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FULL PAPER

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An acetatopalladium(II) complex with 1-benzyl-*N*-(3,5-di-*tert*-butylsalicylidene)piperidin-4-amine: Synthesis, structure and catalytic applications in Suzuki–Miyaura coupling of arylboronic acids with hydroxyaryl halides

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The Schiff base 1-benzyl-*N*-(3,5-di-*tert*-butylsalicylidene)piperidin-4-amine (HL) and its acetatopalladium(II) complex having the formula [Pd(L)(OAc)] were synthesized. Both HL and [Pd(L)(OAc)] were characterized using elemental analysis and various spectroscopic (infrared, UV–visible, ^{1}H NMR and ^{13}C NMR) and mass spectrometric measurements. The molecular structure of the complex was determined using X-ray crystallographic analysis. In the complex, the pincer-like NNO-donor L^{-} and the monodenate OAc^{-} provide a distorted square-planar N_2O_2 coordination environment around the metal centre. The physicochemical properties and the spectroscopic features of [Pd(L)(OAc)] are consistent with its molecular structure. The complex was found to be an effective catalyst for the Suzuki–Miyaura cross-coupling reactions of hydroxyaryl halides with arylboronic acids in predominantly aqueous media. The reactions afforded hydroxybiaryl products in good to excellent yields with a wide substrate scope.

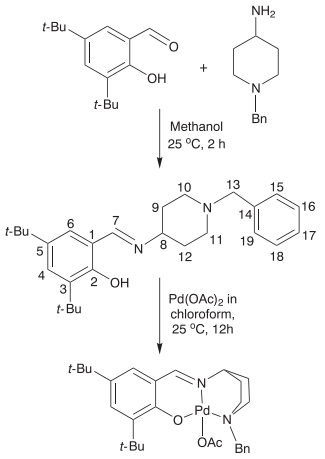
KEYWORDS
catalysis, crystal structure, NNO-donor, palladium(II), Schiff base, Suzuki–Miyaura reaction

1 | INTRODUCTION

The hydroxybiaryl molecular scaffold is of significant interest due to its occurrence in a diverse range of natural products,[1] pharmaceuticals,[2,3] pesticides[4] and functional materials such as sensors and liquid crystals.[5,6] 2-Hydroxybiphenyl and its derivatives are also of particular importance as they are the main substrates for the syntheses of the dibenzofuran frameworks present in a wide variety of biologically active natural products.[7] Biaryls and functionalized biaryls can be conveniently synthesized by employing Suzuki–Miyaura cross-coupling reactions of appropriate aryl halides and arylboronic acids.[8] This very efficient and popular C─C cross-coupling reaction is somewhat less explored in the synthesis of hydroxybiaryls in comparison to other functionalized biaryls using palladium-based catalyst systems. Amongst the few palladium-catalysed methods published so far,[9–11] use of homogeneous catalysts is less common[9,10] than heterogeneous catalysts.[11] A possible disadvantage of one-pot hydroxybiaryl synthesis directly from hydroxyaryl halides and arylboronic acids is low yields, which has been suggested to be due to the formation of the boronates.[9a] A very effective approach to avoid this problem has been the use of a reactive arylboronic acid pinacol ester (Ar-BPin) and an inert haloarylboronic acid *N*-methyliminodiacetic acid ester (Ar′-BMida) to generate the reactive coupled product Ar–Ar′-BPin via chemoselective controlled boron speciation in the presence of a diphosphinedichloropalladium(II) complex as the homogeneous catalyst in tetrahydrofuran at 90 °C and subsequent oxidation of the coupled product to Ar–Ar′-OH.[9a] Instead of free phenol, use of iodophenoxy anchored to

polystyrene-Wang resin for coupling with arylboronic acid in ionic liquid–dimethylformamide mixture in the presence of $Pd(PPh_3)_4$ as catalyst at 110 °C followed by hydrolysis has been demonstrated to be another pathway for the synthesis of hydroxybiaryls.[9b] However, syntheses of hydroxybiaryls from unprotected 2-hydroxyaryl halides and arylboronic acids in homogeneous reactions using wet toluene or dioxane as solvent and phosphine/$Pd(OAc)_2$ as the catalyst system in 48–98% yields have been realized under microwave heating conditions (100–120 °C).[10a] There are couple of reports on the coupling of arylboronic acids in pure aqueous media with unsubstituted bromophenol at elevated temperature (100 °C) or with bromophenol bearing electron-withdrawing substituent at room temperature using water-soluble palladium(II) complexes as catalysts.[10b,c] On the other hand, quite a few procedures for the synthesis of hydroxybiaryls via coupling reactions of unprotected hydroxyaryl halides and arylboronic acids using heterogeneous palladium catalysts are reported.[11] These heterogeneous catalysts range from palladium/carbon[11a–c] to palladium nanoparticles supported on silica or graphite oxide or carbon nanotube or organic polymer[11d–g] to palladium(II) complexes loaded in zeolite[11h] or anchored to an organic polymer.[11i] Thus the sparsity of reports on the synthesis of hydroxybiaryls directly from hydroxyaryl halides and arylboronic acids employing Suzuki–Miyaura cross-coupling reactions using simple and unsupported palladium-based catalyst systems provides a wide scope for the development of new air- and moisture-stable, inexpensive and easy-to-prepare efficient palladium catalysts that will be effective in environmentally benign aqueous media or predominantly aqueous media.[12]

Schiff bases as ligands are very attractive, because their syntheses are simple and convenient and their structural and electronic features can be tuned easily by appropriate choice of primary amines and carbonyls. Consequently, palladium (II) complexes with Schiff bases have recently attracted significant attention for applications as catalysts in Suzuki–Miyaura reactions.[8i] Among such palladium(II) Schiff base complexes used so far, very few feature tridentate Schiff bases.[13] We have prepared the tridentate Schiff base 1-benzyl-*N*-(3,5-di-*tert*-butylsalicylidene)piperidin-4-amine (HL), which can behave as a pincer-like ligand and because of the bulky *tert*-butyl substituents and the piperidine ring it can effectively wrap the palladium centre leaving one coordination site available for a labile mondentate ligand (Scheme 1). Generally such pincer complexes are very stable and can act as effective catalyst systems.[14] Herein, we report the synthesis, characterization and X-ray crystal structure of a palladium(II) complex with HL having the formula [Pd(L)(OAc)], and its application as a catalyst in the Suzuki–Miyaura cross-coupling reactions of hydroxyaryl halides with arylboronic acids in predominantly aqueous media for the synthesis of hydroxybiaryls.



SCHEME 1 Syntheses of 1-benzyl-*N*-(3,5-di-*tert*-butylsalicylidene) piperidin-4-amine (HL) and [Pd(L)(OAc)]

2 | EXPERIMENTAL

2.1 | Materials

1-Benzylpiperidin-4-amine, 3,5-di-*tert*-butylsalicylaldehyde and the substrates (hydroxyaryl halides and arylboronic acids) for the cross-coupling reactions were procured from Sigma Aldrich and used as received. $Pd(OAc)_2$ was purchased from Arora Matthey Ltd, India, and used as supplied. All other chemicals used in this work were of reagent grade available commercially and used without additional purification. All solvents used were purified using standard procedures.[15]

2.2 | Physical measurements

A Thermo Finnigan Flash EA1112 series elemental analyser was used for elemental (CHN) analyses. Mass spectra were recorded with a Bruker Maxis HRMS (ESI-TOF analyser) spectrometer. Magnetic susceptibility of the complex was measured with a Sherwood scientific balance. A Digisun DI-909 conductivity meter was used to measure the electrical conductivity of the complex solution. Infrared (IR) spectra were recorded with a Thermo Scientific Nicolet 380 FT-IR spectrophotometer. A Shimadzu UV-3600 UV–VIS–NIR spectrophotometer was used to collect the electronic spectra. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded with a Bruker spectrometer.

2.3 | Synthesis of HL

In a 100 ml round-bottom flask, 1-benzylpiperidin-4-amine (571 mg, 3 mmol), 3,5-di-*tert*-butylsalicylaldehyde (703 mg, 3 mmol) and methanol (50 ml) were taken and the mixture was stirred at room temperature (25 °C) under aerobic conditions for 2 h. The Schiff base HL separated

as a yellow solid was filtered off and dried in vacuum. This method provided a yield of 1.12 g (92%) of HL having sufficient purity for use in the subsequent preparation of its palladium(II) complex. HRMS (*m/z*) calcd for $C_{27}H_{39}N_2O$ $(M + H)^+$: 407.3062. Found: 407.3061. Anal. Calcd for $C_{27}H_{38}N_2O$ (406.60) (%): C, 79.76; H, 9.42; N, 6.89. Found (%): C, 79.58; H, 9.37; N, 6.95. Selected IR bands (KBr; cm^{-1}): 3422 (OH), 1628 (C═N). ^1H NMR ($CDCl_3$; 400 MHz, δ, ppm): 13.82 (s, 1H, OH), 8.39 (s, 1H, H^7), 7.37–7.19 (m, 6H, H^6, $H^{15–19}$), 7.07 (s, 1H, H^4), 3.54 (s, 2H, $H^{13a,b}$), 3.25 (br m, 1H, H^8), 2.88 (br m, 2H, H^{10a}, H^{11a}), 2.19 (br m, 2H, H^{10b}, H^{11b}), 1.84 (br m, 4H, $H^{9a,b}$, $H^{12a,b}$), 1.45 (s, 9H, protons of ^{t}Bu at C^3), 1.30 (s, 9H, protons of ^{t}Bu at C^5). ^{13}C NMR ($CDCl_3$; 100 MHz, δ, ppm): 163.9 (C^7), 158.1 (C^2), 139.9 (C^{14}), 138.6 (C^5), 136.6 (C^3), 129.1 (C^{15}, C^{19}), 128.2 (C^{16}, C^{18}), 126.9 (C^4), 126.7 (C^{17}), 125.7 (C^1), 117.9 (C^6), 65.5 (C^{13}), 63.1 (C^8), 51.8 (C^{10}, C^{11}), 35.0 (CMe_3 at C^3), 34.1 (CMe_3 at C^5), 33.5 (C^9, C^{12}), 31.5 (methyl-*C*s of ^{t}Bu at C^3), 29.4 (methyl-*C*s of ^{t}Bu at C^5). UV–visible (CH_2Cl_2; λ_{max}, nm (ε, 10^3 M^{-1} cm^{-1})): 328 (5.8), 263 (16.9), 235 (19.8).

2.4 | Synthesis of [Pd(L)(OAc)]

$Pd(OAc)_2$ (225 mg, 1 mmol) was added to a solution of HL (407 mg, 1 mmol) in 30 ml of chloroform and the mixture was stirred at room temperature (25 °C) under aerobic conditions for 12 h. The reaction mixture was then washed with water to remove the acetic acid generated and the solvent was evaporated under reduced pressure to afford the complex [Pd(L)(OAc)] as a yellow solid. It was then recrystallized from chloroform–methanol mixture. The yield was 510 mg (89%). HRMS (*m/z*) calcd for $C_{27}H_{37}N_2OPd$ $(M - OAc)^+$: 511.1941. Found: 511.1979. Anal. Calcd for $C_{29}H_{40}N_2O_3Pd$ (571.06) (%): C, 60.99; H, 7.06; N, 4.91. Found (%): C, 60.92; H, 7.12; N, 4.85. Selected IR bands (KBr; cm^{-1}): 1616 ($C═N/COO_{asymm}$), 1318 (COO_{symm}). ^1H NMR ($CDCl_3$; 400 MHz, δ, ppm): 8.09 (s, 1H, H^7), 7.57 (s, 1H, H^6), 7.36–7.22 (m, 5H, $H^{15–19}$), 6.94 (s, 1H, H^4), 4.23 (s, 2H, $H^{13a,13b}$), 3.60 (br m, 2H, H^{10a}, H^{11a}), 3.50 (s, 1H, H^8), 2.53 (br m, 2H, H^{10b}, H^{11b}), 2.21 (br m, 2H, H^{9a}, H^{12a}), 2.05 (s, 3H, methyl protons of OAc), 1.85 (br m, 2H, H^{9b}, H^{12b}), 1.38 (s, 9H, protons of ^{t}Bu at C^3), 1.24 (s, 9H, protons of ^{t}Bu at C^5). ^{13}C NMR ($CDCl_3$; 100 MHz, δ, ppm): 178.4 (carboxylate-*C* of OAc), 162.4 (C^7), 157.4 (C^2), 139.8 (C^{14}), 136.2 (C^5), 132.8 (C^{15}, C^{19}), 131.0 (C^3), 130.1 (C^4), 128.8 (C^{17}), 128.4 (C^{16}, C^{18}), 127.0 (C^1), 117.5 (C^6), 64.8 (C^{13}), 57.4 (C^8), 48.2 (C^{10}, C^{11}), 35.5 (CMe_3 at C^3), 33.8 (CMe_3 at C^5), 31.3 (methyl-*C*s of ^{t}Bu at C^3), 29.3 (methyl-*C*s of ^{t}Bu at C^5), 28.0 (C^9, C^{12}), 23.4 methyl-*C* of OAc). UV–visible (CH_2Cl_2; λ_{max}, nm (ε, 10^3 M^{-1} cm^{-1})): 401 (5.1), 385^{sh} (4.6), 285 (13.6), 251 (24.5).

2.5 | General procedure for coupling reactions of hydroxyaryl halides with arylboronic acids

A mixture of hydroxyaryl halide (0.5 mmol), arylboronic acid (0.6 mmol), $LiOH·H_2O$ (1.0 mmol), water (2 ml) and [Pd(L)(OAc)] (0.1 or 0.5 mol% in 0.1 ml of dimethylformamide) was stirred under aerobic conditions at room temperature (25 °C) for the required reaction time. The reaction mixture was then extracted with ethyl acetate and the extract was dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using ethyl acetate–hexane as the eluent to afford the corresponding coupled products. All the products were characterized based on their ^1H NMR and ^{13}C NMR spectral data and by comparing the spectra with literature reports.

2.6 | X-ray crystallography

Single crystals of [Pd(L)(OAc)] were grown by slow evaporation of its solution in chloroform–methanol mixture. Determination of the unit cell parameters and the intensity data collection at room temperature (25 °C) were performed using graphite-monochromated Cu K_α radiation (λ = 1.54184 Å) with an Oxford Diffraction Xcalibur Gemini single-crystal X-ray diffractometer. CrysAlisPro software[16] was used for data collection, reduction and absorption correction. Some residual absorption effect was treated with an additional correction using the program XABS2.[17] Structure solution by direct methods and refinement by full-matrix least squares procedures were carried out with SHELX-97 programs[18] embedded in the WinGX software package.[19] The Mercury[20] package was used for molecular graphics. Selected crystal data and the refinement summary are listed in Table 1.

3 | RESULTS AND DISCUSSION

3.1 | Synthesis and characterization

The Schiff base HL was prepared in 92% yield by condensation reaction of equimolar amounts of 1-benzylpiperidin-4-amine and 3,5-di-*tert*-butylsalicylaldehyde in methanol (Scheme 1). The identity and purity of HL were confirmed by elemental analysis, mass spectrometric and spectroscopic (IR, UV–visible, ^1H NMR and ^{13}C NMR) measurements. The complex was synthesized in 89% yield by reacting $Pd(OAc)_2$ with HL in 1:1 mole ratio in chloroform (Scheme 1). The elemental analysis data are consistent with its molecular formula as [Pd(L)(OAc)]. In the positive-ion ESI mass spectrum of the complex, the main peak appeared at *m/z* = 511.1979 with the expected isotopic pattern for the acetate-lacking species $[Pd(L)]^+$. Room

TABLE 1 Selected crystal and refinement data for [Pd(L)(OAc)]

Chemical formula	$C_{29}H_{40}N_2O_3Pd$
Formula weight	571.03
λ (Å)	1.54184
Crystal system	Orthorhombic
Space group	*P*bca
a (Å)	16.3293(5)
b (Å)	15.1530(5)
c (Å)	23.0341(9)
V (Å^3)	5699.5(3)
Z	8
ρ (g cm^{-3})	1.331
μ (mm^{-1})	5.487
Reflections collected	14 353
Reflections unique	5340
Reflections [$I \geq 2\sigma(I)$]	3963
Parameters	322
$R1$, $wR2$ [$I \geq 2\sigma(I)$]	0.0853, 0.2002
$R1$, $wR2$ [all data]	0.1101, 0.2172
GOF on F^2	1.037
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.904, −2.021

temperature magnetic susceptibility measurement showed the diamagnetic character of the complex. Thus in [Pd(L)(OAc)], the palladium centre is bivalent and it is in a square-planar coordination environment. The complex is yellow in colour. It is highly soluble in chloroform, dichloromethane, dimethylformamide and dimethylsulfoxide, moderately soluble in toluene, methanol, ethanol and acetonitrile and insoluble in *n*-hexane. In solution, the complex is electrically non-conducting. Hence, as reflected by the molecular formula, the complex is a neutral species.

3.2 | Description of molecular structure

The complex crystallized without any solvent molecule. The structure was solved in the orthorhombic *P*bca space group. The asymmetric unit contains one complex molecule. The molecular structure of [Pd(L)(OAc)] is illustrated in Figure 1 and the bond parameters involving the metal atom are listed in Table 2. The palladium centre in the complex is in a distorted square-planar N_2O_2 coordination environment. The tridentate pincer-like ligand L^- binds the metal centre through the tertiary amine-N of the piperidine ring, the azomethine-N and the phenolate-O atoms, and the acetate acts as a monodentate O-donor. The metal centre and the four coordinating atoms are in the same plane (r.m.s. deviation = 0.076 Å). The coordination of the ring N-atom induces the boat conformation of the piperidine ring. The O(1)–Pd–N(1) (92.1(2)°) and the N(1)–Pd–N(2) (90.1(3)°) bite angles are comparable and closer to the ideal value of 90° than the remaining two *cis* bond angles (83.6(2)° and 94.2(3)°). The *trans* bond angle (177.7(2)°) involving the two ends (O(1) and N(2)) of L^- is closer to the ideal value of 180° compared to the other *trans* bond angle (170.6(3)°) formed by the azomethine-N and the acetate-O atoms (N(1) and O(2)). Overall, the bond lengths associated with the palladium centre of [Pd(L)(OAc)] are comparable with the bond lengths reported for bivalent palladium complexes having similar coordinating atoms.[21]

3.3 | Spectroscopic characteristics

The IR spectra of both HL and [Pd(L)(OAc)] were recorded in KBr discs. The spectrum of free Schiff base showed the phenolic OH and the C=N stretching absorptions as a broad band at 3422 cm^{-1} and a sharp and strong band at 1628 cm^{-1}, respectively.[21b,d,22] In contrast, the complex did not display the OH stretching band indicating the deprotonation of the phenolic OH. The C=N stretching for the complex is

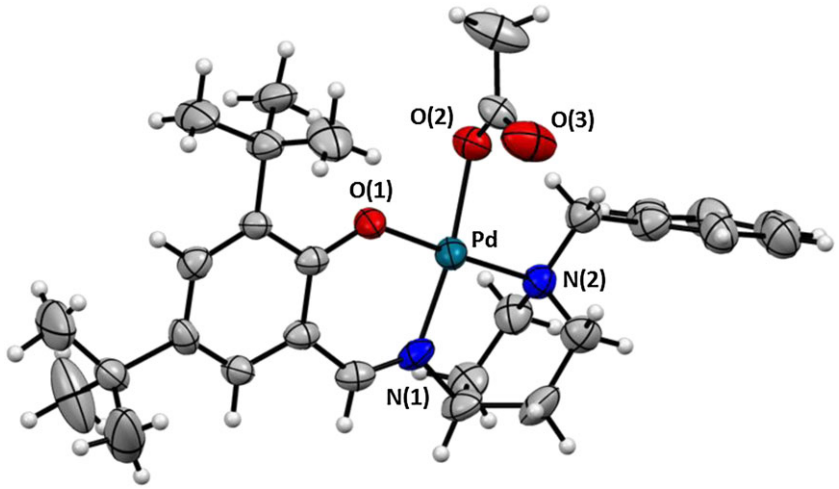


FIGURE 1 X-ray molecular structure of [Pd(L)(OAc)]. Thermal ellipsoids for all non-hydrogen atoms are shown at the 40% probability level. Only non-carbon atoms are labelled for clarity

TABLE 2 Metal-centred bond parameters (Å and °) for [Pd(L)(OAc)]

Pd–O(1)	1.976(5)
Pd–N(1)	1.977(7)
Pd–N(2)	2.104(7)
Pd–O(2)	2.078(6)
O(1)–Pd–N(1)	92.1(2)
O(1)–Pd–N(2)	177.7(2)
O(1)–Pd–O(2)	83.6(2)
N(1)–Pd–N(2)	90.1(3)
N(1)–Pd–O(2)	170.6(3)
N(2)–Pd–O(2)	94.2(3)

expected to appear at a lower frequency compared to that for the free Schiff base due to its coordination to the metal centre.[21a–d,22] A very strong and somewhat broad band was observed at 1616 cm^{-1} for the complex. This band is most likely due to both the metal-coordinated C=N stretching as well as the asymmetric carboxylate stretching of the monodentate OAc^-.[23] A moderately strong band appeared at 1318 cm^{-1} is attributed to the symmetric carboxylate stretching of the monodentate OAc^-.

The ^1H NMR and ^{13}C NMR spectra of HL and [Pd(L)(OAc)] were recorded in $CDCl_3$. All the chemical shift data with tentative assignments are listed in Section 2. The phenolic proton of HL resonated as a singlet at 13.82 ppm. On the other hand, the spectrum of the complex was devoid of any such resonance indicating deprotonation and coordination of the phenolate-O. The azomethine proton (H^7) of HL appeared as a singlet at 8.39 ppm. For the complex, the resonance for this proton was shifted slightly upfield to 8.09 ppm. This upfield shift is perhaps due to significant π-backdonation from metal to azomethine. The methyl protons of the *t*-butyl groups of the salicylaldimine ring of HL appeared as two singlets each of nine protons at 1.45 and 1.30 ppm, while the singlet resonances for the corresponding protons in [Pd(L)(OAc)] were observed at 1.38 and 1.24 ppm, respectively. The spectrum of the complex displayed an additional three-proton singlet at 2.05 ppm corresponding to the methyl protons of OAc^-. The singlet observed for HL at 7.07 ppm is assigned to the salicylaldimine ring proton (H^4) which is flanked by two *t*-butyl groups. The signal due to the other salicylaldimine ring proton (H^6) at the C-atom *ortho* to the metal-free azomethine group overlapped with the multiplet observed in the range 7.37–7.19 ppm due to the aromatic protons of the benzyl group. In the complex, the chemical shift (6.94 ppm) of the singlet for H^4 was comparable to that of HL, but the singlet due to H^6 appeared slightly downfield (7.57 ppm) due to metal coordination to the azomethine-N. Generally the chemical shifts of the benzylic methylene and the piperidine ring protons of [Pd(L)(OAc)] were shifted downfield compared to those of the free HL. This downfield shift is not unusual considering the coordination of the piperidine ring N-atom to the metal centre in the complex. In contrast, the chemical shift range (7.36–7.22 ppm) for the multiplet due to the aromatic benzyl protons of the complex was very similar to that of the free ligand.

The ^{13}C NMR spectra of both HL and [Pd(L)(OAc)] are consistent with the corresponding structures. As such, the spectrum of the complex is comparable with that of the free Schiff base except for the two additional resonances at its two ends. These two additional resonances indicate the presence of monodentate OAc^- in the complex. The carboxylate-C appeared as the most downfield signal (178.4 ppm) and the methyl-C resonated at the highest field (23.4 ppm).

Dichloromethane solutions of HL and [Pd(L)(OAc)] were used to record the electronic spectra. Both spectra are illustrated in Figure 2. The Schiff base displayed three strong absorptions at 328, 263 and 235 nm. Similar absorptions of Schiff bases have been attributed to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions involving the azomethine group and the aromatic ring.[22] The complex also showed three major absorption bands at 401, 285 and 251 nm and a shoulder at 385 nm. Generally the absorption band positions of the complex were red-shifted when compared to those of the free Schiff base. The lowest energy band and the accompanying shoulder are assigned to primarily ligand-to-metal charge transfer transitions and the following two higher energy bands are attributed to $\pi \rightarrow \pi^*$ transitions of the azomethine group and the aromatic ring of L^-.[21b,c,22]

3.4 | Catalytic properties

To evaluate the catalytic activity of [Pd(L)(OAc)] (in 0.1 ml of dimethylformamide) in water (2 ml) at room temperature (25 °C), the Suzuki–Miyaura cross-coupling of 4-iodophenol

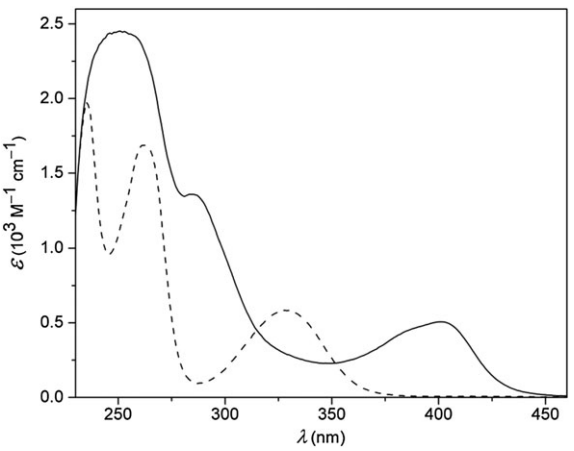
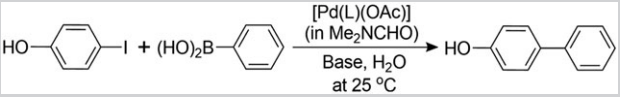


FIGURE 2 Electronic spectra of HL (dashed trace) and [Pd(L)(OAc)] (solid trace) in dichloromethane

and phenylboronic acid under aerobic conditions was chosen as the model reaction to screen the bases and determine the reaction time (Table 3). The reaction proceeded well with the inorganic bases Na_2CO_3, K_2CO_3, K_3PO_4, $NaHCO_3$ and $LiOH{\cdot}H_2O$ and afforded high yield of the desired coupling product (entries 1–5). No reaction was observed with the inorganic strong base NaOH and organic amine bases ($HNC(NMe_2)_2$ and NEt_3) (entries 6–8). Considering the yield and the reaction time, $LiOH{\cdot}H_2O$ was found to be the best base among all the bases used (entry 5). Under otherwise identical conditions, reduction of the catalyst loading by half led to considerably reduced yield in longer reaction time (entry 9). In the control reaction without [Pd(L)(OAc)] as catalyst, no product formation was observed. Further, the solvent effect was examined using $LiOH{\cdot}H_2O$ (1 mmol) as the base. No reaction was observed in pure non-aqueous solvents such as methanol, tetrahydrofuran, dioxane, toluene, dimethylformamide and dimethylsulfoxide. The reaction also did not occur in the 1:1 mixture of water and each of the solvents just mentioned except for methanol and toluene. In water–methanol and water–toluene mixtures the reactions provided good yields (86% in 30 h and 96% in 24 h, respectively), but in longer reaction times than in water (entry 5). Thus the conditions used for entry 5 were found to be optimal, and hence the substrate scope of the reaction was examined under these conditions. Such improved efficiencies in aqueous or predominantly aqueous media have been observed for many palladium-catalysed organic reactions. It is thought that in aqueous environment, the hydrophobicity of the reactant molecules and also of the transition states may lead to their more compact conformations, which in turn facilitates the catalytic steps with negative entropy changes such as insertion or oxidative addition and hence increases their reactivities.[24]

The cross-coupling reactions of both iodo- and bromophenols with various arylboronic acids using [Pd(L)(OAc)] as catalyst were performed (Table 4). *Ortho*-, *meta*- and *para*-iodophenols were treated with phenyl-, 1-naphthyl- and 2-naphthylboronic acids (entries 1–8). Both *para*- and *meta*-iodophenols gave the desired products in high yields (88–99%) at room temperature (25 °C) in the presence of 0.1 mol% of the catalyst in 15 h (entries 1–6). However, the reactions involving *ortho*-iodophenol under the same reaction conditions provided only 40–50% yields for phenyl- and 2-naphthylboronic acids, but no product for 1-naphthylboronic acid due to steric problem. High yields (>90%) were obtained when the reactions were performed for a longer time (24 h) and higher (0.5 mol%) catalyst loading (entries 7 and 8). On the other hand, no reaction was observed in the case of *ortho*-bromophenol, but for *para*- and *meta*-bromophenols, not only higher catalyst loading (0.5 mol%) and longer time (24 h), but also

TABLE 3 Screening of bases[a]



Entry	Base	Time (h)	Yield (%)[b]
1	Na_2CO_3	24	94
2	K_2CO_3	24	96
3	K_3PO_4	24	96
4	$NaHCO_3$	24	92
5	$LiOH{\cdot}H_2O$	15	99
6	NaOH	24	NR[c]
7	$HNC(NMe_2)_2$	24	NR[c]
8	Et_3N	20	NR[c]
9	$LiOH{\cdot}H_2O$	24	64[d]

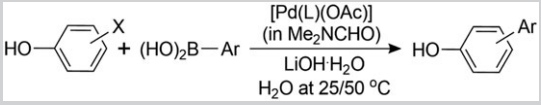
[a]4-Iodophenol: 0.5 mmol; phenylboronic acid: 0.6 mmol; base: 1 mmol; [Pd(L)(OAc)]: 0.1 mol% in 0.1 ml Me_2NCHO; H_2O: 2 ml.

[b]Isolated yield.

[c]No reaction.

[d][Pd(L)(OAc)]: 0.05 mol% in 0.1 ml Me_2NCHO; remaining conditions are same.

TABLE 4 Reactions of hydroxyaryl halides with arylboronic acids[a]



Entry	Hydroxyaryl halide	Ar	Yield (%)[b]
1	4-Iodophenol	Phenyl	99[c]
2	4-Iodophenol	1-Naphthyl	96[c]
3	4-Iodophenol	2-Naphthyl	90[c]
4	3-Iodophenol	Phenyl	97[c]
5	3-Iodophenol	1-Naphthyl	96[c]
6	3-Iodophenol	2-Naphthyl	88[c]
7	2-Iodophenol	Phenyl	94[d]
8	2-Iodophenol	2-Naphthyl	92[d]
9	4-Bromophenol	Phenyl	94[e]
10	4-Bromophenol	1-Naphthyl	90[e]
11	4-Bromophenol	2-Naphthyl	84[e]
12	3-Bromophenol	Phenyl	90[e]
13	3-Bromophenol	1-Naphthyl	88[e]
14	3-Bromophenol	2-Naphthyl	80[e]

[a]Hydroxyaryl halide: 0.5 mmol; arylboronic acid: 0.6 mmol; $LiOH{\cdot}H_2O$: 1 mmol; H_2O: 2 ml.

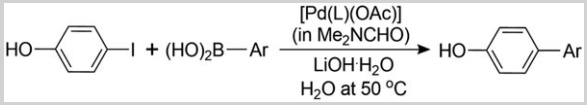
[b]Isolated yield.

[c][Pd(L)(OAc)]: 0.1 mol% in 0.1 ml Me_2NCHO; 25 °C; 15 h.

[d][Pd(L)(OAc)]: 0.5 mol% in 0.1 ml Me_2NCHO; 25 °C; 24 h.

[e][Pd(L)(OAc)]: 0.5 mol% in 0.1 ml Me_2NCHO; 50 °C; 24 h.

TABLE 5 Reactions of 4-iodophenol with various arylboronic acids[a]



Entry	Ar	Yield (%)[b]
1	4-Methylphenyl	86
2	4-Methoxyphenyl	80
3	4-Cyanophenyl	76
4	4-Formylphenyl	70
5	4-Acetylphenyl	74
6	4-Fluorophenyl	80
7	4-Chlorophenyl	84
8	3,5-Dichlorophenyl	76

[a]4-Iodophenol: 0.5 mmol; arylboronic acid: 0.6 mmol; $LiOH{\cdot}H_2O$: 1 mmol; [Pd(L)(OAc)]: 0.5 mol% in 0.1 ml Me_2NCHO; H_2O: 2 ml; 24 h.

[b]Isolated yield.

higher temperature (50 °C) were required for successful coupling and good yields (entries 9–14). The higher reactivities of the iodophenols compared to those of the bromophenols are attributable to the weaker C—X bond in the iodophenols than in the bromophenols.

Further, the scope of the [Pd(L)(OAc)] catalyst was extended to cross-coupling reactions of 4-iodophenol with a variety of substituted phenylboronic acids (Table 5). Optimization of the reaction conditions was done using 4-methylphenylboronic acid. Very low yield (*ca* 25%) was obtained for the coupling of it with 4-iodophenol at room temperature (25 °C) using 0.1 mol% of the catalyst after a reaction time of 24 h. The yield improved to 44% with the increase of reaction temperature to 50 °C. However, an increase of catalyst loading to 0.5 mol% with the increase of temperature to 50 °C was found to be the best conditions for efficient cross-coupling and a very good yield (86%) in 24 h (entry 1). These reaction conditions were applied for other substituted phenylboronic acids (Table 5). The substituents were varied from electron-donating groups such as 4-methyl and 4-methoxy to electron-withdrawing groups such as 4-cyano, 4-formyl, 4-acetyl, 4-flouro, 4-chloro and 3,5-dichloro (entries 1–8). The yields of the corresponding hydroxybiaryls were found to be in the range 70–84% and did not show any significant trend with the variation of the electronic nature of the substituent.

To understand the mechanism of the present catalytic system, a detailed investigation needs to be performed. However, it has been reported in the literature that a bivalent palladium complex used as catalyst in Suzuki–Miyaura reactions in aqueous media produces palladium nanoparticles which first undergo oxidative addition with aryl halide, then exchange of halide for an aryl group from arylboronic acid and finally reductive elimination of the biaryl product with the regeneration of the nanoparticles.[25]

4 | CONCLUSIONS

An acetatopalladium(II) complex with HL has been prepared and characterized. Elemental analysis data and diamagnetic and non-electrolytic behaviour of the complex are in agreement with it being a square-planar palladium(II) species of formula [Pd(L)(OAc)]. The molecular structure of the complex determined using single-crystal X-ray crystallography confirmed a distorted square-planar N_2O_2 coordination environment assembled by the pincer-like NNO-donor L^- and monodentate acetate. The spectroscopic characteristics of the complex concur very well with its X-ray molecular structure. The complex was successfully applied as catalyst for the Suzuki–Miyaura cross-coupling reactions of various hydroxyaryl halides with diversely substituted arylboronic acids in an essentially aqueous medium for the synthesis of a large range of hydroxybiaryls in good to excellent yields.

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SUPPORTING INFORMATION

CCDC 1518767 contains the supplementary crystallographic data for [Pd(L)(OAc)]. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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