bromotoluene (Table-5, entry 3). Further, 4-bromotolune and chlorobenzonitrile can also react with phenylacetylene with good conversions.

Conclusion

In summary, a new type mononuclear palladium(II) Schiff base complexes of general formula $[PdCl(PPh_3)(L)]$ (**1-3**) were synthesized and characterized by elemental analysis, IR, UV-vis and ^1H NMR & ^{13}C NMR. The synthesized complexes contain the uncoordinated sterically hindered Schiff base ligand. The catalytic performance of these palladium complexes towards the carbon-carbon Suzuki-Miyaura and Sonogashira coupling reactions of aryl halides was studied and exhibited the moderate to good conversions.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. V.L. Budarin, P.S. Shuttleworth, J.H. Clark and R. Luque, *Curr. Org. Synth.*, **7**, 614 (2010); https://doi.org/10.2174/157017910794328529
2. A. Dumrath, C. Lübbe and M. Beller, Ed.: A. Molnár, Palladium-Catalyzed Coupling Reactions, Wiley-VCH: Weinheim, Chap. 12, pp. 445-489 (2013).
3. M. Picquet, *Platinum Met. Rev.*, **57**, 272 (2013); https://doi.org/10.1595/147106713X672320

4. C.C.C. Johansson-Seechurn, M.O. Kitching, T.J. Colacot and V. Snieckus, *Angew. Chem. Int. Ed.*, **51**, 5062 (2012); https://doi.org/10.1002/anie.201107017
5. N. Miyaura and A. Suzuki, *Chem. Rev.*, **95**, 2457 (1995); https://doi.org/10.1021/cr00039a007
6. G. Chacon, C. Pradel, N. Saffon-Merceron, D. Madec, M. Gomez and M. Gomez, *French-Ukrain. J. Chem.*, **4**, 37 (2016); https://doi.org/10.17721/fujcV4I1P37-50
7. N. Miyaura and A. Suzuki, *J. Chem. Soc. Chem. Commun.*, **19**, 866 (1979); https://doi.org/10.1039/C39790000866
8. K. Sonogashira, *J. Organomet. Chem.*, **653**, 46 (2002); https://doi.org/10.1016/S0022-328X(02)01158-0
9. R. Chinchilla and C. Najera, *Chem. Soc. Rev.*, **40**, 5084 (2011); https://doi.org/10.1039/c1cs15071e
10. J. Hassan, M. Sévignon, C. Gozzi, E. Schulz and M. Lemaire, *Chem. Rev.*, **102**, 1359 (2002); https://doi.org/10.1021/cr000664r
11. T.E. Barder, S.D. Walker, J.R. Martinelli and S.L. Buchwald, *J. Am. Chem. Soc.*, **127**, 4685 (2005); https://doi.org/10.1021/ja042491j
12. A.F. Littke and G.C. Fu, *Angew. Chem. Int. Ed.*, **41**, 4176 (2002); https://doi.org/10.1002/1521-3773(20021115)41:22<4176::AID-ANIE4176>3.0.CO;2-U
13. S. Kotha, K. Lahiri and D. Kashinath, *Tetrahedron*, **58**, 9633 (2002); https://doi.org/10.1016/S0040-4020(02)01188-2
14. F.S. Han, *Chem. Soc. Rev.*, **42**, 5270 (2013); https://doi.org/10.1039/c3cs35521g
15. A. Suzuki and Y. Yamamoto, *Chem. Lett.*, **40**, 894 (2011); https://doi.org/10.1246/cl.2011.894
16. A. Fihri, M. Bouhrara, B. Nekoueishahraki, J.M. Basset and V. Polshettiwar, *Chem. Soc. Rev.*, **40**, 5181 (2011); https://doi.org/10.1039/c1cs15079k
17. A. Balanta, C. Godard and C. Claver, *Chem. Soc. Rev.*, **40**, 4973 (2011); https://doi.org/10.1039/c1cs15195a
18. R. Zhong, A. Pöthig, Y. Feng, K. Riener, W.A. Herrmann and F.E. Kühn, *Green Chem.*, **16**, 4955 (2014); https://doi.org/10.1039/C4GC00986J
19. S. Yasar, Ç. Sahin, M. Arslan and I. Özdemir, *J. Organomet. Chem.*, **776**, 107 (2015); https://doi.org/10.1016/j.jorganchem.2014.10.047
20. Y. Liu, N. Gu, P. Liu, X. Ma, Y. Liu, J. Xie and B. Dai, *Tetrahedron*, **71**, 7985 (2015); https://doi.org/10.1016/j.tet.2015.08.070
21. N.Y. Baran T. Baran and A. Mentes, *Appl. Catal. A*, **531**, 36 (2017); https://doi.org/10.1016/j.apcata.2016.12.005
22. S. Layek, B. Anuradha, B. Agrahari and D.D. Pathak, *Appl. Organomet. Chem.*, **846**, 105 (2017); https://doi.org/10.1016/j.jorganchem.2017.05.049
23. D. Pandiarajan, R. Ramesh, Y. Liu and R. Suresh, *Inorg. Chem. Commun.*, **33**, 33 (2013); https://doi.org/10.1016/j.inoche.2013.03.032
24. M. Sedighipoor, A.H. Kianfar, G. Mohammadnezhad, H. Görls and W. Plass, *Inorg. Chim. Acta*, **476**, 20 (2018); https://doi.org/10.1016/j.ica.2018.02.007
25. M. Khanmoradi, M. Nikoorazm and A. Ghorbani-Choghamarani, *Catal. Lett.*, **147**, 1114 (2017); https://doi.org/10.1007/s10562-016-1957-5
26. B. Banik, A. Tairai, P.K. Bhattacharyya and P. Das, *Appl. Organomet. Chem.*, **30**, 519 (2016); https://doi.org/10.1002/aoc.3464
27. A.O. Eseola, O. Akogun, H. Görls, O. Atolani, G.A. Kolawole and W. Plass, *J. Mol. Catal. Chem.*, **387**, 112 (2014); https://doi.org/10.1016/j.molcata.2014.02.032
28. M. Kranenburg, P.C.J. Kamer and P.W.N.M. van Leeuwen, *Eur. J. Inorg. Chem.*, **1998**, 155 (1998); https://doi.org/10.1002/(SICI)1099-0682(199802)1998:2<155::AID-EJIC155>3.0.CO;2-T
29. R. Martin and S.L. Buchwald, *Acc. Chem. Res.*, **41**, 1461 (2008); https://doi.org/10.1021/ar800036s
30. P. Bhattacharyya and J. Woollins, *Polyhedron*, **14**, 3367 (1995); https://doi.org/10.1016/0277-5387(95)00103-Y
31. G.C. Fortman and S.P. Nolan, *Chem. Soc. Rev.*, **40**, 5151 (2011); https://doi.org/10.1039/c1cs15088j
32. P. Das, C. Sarmah, A. Tairai and U. Bora, *Appl. Organomet. Chem.*, **25**, 283 (2011); https://doi.org/10.1002/aoc.1755
33. L. Chahen, B. Therrien and G. Suss-Fink, *Eur. J. Inorg. Chem.*, **2007**, 5045 (2007); https://doi.org/10.1002/ejic.200700518
34. L. Botella and C. Najera, *Angew. Chem. Int. Ed.*, **41**, 179 (2002); https://doi.org/10.1002/1521-3773(20020104)41:1<179::AID-ANIE179>3.0.CO;2-O
35. L. Botella and C. Najera, *J. Organomet. Chem.*, **663**, 46 (2002); https://doi.org/10.1016/S0022-328X(02)01727-8
36. I.P. Beletskaya and A.V. Cheprakov, *J. Organomet. Chem.*, **689**, 4055 (2004); https://doi.org/10.1016/j.jorganchem.2004.07.054
37. D.A. Alonso and C. Najera, *Chem. Soc. Rev.*, **39**, 2891 (2010); https://doi.org/10.1039/b821314n
38. A.O. Eseola, H. Görls, J.A.O. Woods and W. Plass, *J. Mol. Catal. Chem.*, **406**, 224 (2015); https://doi.org/10.1016/j.molcata.2015.06.001
39. A.O. Eseola, D. Geibig, H. Görls, W.-H. Sun, X. Hao, J.A.O. Woods and W. Plass, *J. Organomet. Chem.*, **754**, 39 (2014); https://doi.org/10.1016/j.jorganchem.2013.12.041
40. N. Shahnaz, B. Banik and P. Das, *Tetrahedron Lett.*, **54**, 2886 (2013); https://doi.org/10.1016/j.tetlet.2013.03.115
41. B. Banik, A. Tairai, N. Shahnaz and P. Das, *Tetrahedron Lett.*, **53**, 5627 (2012); https://doi.org/10.1016/j.tetlet.2012.08.026
42. I.D. Kostas, B.R. Steele, A. Terzis, S.V. Amosova, A.V. Martynov and N.A. Makhaeva, *Eur. J. Inorg. Chem.*, 2642 (2006); https://doi.org/10.1002/ejic.200600180
43. M. Wang, H. Zhu, K. Jin, D. Dai and L. Sun, *J. Catal.*, **220**, 392 (2003); https://doi.org/10.1016/S0021-9517(03)00306-3
44. F. Marchetti, C. Pettinari, R. Pettinari, A. Cingolani, D. Leonesi and A. Lorenzotti, *Polyhedron*, **18**, 3041 (1999); https://doi.org/10.1016/S0277-5387(99)00230-2
45. M. Schmidt, H. Görls and W. Plass, *RSC Adv.*, **6**, 75844 (2016); https://doi.org/10.1039/C6RA16870A
46. G. Mohammadnezhad, R. Debel and W. Plass, *J. Mol. Catal. Chem.*, **410**, 160 (2015); https://doi.org/10.1016/j.molcata.2015.09.011
47. A. Roth, A. Buchholz, M. Rudolph, E. Schütze, E. Kothe and W. Plass, *Chem. Eur. J.*, **14**, 1571 (2008); https://doi.org/10.1002/chem.200701124
48. A. Roth, E.T. Spielberg and W. Plass, *Inorg. Chem.*, **46**, 4362 (2007); https://doi.org/10.1021/ic070088i
49. G. Bandoli, M. Nicolini, U. Mazzi and F.J. Refosco, *Chem. Soc. Dalton Transact.*, **11**, 2505 (1984); https://doi.org/10.1039/DT9840002505
50. Y.G. Li, D.H. Shi, H.L. Zhu, H. Yan and S.W. Ng, *Inorg. Chim. Acta*, **360**, 2881 (2007); https://doi.org/10.1016/j.ica.2007.02.019
51. S. Güveli and B. Ülküseven, *Polyhedron*, **30**, 1385 (2011); https://doi.org/10.1016/j.poly.2011.02.041
52. S. Priyarega, P. Kalaivani, R. Prabhakaran, T. Hashimoto, A. Endo and K. Natarajan, *J. Mol. Struct.*, **1002**, 58 (2011); https://doi.org/10.1016/j.molstruc.2011.06.046
53. J.J. Fernández, A. Fernández, D. Vázquez-García, M. López-Torres, A. Suárez, N. Gómez-Blanco and J.M. Vila, *Eur. J. Inorg. Chem.*, **2007**, 5408 (2007); https://doi.org/10.1002/ejic.200700478
54. E.M. McGarrigle and D.G. Gilheany, *Chem. Rev.*, **105**, 1563 (2005); https://doi.org/10.1021/cr0306945
55. S. Bilge, Z. Kiliç, Z. Hayvali, T. Hökelek and S. Safran, *J. Chem. Sci.*, **121**, 989 (2009); https://doi.org/10.1007/s12039-009-0128-2
56. S.K. Che Soh and M. Shamsuddin, *J. Chem.*, **2013**, 632315 (2013); https://doi.org/10.1155/2013/632315
57. D. Wang, M. Wang, X. Wang, Y. Chen, A. Gao and L. Sun, *J. Catal.*, **237**, 248 (2006); https://doi.org/10.1016/j.jcat.2005.11.013
58. R. Ferreira, H. Garcia, B. de Castro and C. Freire, *Eur. J. Inorg. Chem.*, **2005**, 4272 (2005); https://doi.org/10.1002/ejic.200500314
59. R. Borhade and B. Waghmode, *Tetrahedron Lett.*, **49**, 3423 (2008); https://doi.org/10.1016/j.tetlet.2008.03.109