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FULL PAPER

Carbonylative Suzuki coupling reactions catalyzed by ONO pincer–type Pd(II) complexes using chloroform as a carbon monoxide surrogate

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Benzoylhydrazone Schiff base–ligated three new ONO pincer–type palladium(II) complexes, [(PdL^1(PPh$_3$)] (**1**), [(PdL^2(PPh$_3$)] (**2**), and [(PdL^3(PPh$_3$)] (**3**), were synthesized by the reaction of the respective ligand, *N*-(2-hydroxybenzylidene)benzohydrazide (HL^1), *N*-(2-hydroxy-3-methoxybenzylidene)benzohydrazide (HL^2), or *N*-(5-bromo-2-hydroxybenzylidene) benzohydrazide (HL^3), with Pd(OAc)$_2$ and PPh$_3$ in methanol and isolated as air-stable reddish-orange crystalline solids in high yields (78%–83%). All three complexes were fully characterized by elemental analysis, Fourier-transform infrared spectroscopy, UV–Visible, ^{1}H nuclear magnetic resonance (NMR), ^{13}C{^{1}H} NMR, and ^{31}P{^{1}H} NMR spectroscopic studies. The molecular structure of all three complexes was established unambiguously by single-crystal X-ray diffraction studies which revealed a distorted square planar geometry of all three complexes. The ONO pincer–type ligands occupied three coordination sites at the palladium, while the fourth site is occupied by the monodentate triphenylphosphine ligand. The catalytic potential of all three complexes was explored in the carbonylative Suzuki coupling of aryl bromides and iodides with arylboronic acids to yield biaryl ketones, using CHCl$_3$ as the source of carbonyl. The reported protocol is convenient and safe as it obviates the use of carbon monoxide (CO) balloons or pressured CO reactors which are otherwise needed for the carbonylation reactions. The methodology has been successfully applied to the synthesis of two antineoplastic drugs, namely, phenstatin and naphthylphenstatin, in good yields (81% and 85%, respectively). Under the optimized reaction conditions, complex **2** exhibited the best catalytic activity in the carbonylative Suzuki couplings. The reported catalysts have wide reaction scope with good functional group tolerance. All catalysts could be retrieved from the reaction after completion and recycled up to three times with insignificant loss in the catalytic activity.

KEYWORDS

carbonylation, catalysis, crystal structure, ONO pincer type, palladium

1 | INTRODUCTION

Palladium catalysts and reagents are becoming extremely versatile and indispensable in modern organic synthesis.[1] Development of efficient methods for the C–C bond formation is one of the enduring research theme in organic chemistry.[2–4] Transition metal-catalyzed carbonylative Suzuki cross-coupling reaction is one of the powerful methods to generate C–C bonds which are an integral part of structural skeleton of a wide variety of natural products, pharmaceutical drugs, agrochemicals, fine chemicals, and organic functional materials[5–10] (Figure 1).

A review of the literature reveals that the direct carbonyl insertion reactions involve the use of carbon monoxide (CO) as a highly toxic gas[11–14] and suffer from one or more drawbacks, such as rigorous reaction conditions, high temperature, difficulty in handling of reactants, and limited utility of high pressurized toxic CO gas, precluding their large-scale industrial applications. To avoid these drawbacks, metal carbonyls,[15–18] formic acid,[19] acid chloride,[20,21] silacarboxylic acids,[22] dimethylformamide (DMF),[23,24] COgen and SilaCOgen,[13] etc. were used as alternative CO surrogates. Although most of these precursors have their own pros and cons, many of them have some limitations.[25–27] Recently, the use of chloroform as a CO surrogate has grabbed the attention of organic chemists for the synthesis of a variety of targeted organic molecules.[28] The *in situ*-generated CO from $CHCl_3$ and a base has been used in various organic reactions such as carboxylation,[29] carbonylative coupling,[30,31] aminocarbonylations,[32,33] Heck-type domino cyclization,[34] and carbonylative Sonogashira coupling.[35] Recently, one of us has elegantly demonstrated the application of this methodology (chloroform as CO surrogates) in aminocarbonylation of 7-azaindole and imidazopyridines, leading to the synthesis of biologically important aminocarbonyl-functionalized 7-azaindole and 2-amidoimidazo[1,2-*a*]pyridines.[36,37] However, all catalysts were generated *in situ* and high loading of the catalyst was required.

Rational design and judicious choice of suitable ligands play a key role in the development and fine-tuning of the catalytic properties and stereoselectivities of metal complexes. The steric and electronic properties imparted by the ligand greatly influence the nature of the reactive species and thus the outcome of a homogeneously catalyzed reaction.[38] In this regard, one of the thriving strategies is to use tridentate ligands, such as pincer ligands, which are well known to form well-defined stable complexes.[39,40] The tridentate coordination of pincer ligands provides strong binding to a metal center by invoking chelate effect and results in high stability of the pincer metal complexes. The robustness of a complex is of special interest for the design of catalysts that need to be stable enough to cope with the harsh reaction conditions. Therefore, it was thought worthwhile to synthesize pincer complexes and use them as catalysts. Complexes having different pincer skeleton such as CCC, NNN, CNC, NCN, PNP, SNS, ONO, and SCS have been used in catalysis and materials science.[41–48] In particular, the ONO pincer–type palladium complexes have proved to be very effective catalysts for Suzuki–Miyaura coupling,[49] C-2 arylation of quinoline scaffolds,[50] Domino reaction of benzoyl chloride with arylboronic acids,[51] and synthesis of tetrazoles,[52] etc. In recent years, hydrazone-based ONO pincer complexes have also been reported to exhibit interesting biological and catalytic properties.[53,54]

Prompted by these reports and our ongoing interest in palladium chemistry,[55,56] we herein report the synthesis and characterization of three new palladium(II) complexes containing hydrazone-based ONO pincer–type ligands and their application in carbonylative Suzuki coupling reactions for the synthesis of a series of biaryl ketones, using chloroform as a cheap and convenient source of CO. To the best of our knowledge, this is the first report on the application of isolated and structurally characterized palladium(II) pincer–type Schiff base complexes in the carbonylative Suzuki coupling reaction (Scheme 1).

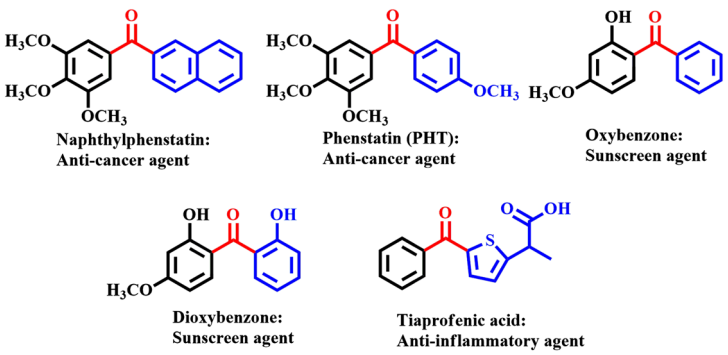
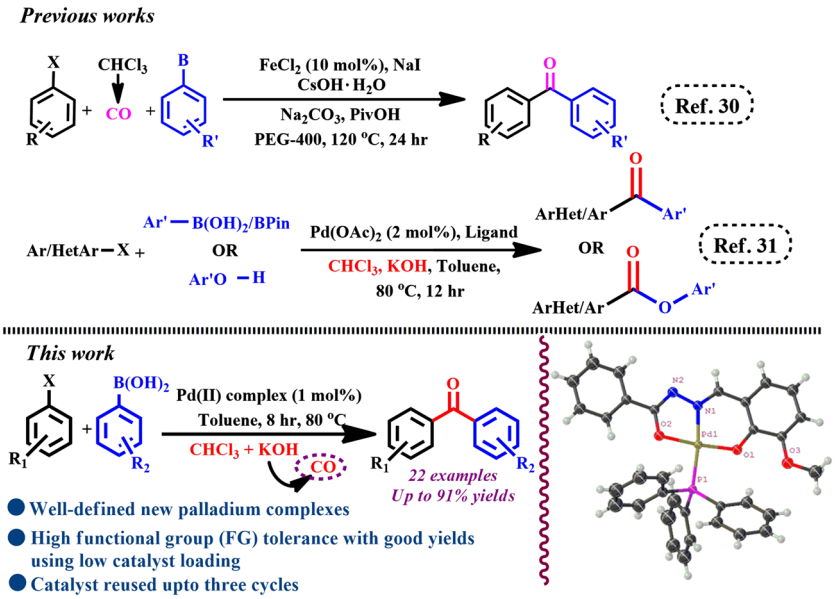


FIGURE 1 Some important molecules containing the biaryl ketone functionality



SCHEME 1 Previous and proposed strategies for the synthesis of biaryl ketones using chloroform as the carbonyl source. See also.[30,31] PEG-400, polyethylene glycol 400

2 | EXPERIMENTAL SECTION

2.1 | Materials and physical measurements

All chemicals and solvent were purchased from Sigma Aldrich, Merck (India) Limited, Alfa Aesar and TCIchemicals. Silica gel (100–200 mesh, Merck) was used for column chromatography. The thin-layer chromatography was performed on Merck-pre-coated silica gel 60-F254 plates andvisualized by UV-light. The FT-IR spectra were recorded on a Perkin Elmer Spectrometer (Model: Cary660) in the range of 400–4000 cm-1 using KBr pellets in which MCT used as a detector with scan number 20, and resolution 4 cm-1. Electronic absorption spectral analysis was recorded on a Shimadzu UV-1800 Spectrophotometer in the wave length range of 250–800 nm. The NMR spectra of complexes were recorded in CDCl3/DMSO-d6on a Bruker 75 AvIII HD-400 MHz spectrometer using TMS as the internal standard.

2.2 | General procedure for the synthesis of ligands HL^1–HL^3

All three ligands were synthesized by reported methods.[57–59] In brief, in a round-bottomed flask, ethanolic solutions (5 mL) of benzoylhydrazine (1.0 mmol) and the corresponding aldehyde (1.0 mmol) were stirred and refluxed at 80 °C in ethanol (5 mL) for 7 hr. Upon cooling to room temperature, a solid precipitate was formed from the reaction mixture. After this, the solid was filtered, washed with cold ethanol, and dried in vacuum over anhydrous $CaCl_2$. The details of experimental procedure for these Schiff base ligands and their spectroscopic data and spectra are given in the Supporting Information.

2.2.1 | Schiff base ligand *N*-(2-hydroxybenzylidene)benzohydrazide (HL^1)

Benzoylhydrazine (0.136 g, 1.0 mmol), salicylaldehyde (0.122 g, 1.0 mmol), and ethanol (10 mL) afforded the title compound as a white crystalline solid.

Yields: 0.246 g, 87%, Selected Fourier-transform infrared (FT-IR; KBr), cm^{-1}: 3440 (ν OH), 3264 (ν NH), 1671 (ν C=O), 1623 (ν C=N),1539 (ν C=C); ^{1}H nuclear magnetic resonance (NMR) (dimethyl sulfoxide [DMSO]-d_6, 25 °C, 400 MHz): δ 12.020 (s, 1H, phenolic O*H*), 11.212 (s, 1H, N*H*), 8.547 (s, 1H, –N=C*H*–), 7.842 (d, 3H, Ar *H*),7.521–7.435 (m, 4H, Ar *H*), 6.850–6.798 (m, 2H, Ar *H*).

2.2.2 | Schiff base ligand *N*-(2-hydroxy-3-methoxybenzylidene)benzohydrazide (HL^2)

Benzoylhydrazine (0.136 g, 1.0 mmol), *ortho*-vaniline (0.152 g, 1.0 mmol), and ethanol (10 mL) afforded the title compound as an off-white crystalline solid.

Yields: 0.225 g, 83%, Selected FT-IR (KBr), cm^{-1}: 3369 (ν OH), 3212 (ν NH), 1652 (ν C=O), 1602 (ν C=N),1570 (ν C=C); ^{1}H NMR (DMSO-d_6, 25 °C, 400 MHz): δ 11.976 (s, 1H, phenolic O*H*), 10.848 (s, 1H, N*H*), 8.547 (s, 1H, –N=C*H*–), 7.830 (d, 2H, Ar *H*), 7.523–7.418 (m, 3H, Ar *H*),

7.206–6.923 (m, 2H, Ar *H*), 6.762 (t, 1H, Ar *H*), 3.709 (s, 3H, –OC*H*$_3$).

2.2.3 | Schiff base ligand *N*-(2-hydroxy-5-bromobenzylidene)benzohydrazide (HL^3)

Benzoylhydrazine (0.136 g, 1.0 mmol), 5-bromosalicylaldehyde (0.201 g, 1.0 mmol), and ethanol (10 mL) afforded the title compound as an off-white crystalline solid.

Yields: 0.252 g, 81%, Selected FT-IR (KBr), cm^{-1}: 3429 (ν OH), 3223 (ν NH), 1649 (ν C=O), 1605 (ν C=N),1542 (ν C=C); ^{1}H NMR (DMSO-d_6, 25 °C, 400 MHz): δ 12.063 (s, 1H, phenolic O*H*), 11.552 (s, 1H, N*H*), 8.522 (s, 1H, –N=C*H*–), 7.952 (d, 2H, Ar *H*),7.595–7.483 (m, 4H, Ar *H*), 7.342 (d, 1H, Ar *H*), 6.872 (d, 1H, Ar *H*).

2.3 | General procedure for the synthesis of palladium(II) complexes 1–3

A solution of the Schiff base ligand HL^{1-3} (1.0 mmol) in 3 mL methanol was added dropwise to the 5 mL methanolic solution of $Pd(OAc)_2$ (0.224 g, 1.0 mmol) with constant stirring at room temperature. After stirring the solution for 5 min, PPh_3 (0.264 g, 1.0 mmol) was added as a co-ligand to the reaction mixture. After 8 hr of stirring at room temperature, the resultant colored precipitate was filtered, washed with cold methanol, and dried in vacuum over anhydrous $CaCl_2$. The precipitate was recrystallized from DMF. Suitable single crystals for X-ray crystallography were obtained on slow evaporation over a period of 2–3 weeks from a concentrated solution of the complex in DMF.

2.3.1 | $[Pd(L^1)(PPh_3)]$ (1)

Yield: 504.57 mg, 83%. Elemental analysis (%) calculated for $C_{32}H_{26}N_2O_2PPd$: C, 63.32; H, 4.15; N, 4.62. Found (%) C, 63.69; H, 4.23; N, 4.38. Selected IR bands (KBr, ν in cm^{-1}): 1603 (ν C=N), 1527 (ν C=C), 531 (ν Pd–O), 506 (ν Pd–N); UV–Vis [λ_{max} (nm), ε (L mol^{-1} cm^{-1})]: 314 (15500), 339 (10400), 402 (9080); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 8.52 (d, J = 15.6 Hz, 1H, –C*H*=N–), 7.67 (d, J = 24 Hz, 2H, Ar *H*), 7.62–7.61 (m, 7H, Ar *H*), 7.58–7.52 (m, 11H, Ar *H*), 7.50 (t, J = 7.6 Hz, 1H, Ar H), 7.48 (t, J = 7.2 Hz, 1H, Ar H), 6.62–6.56 (m, 2H, Ar *H*); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 162.20, 146.97, 134.63, 134.52, 133.72, 132.69, 131.77, 133.02, 129.16, 128.68, 128.01, 121.19, 119.70, 115.56; ^{31}P NMR ($CDCl_3$, 160 MHz, δ ppm): 21.11.

2.3.2 | $[Pd(L^2)(PPh_3)]$ (2)

Yield: 515.90 mg, 81%. Elemental analysis (%) calculated for $C_{33}H_{27}N_2O_3PPd$: C, 62.22; H, 4.27; N, 4.40. Found (%) C, 62.45; H, 4.13; N, 4.59. Selected IR bands (KBr, ν in cm^{-1}): 1594 (ν C=N), 1537 (ν C=C), 532 (ν Pd–O), 508 (ν Pd–N); UV–Vis [λ_{max} (nm), ε (L mol^{-1} cm^{-1})]: 320 (15700), 347 (11000), 404 (5700); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 8.35 (d, J = 16 Hz, 1H, –C*H*=N–), 7.88–7.83 (m, 8H, Ar *H*), 7.58–7.54 (m, 3H, Ar *H*), 7.50–7.42 (m, 5H, Ar *H*), 7.48–7.40 (m, 1H, Ar H), 7.38–7.29 (m, 3H, Ar H), 7.11 (d, 8 Hz, 1H, Ar *H*), 6.88 (d, 6.4 Hz, 1H, Ar *H*), 6.67 (t, 7.8 Hz, 1H, Ar *H*), 3.69 (s, 3H, –OC*H*$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 173.34, 153.74, 151.95, 134.77, 134.65, 131.62, 131.07, 130.16, 130.03, 129.44, 129.34, 128.97, 128.52, 127.98, 125.97, 119.68, 114.81, 56.49; ^{31}P NMR ($CDCl_3$, 160 MHz, δ ppm): 17.69.

2.3.3 | $[Pd(L^3)(PPh_3)]$ (3)

Yield: 534.93 mg, 78%. Elemental analysis (%) calculated for $C_{32}H_{24}BrN_2O_2PPd$: C, 56.04; H, 3.53; N, 4.08. Found (%) C, 56.25; H, 3.84; N, 4.19. Selected IR bands (KBr, ν in cm^{-1}): 1596 (ν C=N), 1516 (ν C=C), 531 (ν Pd–O), 499 (ν Pd–N); UV–Vis [λ_{max} (nm), ε (L mol^{-1} cm^{-1})]: 312 (16900), 339 (11600), 410 (9300); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 8.26 (d, J = 16 Hz, 1H, –C*H*=N–), 7.95 (d, J = 8 Hz, 2H, Ar *H*), 7.79 (t, J = 10 Hz, 6H, Ar *H*), 7.57–7.48 (m, 10H, Ar *H*), 7.42 (t, J = 8 Hz, 1H, Ar *H*), 7.35 (t, J = 6 Hz, 2H, Ar H), 7.27 (d, J = 12 Hz, 1H, Ar H), 6.69 (d, J = 12 Hz, 1H, Ar *H*); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 161.45, 145.77, 134.77, 134.58, 134.47, 131.15, 128.73, 128.67, 128.57, 128.05, 106.62, 106.33; ^{31}P NMR ($CDCl_3$, 160 MHz, δ ppm): 21.24.

2.4 | General procedure for carbonylative Suzuki–Miyaura coupling

A 10-mL sealed tube was charged with arylboronic acid (1.2 mmol), aryl halide (1.0 mmol), KOH (8.0 mmol, 0.49 g), $CHCl_3$ (4.0 mmol, 326 μL), toluene (2 mL), and palladium(II) complex (1 mol%). The tube was sealed tightly and stirred vigorously at 80 °C for 8–10 hr. After completion of the reaction, the reaction mixture was allowed to cool to room temperature and the combined organic layer was extracted with ethyl acetate, washed with water, dried over Na_2SO_4, and concentrated under reduced pressure over a rotary evaporator. The residue was purified by column

chromatography through silica gel using ethyl acetate–petroleum ether as eluent to afford the desired benzophenone product. The isolated organic products were characterized with ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra (see Figures S18–S53).

2.5 | Crystallographic studies

Diffraction quality crystals of complexes **1**, **2**, and **3** were obtained over a period of few days from a concentrated solution of the complex in DMF at room temperature and the structure of the complexes was elucidated by single-crystal X-ray diffraction. The X-ray diffraction intensity data were measured with a Bruker Kappa diffractometer equipped with a charge-coupled device detector, employing Mo-Kα radiation (λ = 0.71073 Å), with the SMART suite of programs. All data were processed and corrected for Lorentz and polarization effects with SAINT and for absorption effects with SADABS. Structural solution and refinement were carried out with the SHELXTL suite of programs. The structures were refined (weighted least squares refinement on F^2) to convergence.

3 | RESULTS AND DISCUSSION

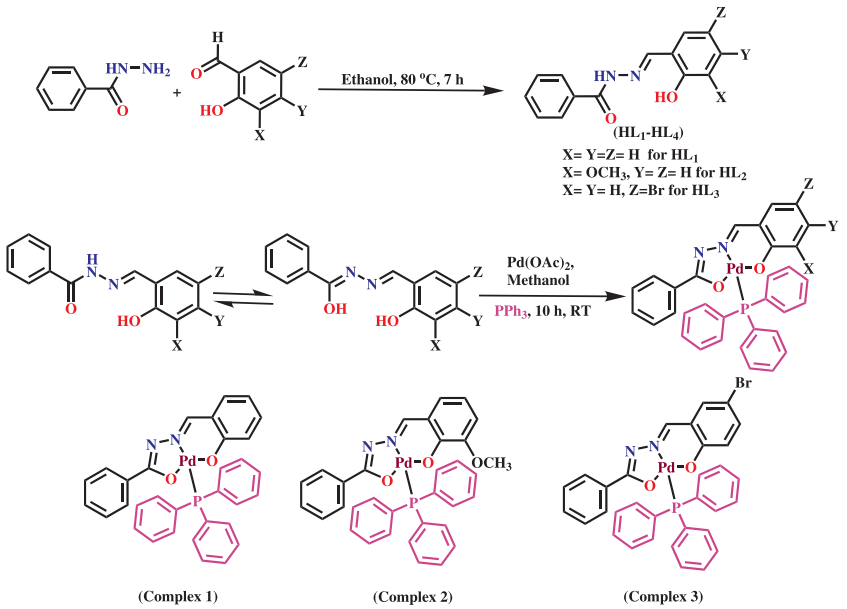
3.1 | Catalysts synthesis

Benzoylhydrazone-based ONO pincer–type three Schiff base ligands (HL^{1-3}) were synthesized by the reported methods and isolated as white crystalline solids.[57–59] Using these ligands, three new pincer-type palladium(II) Schiff base complexes of the type $[Pd(L^{1-3})(PPh_3)]$ were synthesized as shown in Scheme 2. The reaction of the Schiff base ligands precursor with palladium acetate in a 1:1 molar ratio with PPh_3 as a co-ligand in methanol at room temperature for 10 hr afforded the corresponding complexes, $[Pd(L^1)(PPh_3)]$ **(1)**, $[Pd(L^2)(PPh_3)]$ **(2)**, and $[Pd(L^3)(PPh_3)]$ **(3)** in 78%–83% yields as air-stable, reddish-orange crystalline solids. The complexes were found to be soluble in polar solvents such as CH_2Cl_2, CH_3CN, DMF, and DMSO and sparingly in nonpolar solvents such as *n*-hexane and diethyl ether. Single crystals of complexes **1**, **2**, and **3**, suitable for X-ray crystallography, were grown over a period of few days on standing a concentrated solution of the complex in DMF. All complexes were characterized by elemental analysis, FT-IR, UV–Visible, ^{1}H NMR, $^{13}C\{^{1}H\}$ NMR, and $^{31}P\{^{1}H\}$ NMR spectroscopic techniques and their structures were also confirmed by single-crystal X-ray diffraction studies.

3.2 | Catalysts characterization

3.2.1 | FT-IR analysis

The FT-IR spectra of Schiff base ligands HL^{1-3} and their corresponding palladium(II) complexes **1**, **2**, and **3** are presented in Figures S1–S3, respectively. The FT-IR spectra of the ligands displayed broad bands in the range of 3369–3440 cm^{-1} attributed to ν OH and bands at 3212–3264 cm^{-1} due to ν NH, respectively. In addition to these, ligands HL^1, HL^2, and HL^3 exhibited sharp and high-intensity bands at 1671, 1652, and 1649 cm^{-1}, respectively, owing to ν C=O. The existence of ν NH and ν C=O clearly indicated that the ligands HL^{1-3} existed



SCHEME 2 Synthesis of ONO pincer–type Pd(II) Schiff base complexes **1–3**. RT, room temperature

mainly in keto form in the solid state.[60] The bands at 1623, 1602, and 1605 cm^{-1} were attributed to the azomethine (ν C=N) group of the corresponding ligands **1**, **2**, and **3**. However, the FT-IR spectra of complexes **1**, **2**, and **3** exhibited bands at 1603, 1594, and 1596 cm^{-1}, respectively, assignable to the ν C=N stretching frequency. A comparison of the FT-IR of the free ligands and their corresponding complexes clearly indicated that the ν C=N stretching frequency was shifted to a lower wave number by $\Delta\nu$ 20, 8, and 9 cm^{-1} in complexes **1**, **2**, and **3**, respectively. The shifting of azomethine stretching frequency to a lower wave number may be taken as an evidence for the coordination of the nitrogen atom to the metal. In the FT-IR spectra of complexes, the vanishing of ν OH peak and appearance of peaks in the range of 531–532 and 499–508 cm^{-1} assignable to ν Pd–O and ν Pd–N, respectively, support the formation of the complexes.[61]

3.2.2 | UV–Visible analysis

The electronic spectra of palladium(II) complexes (**1–3**) were recorded in DMF solutions (10^{-4} M) in the wavelength range of 250–800 nm and are shown in Figure S4. All spectra are very similar and exhibit three strong absorption bands in the following regions: 312–320 nm, 339–347 nm, and 402–410 nm. The strong and high-energy peaks in the region 312–320 nm were attributed to the π–π* transition of the aromatic fragment of the ligand. In all complexes, the n–π* transition corresponding to the azomethine groups was observed in the range of 339–347 nm. The lower energy absorptions between 402 and 410 nm for all three complexes were due to ligand-to-metal charge transfer.

3.2.3 | NMR analysis

The ^{1}H NMR spectra of all ligands (HL^{1-3}) were recorded in DMSO-d_6 at room temperature (Figures S5, S9, and S13). The ^{1}H NMR spectra of all three Schiff base ligands showed a singlet at δ 12.02, δ 11.98, and δ 12.06 for HL^1, HL^2, and HL^3, respectively, due to the O*H* proton. The other characteristic resonance that appeared at δ 11.21, δ 10.85, and δ 11.55 as singlet was assigned to the –N*H* proton for ligands HL^1, HL^2, and HL^3, respectively. The azomethine (*H*C=N–) proton in ligands HL^1, HL^2, and HL^3 was observed as a sharp singlet at δ 8.55, δ 8.55, and δ 8.52, respectively. The ^{1}H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ spectra of all complexes were recorded in $CDCl_3$ and their spectral data are summarized in Table S1. The ^{1}H NMR spectra of complexes **1–3** (Figures S6, S10, and S14) did not display any signal corresponding to N*H* protons. The disappearance of the –N*H* resonance in the complexes clearly indicated that ligands had undergone keto to enol tautomerism before complexation followed by deprotonation. In addition, the disappearance of O*H* protons (phenolate) in the ^{1}H NMR of the complexes indicated the deprotonation of the hydroxy groups on coordination. However, in complexes **1**, **2**, and **3**, the resonance corresponding to the azomethine proton was observed at δ 8.52, δ 8.35, and δ 8.26, respectively. The upfield shift of the azomethine proton in all three complexes as compared with the free ligands supported the coordination of the nitrogen of the azomethine group to the metal ion. The upfield shifting of azomethine protons may be due to the sterical and geometrical constraints experienced by the ligand upon complex formation.[62] In complex **2**, the –O*C*H_3 protons of the *o*-vaniline moiety were observed as a singlet at δ 3.695. In the free ligand HL^2, these protons were observed at the same position, which clearly reflected that the methoxy group remains unperturbed during complexation.

The $^{13}C\{^1H\}$ NMR spectra of the complexes **1**, **2**, and **3** (Figures S7, S11, and S15) exhibited a sharp signal at δ 162.20, δ 173.34, and δ 161.45, corresponding to azomethine carbon (–*C*H=N–) of the coordinated ligand, respectively. The signals that appeared in the region of δ 106.33–δ 153.74 were assigned to various aromatic carbons of the complexes. In complex **2**, the methoxy carbon (–O*C*H_3) of the *o*-vaniline moiety was observed at δ 56.49.

The $^{31}P\{^1H\}$ NMR spectra of complexes **1**, **2**, and **3** (Figures S8, S12, and S16) showed a sharp singlet at δ 21.11, δ 17.70, and δ 21.24, respectively. The free *P*Ph_3 ligand exhibited a resonance at δ –6.4. It is evident from the ^{31}P NMR data of the complexes that the triphenylphosphine ligand experienced a downfield shift (Δ = 24–27 ppm) which clearly confirms the coordination of the PPh_3 ligand through the P atom to the metal center.[63]

3.2.4 | X-ray crystal structure determinations

Single crystals of complexes **1**, **2**, and **3**, suitable for X-ray crystallography, were grown over a period of few days on a standing concentrated solution of the respective complex in DMF. The mode of coordination of the ONO pincer–type ligands to palladium ion in all three complexes was determined from the single-crystal X-ray structure and the ORTEP representations of the three new palladium(II) complexes including the non-C and non-H atoms numbering scheme (Figures 2–4). X-ray

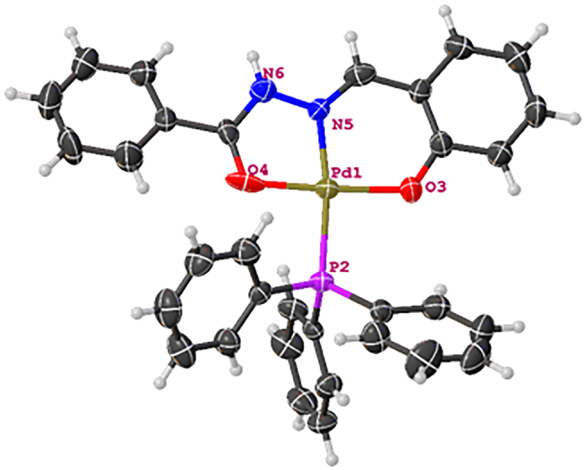


FIGURE 2 ORTEP (Oak Ridge Thermal Ellipsoid Plot) diagram of complex **1** with the non-C and non-H atoms labeling scheme (thermal ellipsoids are drawn at the 50% probability level)

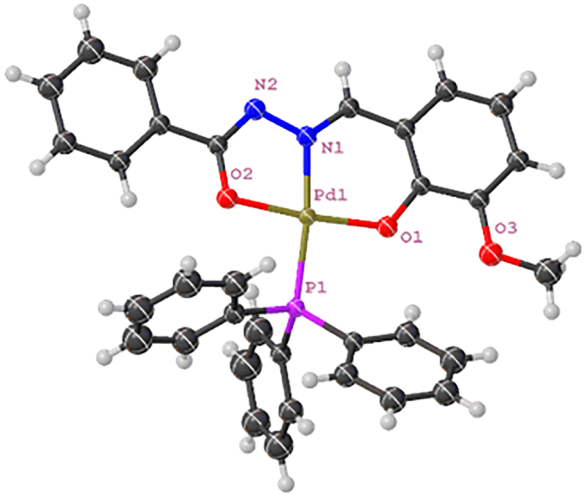


FIGURE 3 ORTEP (Oak Ridge Thermal Ellipsoid Plot) diagram of complex **2** with the non-C and non-H atoms labeling scheme (thermal ellipsoids are drawn at the 50% probability level)

investigation revealed that complexes **1** and **2** crystallized in the monoclinic system in space groups $P2_1/c$ and $C2/c$, respectively. However, complex **3** crystallized in the orthorhombic system in the space group *Pbca*. The molecular structures of these complexes were found to be almost similar and revealed that the Pd(II) center in all complexes has a distorted square planar geometry, as reflected in the bond parameters around the metal center (Table S2). Distortion is mainly caused by the presence of the double deprotonated tridentate Schiff base ligand. In all complexes, the metal centre Pd(II) is surrounded by the ONO pincer–type ligand occupying three coordination sites and a monodentate triphenylphosphine ligand.

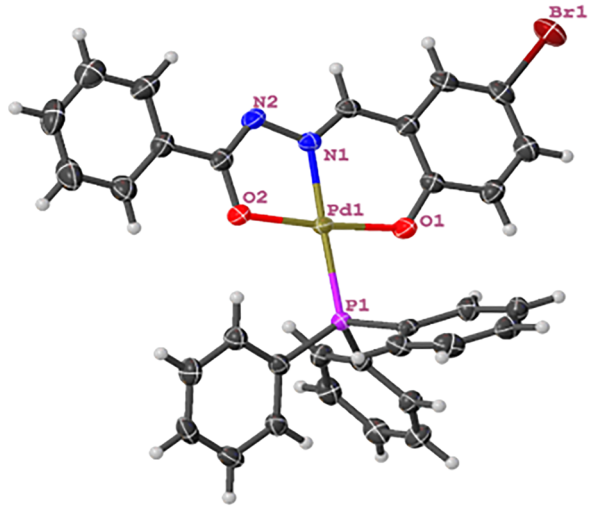


FIGURE 4 ORTEP (Oak Ridge Thermal Ellipsoid Plot) diagram of complex **3** with the non-C and non-H atoms labeling scheme (thermal ellipsoids are drawn at the 50% probability level)

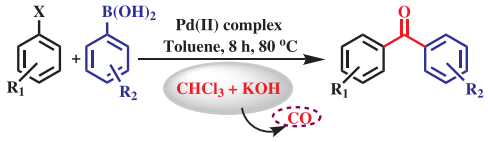
Two rings, one five-membered and one six-membered chelating rings, were formed when the pincer-type ligand coordinated through the O, N, and O donors to the palladium(II). A summary of the crystallographic and refinement data of complexes is furnished in Table 1 with selected bond lengths and bond angles given in Table S2. The N(5)–Pd(1)–O(3), N(5)–Pd(1)–O(5), O(3)–Pd(1)–P(2), and O(4)–Pd(1)–P(2) chelate bite angles of the complexes **1** are 94.83(19), 80.21(19), 93.83(14), and 171.33(15), respectively. The N(1)–Pd(1)–O(1), N(1)–Pd(1)–O(2), O(1)–Pd(1)–P(1), and O(2)–Pd(1)–P(1) chelate bite angles of complexes **1** and **2** are in the range of 93.66(9)–94.47(11), 79.92(11)–80.09(9), 85.38(7)–94.09(5), and 92.16(6)–100.30(7), respectively. The Pd–O, Pd–N, and Pd–P bond lengths in all complexes are in the range of 1.926(6)–1.993(2) Å, 1.968(5)–1.975(3) Å, and 2.2837(9)–2.2965(7) Å, respectively, which are in the normal range and similar to other structurally characterized analogous palladium(II) complexes.[64–66]

3.3 | Catalytic studies: carbonylative Suzuki coupling reaction

After the synthesis and characterization of the complexes **1–3**, the catalytic potential of all three complexes was explored in the synthesis of a wide range of biaryl ketones via the carbonylative Suzuki–Miyaura coupling reaction of various aryl bromides/iodides with different arylboronic acids using $CHCl_3$ as the source of CO (Scheme 3).

TABLE 1 Crystallographic and refinement data for [($PdL^1(PPh_3)$] **(1)**, [($PdL^2(PPh_3)$] **(2)**, and [($PdL^3(PPh_3)$] **(3)** complexes

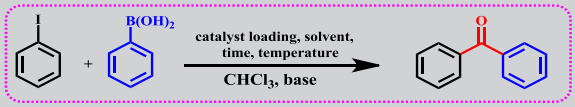
Complex	[($PdL^1(PPh_3)$]	[($PdL^2(PPh_3)$]	[($PdL^3(PPh_3)$]
CCDC number	1915066	1526697	1862709
Chemical formula	$C_{32}H_{25}N_2O_2PPd$	$C_{33}H_{27}N_2O_3PPd$	$C_{32}H_{24}BrN_2O_2PPd$
Formula weight	607.92 g/mol	636.93 g/mol	685.81 g/mol
Temperature	293 K	103(2) K	153(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal size (mm)	0.08 × 0.18 × 0.21	0.24 × 0.32 × 0.40	0.14 × 0.18 × 0.22
Crystal habit	Block, red	Block, red	Block, red
Crystal system	Monoclinic	Monoclinic	orthorhombic
Space group	$P2_1/c$	$C2/c$	$Pbca$
Unit cell dimensions			
a (Å)	14.7005(8)	33.1424(16)	22.8515(8)
b (Å)	10.3418(6)	9.5982(5)	8.5215(3)
c (Å)	17.4996(9)	18.3665(9)	27.7953(10)
α (degrees)	90	90	90
β (degrees)	91.953(5)	107.7741(10)	90
γ (degrees)	90	90	90
V (Å^3)	2658.9(3)	5563.6(5)	5412.6(3) Å^3
Z	4	8	8
Density (calculated)	1.519 mg m^{-3}	1.521 g cm^{-3}	1.683 g cm^{-3}
Absorption coefficient	0.791 mm^{-1}	0.763 mm^{-1}	2.255 mm^{-1}
F(000)	1236.0	2592	2736
Goodness-of-fit on F^2	1.013	1.046	1.020
R_{int}	0.0565	0.0929	0.0657
$R_1[I > 2\delta(I)]$	0.0658	0.0582	0.0328
wR_2 (all data)	0.1704	0.1542	0.0795
Largest diffraction peaks and hole	0.48 and −0.66 eÅ^{-3}	1.088 and −1.255 eÅ^{-3}	1.803 and −0.732 eÅ^{-3}



SCHEME 3 Palladium(II) complex–catalyzed carbonylative Suzuki reactions

Our investigation began by carrying out the carbonylative Suzuki–Miyaura coupling reaction of iodobenzene (1.0 mmol) with phenylboronic acid (1.2 mmol) in the presence of $CHCl_3$ (4 equiv.) and KOH (8 equiv.) in a sealed tube. This reaction was conducted in various solvents at different temperatures in the presence of varying amounts of complexes in order to optimize the reaction parameters such catalyst loading, solvent, time, and temperature. The results are summarized in Table 2. As shown in Table 2, when the reaction was carried out in the presence of 0.5 mol. % of complex **1**, in toluene (2 mL) as solvent at 80 °C for 8 hr, the desired product was obtained in only 58% yield (Table 2, Entry 1). The reaction with complexes **2** and **3**, under identical conditions, afforded the product in 70% and 62% yield (Table 2, Entries 2 and 3). Because the best yield was obtained with complex **2**, we focused our attention to further increase the yield of the carbonylative products. Therefore, on increasing the catalyst **2** loading from 0.5 to 1 mol%, the corresponding product was obtained in 85% yield (Table 2, Entry 4). However, further enhancement in the catalyst loading beyond 1.0 mol % did not give any fruitful result on the yield (Table 2, Entry 5). To see the effect of temperature and reaction time, the reaction was also carried out at different temperatures and reaction times (Table 2, Entries 6–9). It can be seen from the table that the best yield of the product

TABLE 2 Optimization of the reaction conditions[a]



Entry	Catalyst	Catalyst loading (mol%)	Solvents	Base	Temp (°C)	Time (hr)	Yield (%)[b]
1	Complex **1**	0.5	Toluene	KOH	80	8	58
2	Complex **2**	0.5	Toluene	KOH	80	8	70
3	Complex **3**	0.5	Toluene	KOH	80	8	62
4	Complex **2**	1.0	Toluene	KOH	80	8	85
5	Complex **2**	1.2	Toluene	KOH	80	8	85
6	Complex **2**	1.0	Toluene	KOH	60	8	74
7	Complex **2**	1.0	Toluene	KOH	100	8	85
8	Complex **2**	1.0	Toluene	KOH	80	6	70
9	Complex **2**	1.0	Toluene	KOH	80	12	86
10	Complex **2**	1.0	EtOH	KOH	80	8	45
11	Complex **2**	1.0	Dimethylformamide	KOH	80	8	30
12	Complex **2**	1.0	Dioxane	KOH	80	8	42
13	Complex **2**	1.0	CH_3CN	KOH	80	8	25
14	Complex **2**	1.0	Toluene	NaOH	80	8	54
15	Complex **2**	1.0	Toluene	LiOH	80	8	45
16	Complex **2**	1.0	Toluene	$Mg(OH)_2$	80	8	30
17	Complex **2**	1.0	Toluene	$Cs(OH)\cdot H_2O$	80	8	80
18	Complex **3**	1.0	Toluene	KOH	80	8	70
19	–	–	Toluene	KOH	80	24	n.r.
20[c]	$Pd(OAc)_2$	1.0	Toluene	KOH	80	8	48

[a]Reaction conditions: iodobenzene (1.0 equiv.), phenyl boronic acid (1.2 equiv.), base (8.0 equiv.), $CHCl_3$ (4.0 equiv.), and solvent (2 mL).
[b]Yield after column chromatography.
[c]5 mol% PPh_3 was used as ligand.

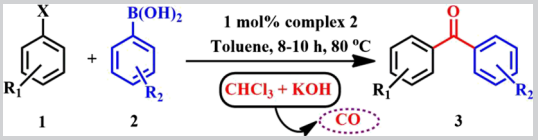
was obtained with 1 mol% of catalyst **2** at 80 °C for 8 hr. The reaction was also carried out in EtOH, CH_3CN, DMF, and dioxane (Table 2, Entries 10–13) to see the solvent effect, but none of the solvent afforded higher yield of the product. Therefore, toluene was found to be the best solvent for the reaction.

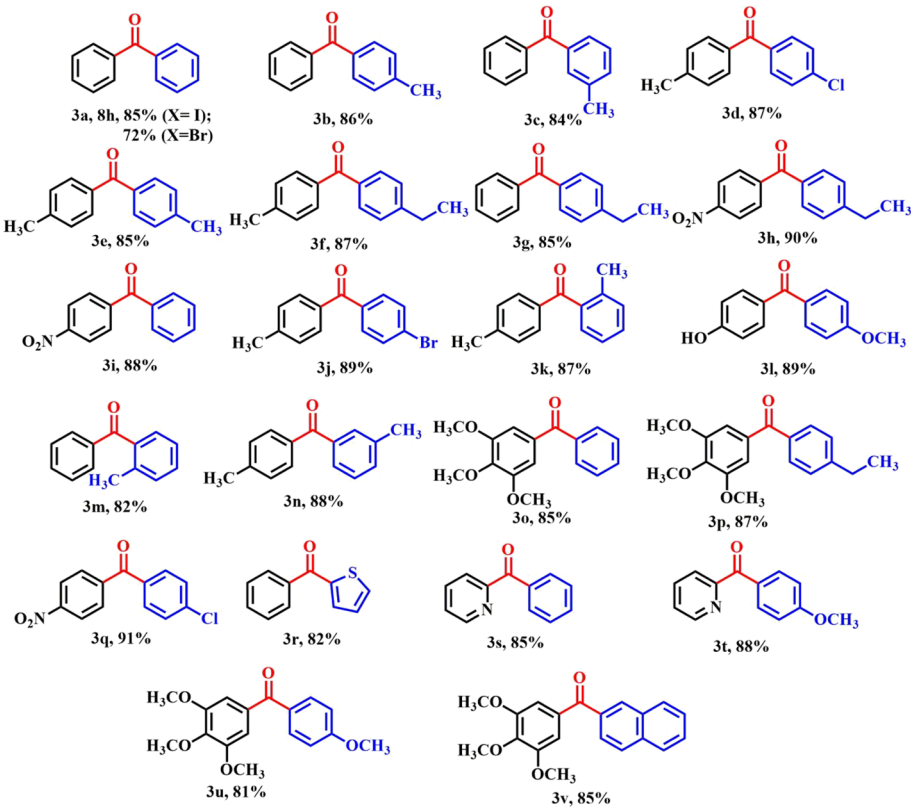
Chloroform in presence of a base is known to generate carbene which undergoes *in situ* hydrolysis to produce CO.[30] Therefore, a number of bases, such as NaOH, LiOH, $Mg(OH)_2$, and $CsOH\cdot H_2O$, were investigated to optimize the generation of CO from chloroform. Among all bases used, KOH provided the best yield of the desired product (Table 2, Entries 14–17).

To demonstrate the role of the palladium complex as catalyst, a blank reaction (without complex) was carried out under identical conditions; however, the reaction did not yield any product (Table 2, Entry 19). Further, the reaction in presence of $Pd(OAc)_2$ and PPh_3 (as ligand) resulted in low yield of the desired products (Table 2, Entry 20). Hence, the pre-formed complex as a catalyst resulted in better yield as compared with *in situ*-generated palladium complex. The enhanced catalytic activity using the isolated palladium(II) complexes may be ascribed to the stabilization of the reaction intermediates by chelation of ONO pincer–type Schiff base ligand, in addition to the fine-tuning of electronic and steric properties of the complex to facilitate the formation of the desired product. Complex **2**, containing a methoxy group at *o*-position, exhibited the best catalytic activity which may be rationalized in terms of strong electron-donating properties of the methoxy group.

After optimization of the reaction conditions, the scope of palladium(II)-catalyzed carbonylative Suzuki couplings was extended to a library of halides (aromatic

TABLE 3 Carbonylative Suzuki coupling reactions of various halides with aryl boronic acids[a,b]





[a]Reaction conditions: Aryl halide (**1**) (1.0 mmol, 1.0 equiv.), boronic acid (**2**) (1.2 mmol, 1.2 equiv.), Complex **2** (1 mol%), KOH (8 equiv.), and $CHCl_3$ (4.0 equiv.) in toluene (2 mL) at 80 °C.
[b]Isolated Yields.

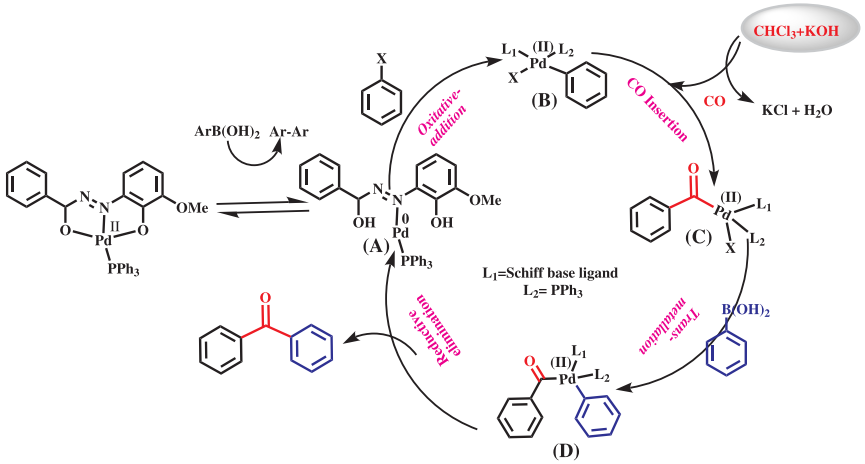
and heteroaromatic) and several substituted and unsubstituted boronic acids in the presence of $CHCl_3$ and KOH and complex **2**, and the results are summarized in Table 3. In general, all the investigated reactions of different types of iodobenzene having a variety of functional groups such methyl, hydroxy, nitro, and trimethoxy on the aryl ring with different boronic acids having *ortho*-, *meta*-, and *para*-substituents on the aryl ring underwent smooth carbonylative coupling under the optimized reaction conditions to afford the corresponding biaryl ketones in very good yields (Table 3) with negligible biaryl formation, which may be formed as a result of homocoupling reaction of aryl boronic acids. The electron-withdrawing $-NO_2$ group containing iodobenzene also presented satisfactory yields (Table 3, Entries 3h, 3i, and 3q). Aryl bromides in the place of iodides behaved well in the carbonylative Suzuki coupling reactions, but produced relatively low yields (Table 3, Entry 3a). The heteroaryl iodobenzene, 2-iodopyridine, also produced the corresponding biaryl ketone product in high yield, indicating that catalyst poisoning does not occur during catalysis. Unfortunately, the reaction of chloro substrates, instead of bromo and iodo substrates, did not succeed under the optimized conditions, presumably owing to less reactivity of the C–Cl bond.

Arylboronic acid bearing both electron-donating and electron-withdrawing substituents reacted well to afford the corresponding carbonylative coupling products in

TABLE 4 Comparison of catalytic activity of the palladium(II) complex with reported catalysts for the synthesis of biphenyl ketones using $CHCl_3$ as the source of carbonyl

Entry	Reaction conditions	Yields (%)	TON	TOF (hr^{-1})	Reference
1	$FeCl_2$ (10 mol%), NaI (50 mol%), $CsOH{\cdot}H_2O$ (5 equiv.), Na_2CO_3 (2 equiv.), PivOH (1.5 equiv.), PEG-400 (2 mL), 24 hr, 120 °C	94	9.4	0.40	[30]
2	$Pd(OAc)_2$ (2 mol%), DMAP (20 mol%), KOH (5 equiv.), toluene (2 mL), 12 hr, 80 °C	75	37.5	3.13	[31]
3	Pd(II) pincer–type complex **2** (1 mol%), toluene (2 mL), 8 hr, 80 °C	85	85.0	10.63	This work

TOF, turnover frequency; TON, turnover number; PEG-400, polyethylene glycol 400.



SCHEME 4 Plausible mechanism for the synthesis of biaryl ketone

high yields (Table 3). Both *m*- or *p*-substituted phenylboronic acids gave very good yields of the corresponding benzophenone (Table 3, Entries 3b and 3c) as compared with that of *o*-substituted arylboronic acid (Table 3, Entry 3m). The low yield with *o*-substituted aryl boronic acids may be rationalized in terms of steric hindrance. Under optimized conditions, the reaction of hetero-arylboronic acid (i.e. thiophene-2-phenylboronic acid) also proceeded smoothly to afford the corresponding product in high yield (Table 3, Entry 3r).

Finally, to validate the practical utility of the developed catalytic system, the synthesis of two pharmaceutically important antineoplastic drugs (4-methoxyphenyl) (3,4,5-trimethoxyphenyl)methanone and (2-naphthyl) (3,4,5-trimethoxyphenyl)methanone (phenstatin scaffolds) was carried out. As reported in Entries 3u–3v (Table 3), the carbonylative Suzuki cross-coupling of 5-iodo-1,2,3-trimethoxybenzene with 4-methoxy phenylboronic acid and 2-naphthylboronic acid afforded (4-methoxyphenyl) (3,4,5-trimethoxyphenyl)methanone and (2-naphthyl) (3,4,5-trimethoxyphenyl)methanone in very good yields (81% and 85%, respectively). Both compounds belong to the phenstatin family and exhibited good cytotoxic properties and inhibited tubulin polymerization in cancerous cells.[67,68]

Furthermore, we performed a comparison of the catalytic activity of the synthesized palladium(II) complexes with the state-of-the-art catalysts.[30,31] The results showed that complex **2** has better catalytic activity than other catalysts in terms of yield, catalyst loading, reactions time, turnover number (TON), turnover frequency (TOF), and reusability as shown in Table 4.

A plausible mechanism of this catalytic system is proposed in Scheme 4, based on previous reports.[30,31] The proposed mechanism entails a $Pd^{II/0/II}$ catalytic cycle. First, the catalyst $[Pd^{II}(L)(PPh_3)]$ undergoes a two-electron reduction in presence of arylboronic acid to produce $[Pd^{0}(L)(PPh_3)]$ **(A)**.[51] In the next step, **(A)** reacts with any aryl halide to generate an arylpalladium(II) intermediate **(B)** by an oxidative addition step. The intermediate **(B)** undergoes insertion of CO (generated *in situ* from chloroform and KOH) between the Pd(II) and carbon of the aryl group to form the intermediate **(C)**. Subsequently, intermediate **(C)** reacts with a phenyl anion (nucleophile generated from arylboronic acid) and undergoes transmetalation to form the intermediate **(D)**.

Finally, the intermediate **(D)** undergoes reductive elimination to yield the carbonylative Suzuki-coupling product (biraryl ketone) and regenerate the $[Pd^{II}(L)(PPh_3)]$ catalyst by oxidation of $[Pd^{0}(L)(PPh_3)]$ species.

3.3.1 | Catalytic recyclability

The catalyst recyclability is an important step in catalysis as it trims down the overall cost of the process. The recyclability of complex **2** for the synthesis of biphenyl ketones via carbonylative Suzuki coupling of iodobenzene with phenylboronic acid was studied. The complex showed good catalytic activity until the third cycle with insignificant decrease in efficiency. The results of recycling experiments with complex **2**, with respective yields after each run, are depicted in Figure 5.

A 10-mL sealed tube was charged with phenylboronic acid (0.133 g, 1.2 mmol), iodobenzene (0.204 g, 1.0 mmol), KOH (8.0 mmol, 0.49 g), $CHCl_3$ (4.0 mmol, 326 μL), toluene (2 mL), and palladium(II) complex (1 mol%). The tube was sealed tightly and stirred vigorously at 80 °C for 8 hr. After completion of the reaction, the reaction mixture was allowed to cool to room temperature and the organic layer was extracted with ethyl acetate (3 × 10 mL), washed with water, dried over anhydrous Na_2SO_4, and concentrated on a rotary evaporator. The desired carbonylative product and catalyst were separated from the crude reaction mixture by column chromatography on silica using ethyl acetate and petroleum ether as eluent. On the column, organic products moved first, followed by catalyst. The recovered catalyst was dried and utilized in successive cycles under the same reaction conditions and results showed that the catalyst exhibited good catalytic activity up to three cycles. A comparison of the ^1H NMR spectra (Figure S17) of the freshly prepared catalyst with the recovered catalyst clearly showed that there was no significant changes in complex **2**.

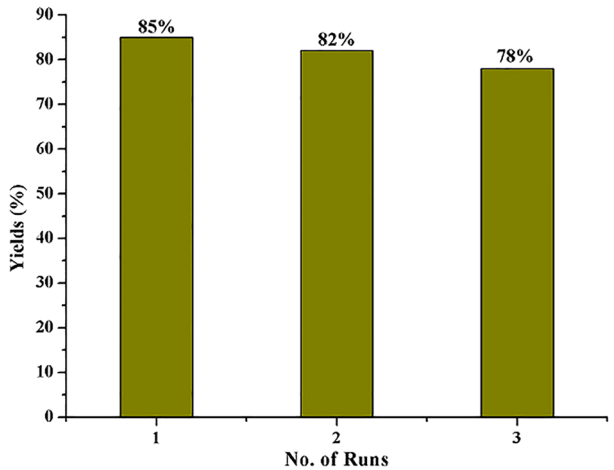


FIGURE 5 Recyclability of the catalyst

3.3.2 | Mercury poisoning test

To confirm the homogeneous nature of the catalytic system, mercury poisoning test[69] was carried out. Under optimized conditions, in presence of an excess of mercury, the reaction of phenylboronic acid, iodobenzene, and $CHCl_3$ using palladium complex as the catalyst proceeded smoothly to afford the benzophenone product without any significant effect on the yield of the product. Therefore, it can be inferred from the test result that the reaction follows a homogeneous catalytic pathway.

4 | CONCLUSIONS

In summary, three new ONO pincer–type palladium(II) Schiff base complexes **1**, **2**, and **3** were synthesized and characterized by elemental analysis, FT-IR, UV–Visible, ^1H NMR, $^{13}C\{^1H\}$ NMR, and $^{31}P\{^1H\}$ NMR and their molecular structures confirmed by single-crystal X-ray diffraction studies. The catalytic activity of the complexes was explored in the carbonylative Suzuki coupling reactions of aryl halides with arylboronic acids, using $CHCl_3$ as the source of CO. Of the three complexes, complex **2** exhibited the best catalytic activity. The key feature of the reported methodology is that it offers safe alternative to the use of CO balloons or pressured CO reactors, which are otherwise required for the carbonylation reactions. The practical utility of complex **2** is successfully demonstrated in the synthesis of two anti-neoplastic phenstatin scaffolds. High values of TON and TOF were achieved by complex **2**, as compared with the previous reported catalysts. The catalyst can be recycled up to three times with insignificant loss in the catalytic activity. The efficiency, reusability, and operational simplicity are the main features of the reported catalytic system. Presently, efforts are in progress to replace expensive palladium with alternative cheap and earth-abundant metals for the carbonylative Suzuki coupling reactions.

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