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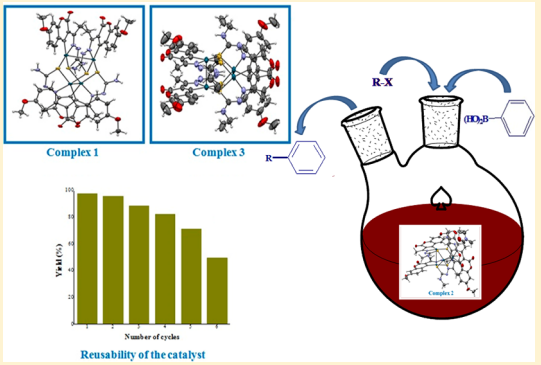
Tetranuclear Palladacycles of 3-Acetyl-7-methoxy-2*H*-chromen-2-one Derived Schiff Bases: Efficient Catalysts for Suzuki−Miyaura Coupling in an Aqueous Medium

Sivadasan Dharani,[‡] Giriraj Kalaiarasi,[‡] Dharmalingam Sindhuja,[†] Vincent M. Lynch,[§] Ramasamy Shankar,[∥] Ramasamy Karvembu,*[,†] and Rathinasabapathi Prabhakaran*[,‡]

[‡]Department of Chemistry, Bharathiar University, Coimbatore 641 046, India
[†]Department of Chemistry, National Institute of Technology, Tiruchirappalli 620015, India
[§]Department of Chemistry, University of Texas, Austin, Texas 78712-1224, United States
[∥]Department of Physics, Bharathiar University, Coimbatore 641 046, India

Supporting Information

ABSTRACT: Tetranuclear organopalladium(II) complexes **1**−**3** and mononuclear complex **4** have been synthesized by the complexation of 3-acetyl-7-methoxy-2*H*-chromen-2-one derived Schiff bases with potassium tetrachloropalladate $K_2[PdCl_4]$. Structural confirmation for the complexes (**1**−**3**) has been achieved by single-crystal X-ray diffraction analysis. The ligands are found to bind with the palladium ion through its azomethine nitrogen, thiolate sulfur, and C4 carbon atom of the coumarin moiety subsequent to C−H activation. The monomeric nature of complex **4** was confirmed from its mass spectroscopic data. In complex **4**, coordination occurred via the lactone oxygen, azomethine nitrogen, and thiolate sulfur atoms. Computational study has been used to determine the optimized molecular structures of the complexes. An explanation on the energies of their highest occupied and lowest unoccupied molecular orbital levels and their electronic spectra has also been provided on the basis of the theoretical calculations. A systematic study of the application of these complexes as catalysts in Suzuki−Miyaura coupling (SMC) has been done with different aryl halides and phenyl boronic acid in an aqueous medium. Optimization of the reaction indicated that complex **2** exhibits greater efficiency than other complexes. An appreciable yield of the coupled products was observed with the minimum use of catalyst (μmol), and the C−C coupling has been confirmed by GC/GC-MS. An interesting result of our catalyst is the coupling of four different chloroquinolines with phenyl boronic acid to afford the coupled products in good yields.



INTRODUCTION

Palladium-catalyzed coupling reactions have become a matter of interest in synthetic chemistry since the awarding of the Noble prize in 2010 to Heck, Negishi, and Suzuki.[1] Suzuki−Miyaura coupling, in particular, is able to operate at moderate reaction conditions and can afford complex molecules from simple starting materials.[2] Many coupling reactions using organozinc and organotin compounds are known,[3] but the special attention given to organoboron reagents is mainly due to their low toxicity and thermal stability and the easy removal of the boronic byproducts.[4] Among the palladium catalyst systems, prominent are the palladacycles.[5] Their steric and electronic properties can be tuned by simply changing (i) the size of the palladacyclic ring (3−10 members), (ii) nature of the cyclometalated carbon (aromatic, aliphatic, etc.), (iii) type of the donors present in the ligand system (N, O, S, P, etc.), and (iv) their substituents.[6] Simple palladium precursors like $Pd(OAc)_2$, $Pd(PPh_3)_4$, and $Pd_2(dba)_3$ catalyze a number of SMC reactions.[7−10] Modulation of the organoborane coupling partners has been carried out by Barbeiro et al.[11] and Molander et al.,[12] who utilized trifluoroborates to arrive at the biaryl products. Some palladium catalysts not only end up in the formation of a single C−C bond but also form more than one bond, resulting in domino reactions in one-pot synthesis.[9,10,13,14] Such reactions are quite advantageous in the synthesis of natural products and pharmaceuticals.[15] To improve the efficiency of catalysts, it is important to develop newer ligands as well as newer catalytic precursors. The elimination of expensive and air- and moisture-sensitive phosphine ligand systems is also important. It is often noted in literature reports that the catalyst is generated in situ. However, defined palladium complexes are better catalysts than the similar in situ generated systems.[16−18] The Suzuki−Miyaura coupling reaction aids in medicinal chemistry for the development of drugs which involve nitrogen-containing

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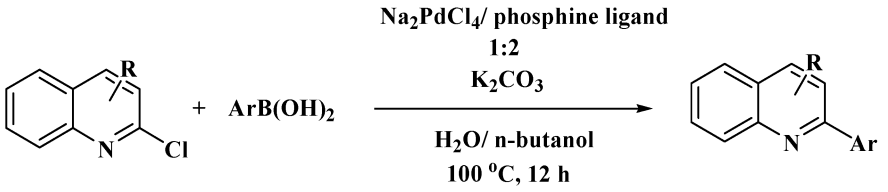
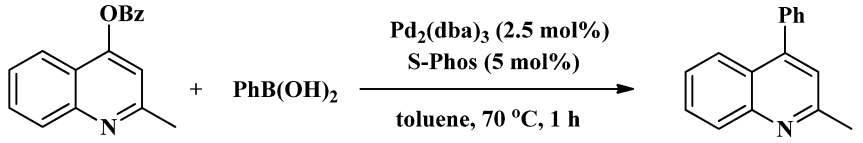
Scheme 1. Selective Strategies for SMC Coupling of Quinoline Derivatives Using Palladium Catalysts

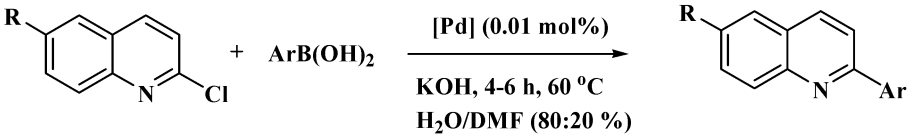
Previous works



R = H, CH_3 or CHO (6)

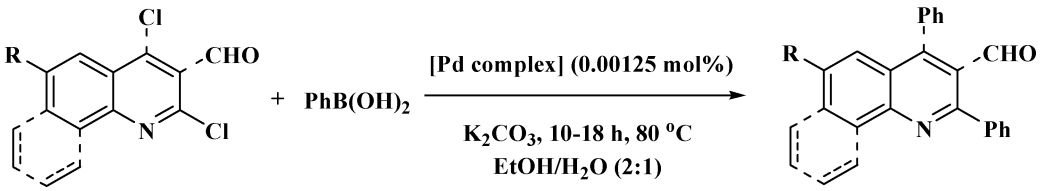


(7)



R = H or CH_3 (8)

This work



heterocycles as substrates. Cross coupling of nitrogen-containing heterocycles is a challenge, which becomes detrimental when palladium is employed.[19,20] Efficient catalytic precursors should be developed to couple nitrogen-based heterocycles like quinolines. Previous works on quinoline coupling using palladium catalysts are shown in Scheme 1.[21−23] Many reports are available for mononuclear palladium complexes catalyzing Suzuki−Miyaura coupling reactions,[24−29] but the application of multinuclear complexes is less explored, particularly in an aqueous medium, and only a handful can be found in the literature.[30]

Thiosemicarbazones are among the Schiff base ligands, whose study in bioinorganic applications is prolific.[31−33] Only a few reports quote their catalytic activity.[34,35] Coumarin derivatives (1,4-benzopyrones) condensed with thiosemicarbazides form Schiff base ligands, whose metal complexes were found to be active in anticancer studies, as discussed in our earlier articles.[36−38] However, not much reports are available for coumarin appended palladium complexes employed as catalysts. Hence, in order to present a simple catalytic methodology which proceeds smoothly in an aqueous medium and in a view to expand the purview of tetranuclear palladium complexes in catalysis, we have carried out a catalytic study for four newly synthesized palladium(II) complexes.

RESULTS AND DISCUSSION

Reactions of the palladium(II) precursor $K_2[PdCl_4]$ with 3-acetyl-7-methoxy-2*H*-chromen-2-one-4(*N*)-substituted thiosemicarbazones $\mathbf{H_2L^{1-4}}$ in dichloromethane/methanol resulted in the formation of tetranuclear and mononuclear complexes as depicted in Scheme 2. The formation of complexes was confirmed by spectroscopic techniques including Fourier transform infrared (FT-IR), ultraviolet−visible (UV−vis) (Figures S1 and S2), ^{1}H NMR (Figures S3−S6 (DMSO-d_6 as solvent); Figures S7−S13 ($CDCl_3$ as solvent)), and X-ray diffraction (XRD) analysis. Mass spectra were recorded for all the complexes (Figures S14−S17).

X-ray Crystallographic Analysis. The molecular structures of complexes **1**−**3** were unequivocally confirmed by XRD analysis (Figures 1−3 and Tables S2 and S3). They were found to be tetranuclear, in which each ligand $(L)^{2-}$ was bound to one palladium ion through azomethine nitrogen with Pd(1)−N(1) bond distances of 2.010(6) Å for complex **1**, 1.988(3) Å for complex **2**, and 1.997(6) Å for complex **3**; thiolate sulfur with Pd(1)−S(1) bond distances of 2.330(19) Å for complex

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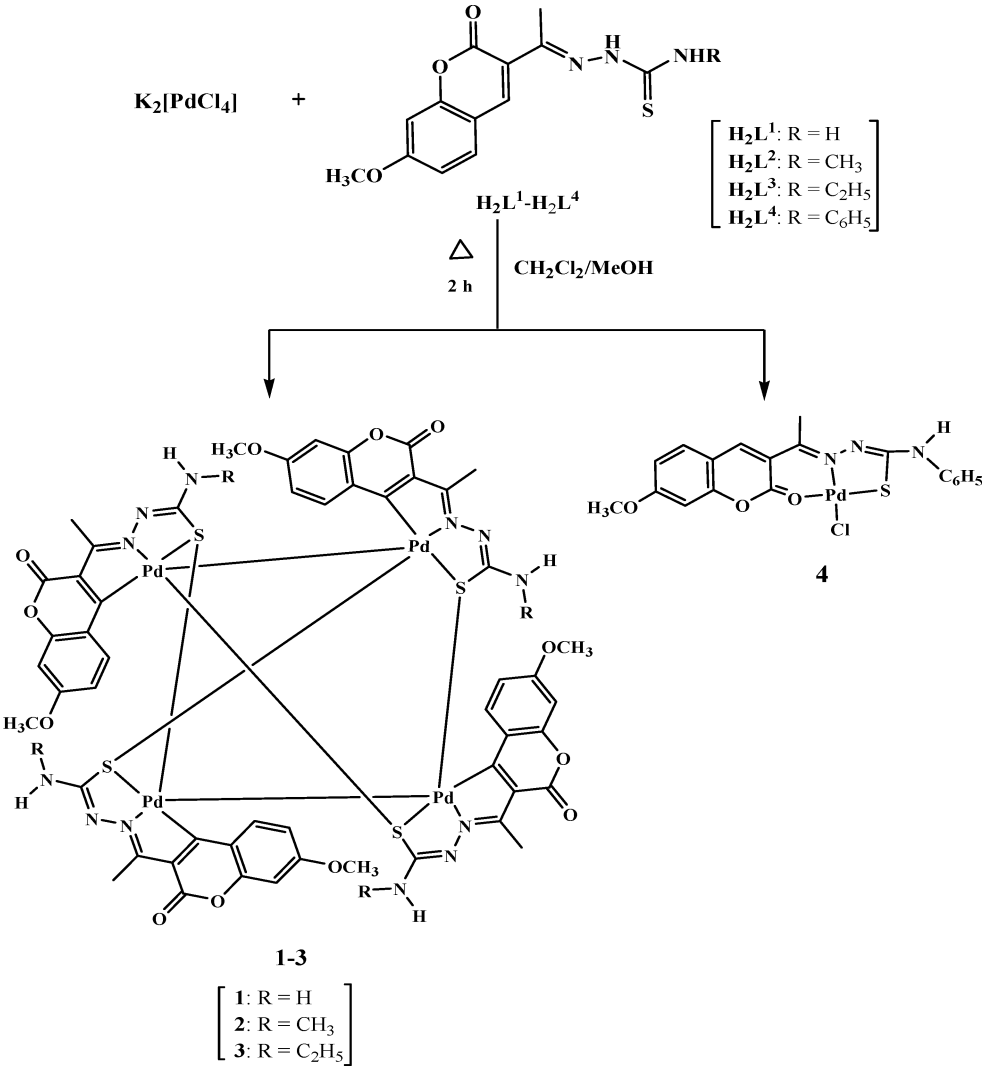
Scheme 2. Synthesis of Tetranuclear and Mononuclear Pd(II) Complexes



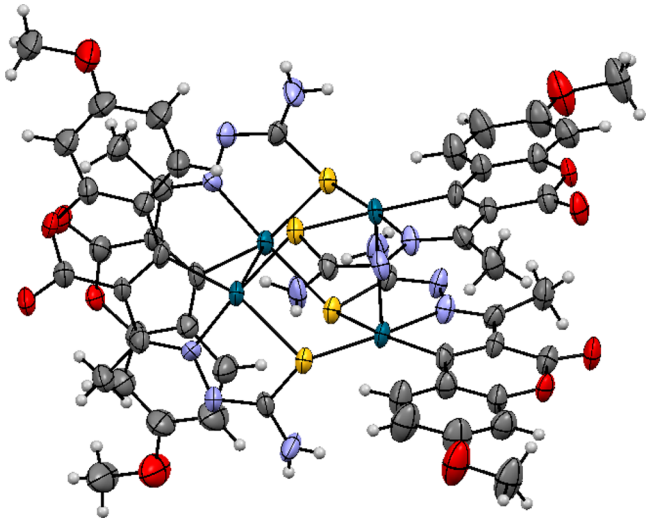


Figure 1. ORTEP diagram of complex **1** (thermal ellipsoid at 50% probability level).

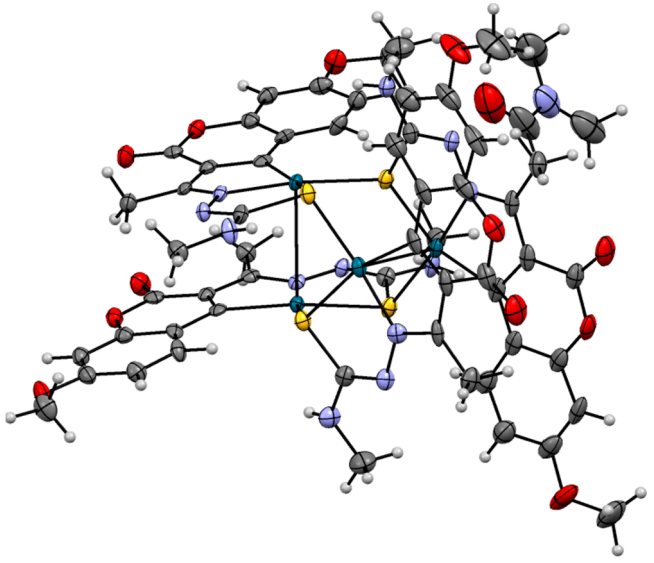


Figure 2. ORTEP diagram of complex **2** (thermal ellipsoid at 50% probability level).

1, 2.347(10) Å for complex **2**, and 2.337(16) Å for complex **3**; and C4 carbon atom of the coumarin moiety with Pd(1)–C(1) bond distances of 2.060(7) Å for complex **1**, 2.043(4) Å

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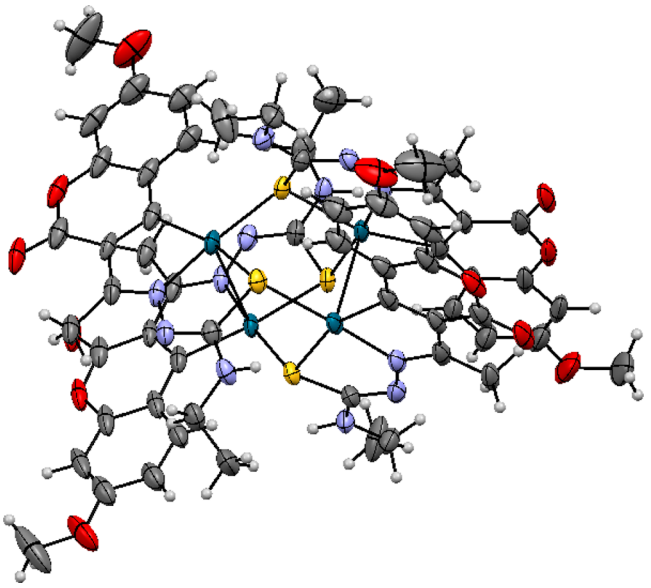

Figure 3. ORTEP diagram of complex **3** (thermal ellipsoid at 50% probability level).

for complex **2**, and 2.065(7) Å for complex **3**. This coordination resulted in a 5,5-member fused chelate ring. The fourth coordination was through the thiolate sulfur of the neighbor ligand, which formed a bridge between two metal centers. The Pd(1)−S(4) bond distances were observed as 2.336(19) Å for complex **1**, 2.320(10) Å for complex **2**, and 2.338(18)Å for complex **3**. The bite angles N(1)−Pd(1)−C(1) and N(1)−Pd(1)−S(1) were found as 81.3(3)° and 82.49(17)° for complex **1**, 80.99(13)° and 83.25(9)° for complex **2**, and 80.8(3)° and 82.62(17)° for complex **3**. The *trans* angles C(1)−Pd(1)−S(1) of complexes **1** (162.6(2)°), **2** (160.66(10)°), and **3** (161.5(2)°) showed considerable deviation from 180°, implying significant distortion in the square planar geometry of the complexes. The bond distances and angles pertaining to the metal and the coordinated ligands are similar to those of reported Pd(II) complexes.[39−42] The distance between the two Pd−Pd bonds was 3.242 Å for complex **1**, 3.195−3.207 Å for complex **2**, and 3.186 Å for complex **3**, while that between the four Pd−S−Pd fragments was found to be 3.943 Å for complex **1**, 3.933−3.944 Å for complex **2**, and 3.939 Å for complex **3**.[43a] The Pd−Pd distance found here is similar to the Vanderwaal's radii (3.26 Å) observed in other Pd(II) complexes. Thus, the two Pd−Pd bonds seen in complexes **1**−**3** may be considered to be intramolecular secondary bonding interactions.[43b] All these complexes contain hydrogen bonding, which resulted in a 3D chain network (Figures S18−S20 and Table S4).

Density Functional Theory Study. Density functional theory (DFT) calculations have been carried out to understand the geometrical and electronic properties of synthesized complexes **1**−**4**. The results confirmed the optimized geometry of all the complexes at a stationary point of the potential energy surface without any imaginary frequency. The bond lengths between the metal and coordinated atoms of the ligands agreed with the experimental values, which are given in Table S5. The optimized structures of the complexes are shown in Figures S21−S24.

The frontier molecular orbital diagram showed that both the highest occupied molecular orbitals (HOMOs) of complexes **1**−**3** delocalized on nitrogen, oxygen atoms of the coordinated ligands, and palladium atoms (Figures 4 and S25). However, on account of the lowest unoccupied molecular orbital (LUMO), the electron density is highly localized in C4 carbon, azomethine carbon, nitrogen atoms of the coordinated ligands, and palladium atoms. In complex **4**, the LUMO is mainly delocalized on the coumarin ring; carbon, oxygen, nitrogen atoms of the coordinated ligand; and the palladium atom, whereas the HOMO exhibits its delocalization on the phenyl ring, coordinated atoms of the ligand (carbon, nitrogen, sulfur, and chloride atoms), and on the palladium atom. Both complexes **1** and **3** have the same band gap of 2.99 eV. Complex **2** has the HOMO value of −5.66 eV and LUMO value of −2.68 eV with the band gap of 2.98 eV. The calculated band gap for complex **4** is 2.46 eV with the HOMO value of −5.74 eV and LUMO value of −3.28 eV. Further, solvent corrections (in DMSO (Figures 4 and S25) and ethanol/water) were carried out, and the band gap of the complex structures has changed slightly (Table S6). The percentage composition of frontier molecular orbitals of the complexes is provided in Table S7.

The electronic properties of complexes **1**−**4** are calculated by frontier molecular orbital analysis. The UV absorbance calculations are carried out at the B3LYP/LANL2DZ level of theory in the presence of DMSO by varying the number steps to 20, 50, and 100, and the maximum absorption peaks are observed from 300 to 600 nm for complexes **1**−**3** and from 250 to 600 nm for complex **4**. The spectra of complexes **1**−**3** exhibited bands around 320, 430, and 480 nm (Figure S26). In complex **1**, maximum energy absorptions were seen at 322, 419, and 481 nm, out of which the band at 322 nm corresponded to the transition from H^{-19} orbital to L orbital ($HOMO^{-19}$−LUMO); the band at 419 nm corresponded to the transition from the H^{-3}−L^{3} orbital; and 481 nm corresponded to transition from the H^{2}−L orbital. Similarly, the highest-energy orbital transitions of each complex corresponding to the absorption maxima, along with their energies of transition, are provided in Table S8. Complex **4** exhibited three absorption bands at 264 nm (H−L^{5}), 328 nm (H^{-9}−L^{2}), 432 nm (H^{-1}−L), and 498 nm (H−L) (Figure S26). Experimentally, this complex showed absorption maxima at 263, 329, and 432 nm, and the theoretical values agree well with experimental values. The band around 480−490 nm in complexes **1**−**4** were not observed under experimental conditions, which may be due to the masking of weaker d−d transitions by the stronger charge-transfer transitions.

Application as Catalyst in Suzuki−Miyaura Coupling. Because the palladium-catalyzed cross coupling reactions find applications in synthetic organic chemistry and industry,[44] we have carried out a systematic study to test the catalytic efficiency of our palladium complexes in the SMC reaction. First, the reaction conditions were optimized using bromobenzene (1 mmol) and phenyl boronic acid (1.2 mmol) as model substrates and with complex **1** (0.005 mmol) as catalyst. This reaction was made to proceed at 70 °C with stirring. Among the different solvents and bases tested, ethanol−water mixture (4:1) and potassium carbonate (1.5 mmol) (Table S9, entry 13) gave an appreciable yield of biphenyl. Without addition of the catalyst, only a trace amount of the product was isolated (Table S9, entry 15), with the recovery of almost 90% of the reactants. This suggested that the catalyst is necessary for the reaction to progress.

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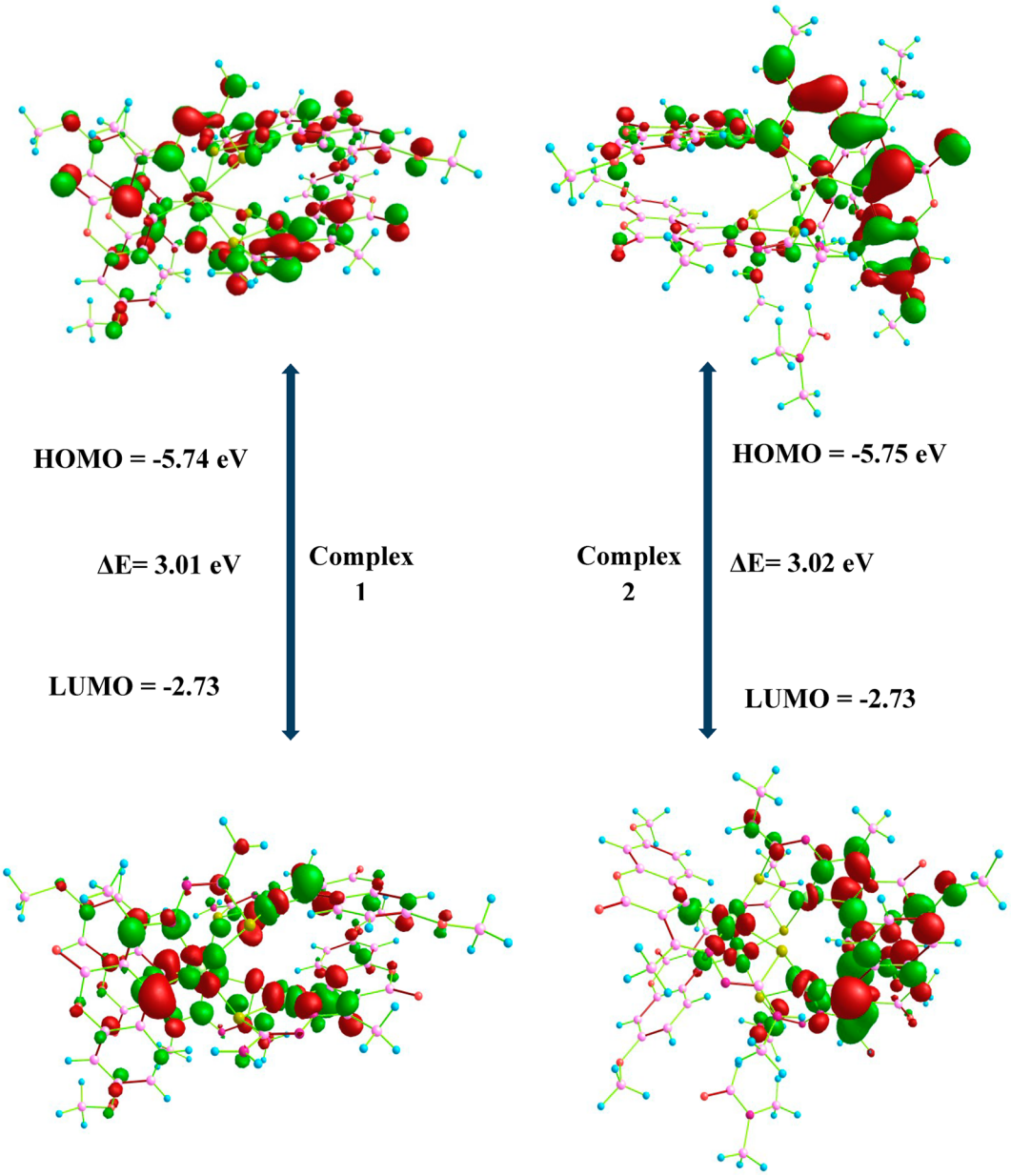

Figure 4. Energy level diagram between HUMO and LUMO of complexes **1** and **2** (in DMSO).

The activities of other palladium complexes were studied under identical reaction conditions as with complex **1**. Out of the four complexes, **1**, **2**, and **3** are tetranuclear, while complex **4** is mononuclear. Hence, for comparison the reaction using complex **4** was carried out with 0.02 mmol (assuming to be accounting for four Pd centers). The maximum yield (87%) of biphenyl was obtained in the case of complex **2** (Table S9, entry 18), and it was found to be the better catalyst in the SMC reaction. Varying the ratio of ethanol and water brought about a considerable difference in the yield (Table S10), and the outcomes suggested a 2:1 ethanol−water mixture to be the appropriate solvent for the catalytic reaction (Table S10, entry 3). Knowing that complex **2** is the better catalyst, catalyst loading was varied in a geometric sequence. Surprisingly, the reaction loaded with one-fourth amount of complex **2**, i.e., 0.00125 mmol, was found to give almost 97% yield of the product (Table S11, entry 3).

Having the optimized reaction conditions in hand, the scope of the SMC reaction is extended with various aryl halides and phenyl boronic acid (Table 1). The reactions were shown to proceed well with both electron-donating and electron-withdrawing substituents, producing an appreciable yield in all the cases. The scope of our catalytic system was extended to various chloroquinolines. It is interesting to note that the reactions of different chloroquinolines with phenyl boronic acid yielded the corresponding coupled products (Table 1, entries 17−20). These reactions required a higher temperature and reaction time when compared to others. In the case of dichloroquinoline (Table 1, entry 20), the formation of both monocoupled and dicoupled products was observed. The GC-MS chromatogram of entry 20 showed three prominent peaks, with two peaks of the same mass, which confirmed the formation of two monocoupled products because the coupling can occur at two positions. This is an indication that the used complex can be effectively applied as a catalyst for the coupling

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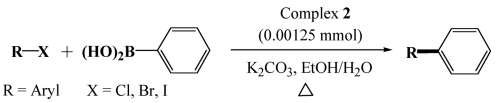
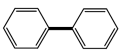
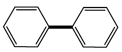
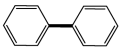
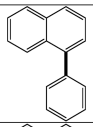
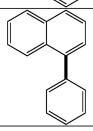
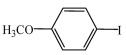
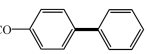
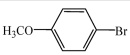
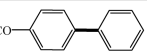
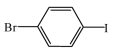
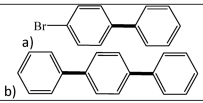
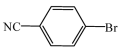
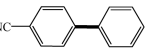
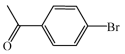
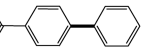
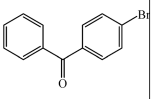
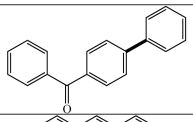
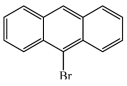
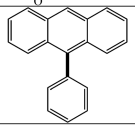
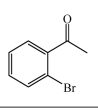
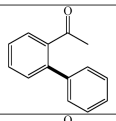
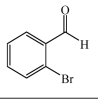
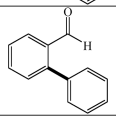
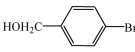
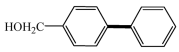
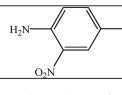
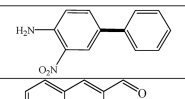
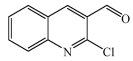
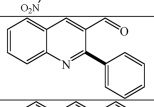
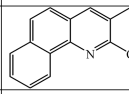
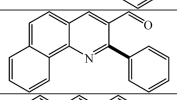
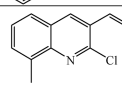
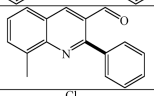
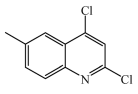
Table 1. Extension of Scope Using Catalyst 2 under Optimized Reaction Conditions[a]



Entry	R-X	Product	Temperature (°C)	Time (h)	Yield (%)[b]
1			70	3	99 (98)[c]
2			65	2	(99)[c]
3			70	5	(94)[c]
4			65	2	99 (98)[c]
5			70	3	99 (96)[c]
6			65	1.5	99 (98)[c]
7			65	2	(97)[c]
8[d]			70	4	a) 17 b) 83
9			70	4	99 (91)[c]
10			70	3	99 (96)[c]
11			62	2	98 (97)[c]
12			65	2	99 (93)[c]

Entry	R-X	Product	Temperature (°C)	Time (h)	Yield (%)[b]
13			70	1.5	51
14			65	2	91 (88)[c]
15			70	40 min	86
16			60	3	99(96)[c]
17			75	10	55
18			80	12	99
19			82	18	(65)[c]
20[d]			80	18	75 9

[a]Reaction conditions: aryl halide (1 mmol), phenyl boronic acid (1.2 mmol), K_2CO_3 (1.5 mmol), **2** (0.00125 mmol), EtOH−water (2:1). [b]Yield was determined by GC and GC-MS. [c]Isolated yield is given in parentheses. [d]Aryl halide (1 mmol), phenyl boronic acid (2.4 mmol), K_2CO_3 (1.5 mmol), **2** (0.00125 mmol), EtOH−water (2:1).

of quinoline substrates with boronic acids with appreciable yields. During the progress of all the reactions, palladium black formation was not observed, and hence, it is assumed that the catalysis entirely proceeds in a homogeneous way. The GC and GC-MS chromatograms of the coupled products are provided in Figures S27−S43. ^{1}H NMR spectra have been recorded for quinoline coupled products (Figures S44−S47).

With a view to extend the present approach for large-scale production, we intended to carry out a gram-scale synthesis using the reaction between 4-bromo anisole (5 mmol) and phenyl boronic acid (6 mmol). As expected, the product 4-methoxy biphenyl was obtained with 92% yield. To check the effectiveness of the catalyst, its reusability was assessed in parallel by taking bromobenzene and phenyl boronic acid as substrates. The catalyst has shown to be active for five cycles affording the yields of 97%, 96%, 88%, 83%, and 71%. On extension to the sixth cycle, almost 50% of its activity is lost (Figure 5).

The powder XRD patterns for the catalysts regenerated after first (**C1**), third (**C3**) and fifth (**C5**) cycles are shown in the Figure S48. In **C1** and **C3**, no peaks were observed at $2\theta = 40°$, 46°, 68°, 82°, and 86°, corresponding to (111), (200), (220), (311), and (222) indices of metallic Pd in a face centered cubic lattice. The obtained PXRD pattern clearly indicated that the activity of the catalyst is not due to any Pd(0) nanoparticle.[45] Instead, the catalysts have shown peaks at around 10.4°, 15.5°, and 26.4°. The pattern suggested **C1** and **C3** to be almost similar. Whereas in **C5**, there was a peak at 40.5°, which may be due to the formation of palladium nanoparticles (matching with JCPDS file no. 46-1043). For comparison, the PXRD spectrum of the catalyst (**C**) before performing the catalysis reaction was recorded (Figure S48).

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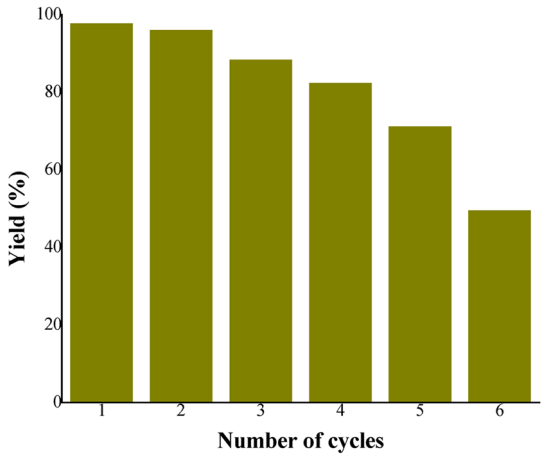


Figure 5. Reusability of the catalyst.

Peaks were found at 10.3°, 14.1°, 15.4°, 25.3°, and 26.5°, which are comparable with those observed for **C1** and **C3**.

The ^{1}H NMR spectra of the catalysts regenerated after the first (**C1**) and third (**C3**) cycles are provided in Figures S49 and S50. There were not many changes when we compare the spectrum taken originally (Figure S4) with the spectra taken after the first (Figure S46) and third cycles (Figure S50). This clearly indicated that the catalysts retained their nature even after three cycles.

A plausible mechanism for the formation of the coupled products is shown in Scheme 3, taking 4-bromoanisole and phenyl boronic acid as the model substrates. Initially, the tetranuclear complex breaks into a mononuclear complex, and oxidative addition of 4-bromoanisole results in the oxidation of Pd(II) (**A**) to Pd(IV) (**B**). Upon addition of the base, the intermediate **B** generates an intermediate **C** because of the metathetic exchange. Then, the intermediate **C** undergoes transmetalation with phenyl boronic acid to give **D**, which on reductive elimination gives the desired product.[4,46]

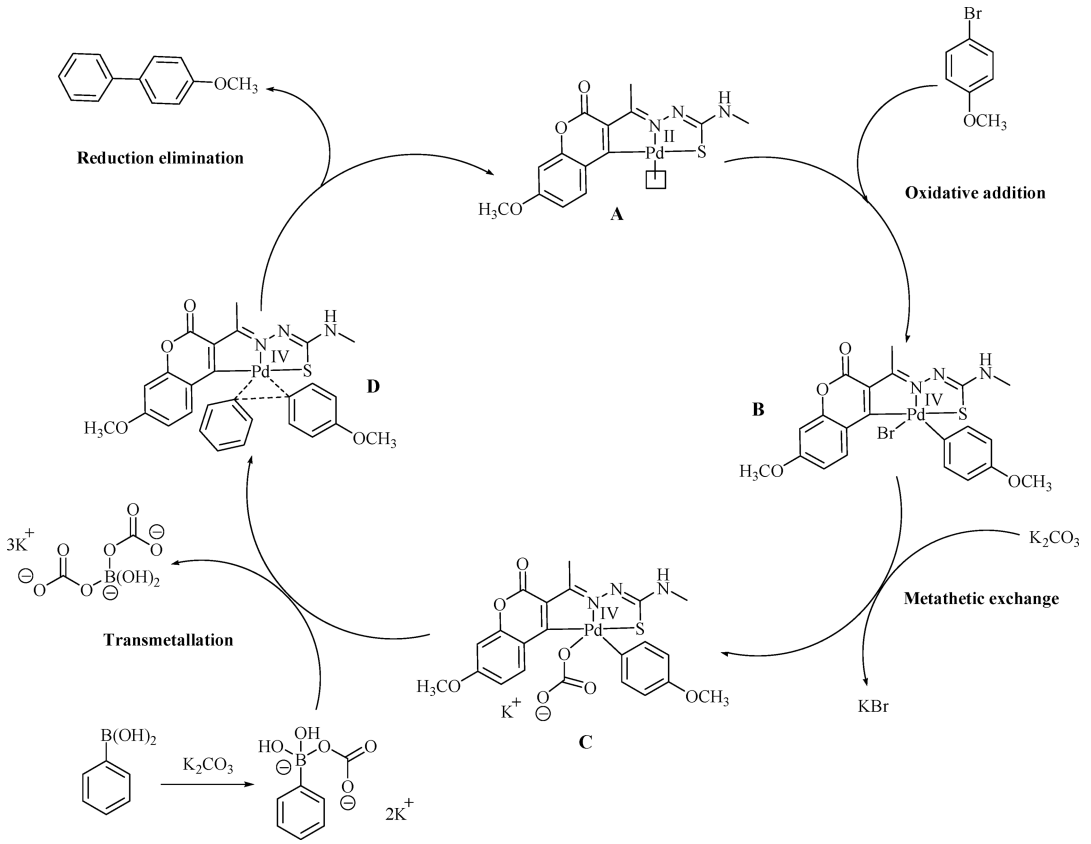
A comparison was made between the catalytic efficiency of our complex **2** and a few reported tetranuclear palladium(II) complexes (Table 2). Our catalyst showed activity comparable to the reported ones in an aqueous medium.

Table 2. Comparison of the Catalytic Activity with Literature Reports for the Coupling of 4-Bromoacetophenone with Phenyl Boronic Acid

entry	catalyst (mol %)	solvent	temperature (°C)	time (h)	yield (%)
1[47,a]	$Pd_4L_4(OAc)_4$ (0.012)	NMP/H_2O (1:1)	RT	1	86
2[48,b]	[Pd(4-CH_3O−C_6H_3−CH=N−NH−CO−2-C_4H_3O)(μ-Cl)]$_4$(0.02)	toluene	60	2	99
3[30a,a]	[$Pd_4L_4(\mu$-S)$_4Br_2$]·$2BF_4$(0.0005)	H_2O	60	24	48
4[c]	Pd_4L_4(0.00125)	EtOH/H_2O (2:1)	70	3	99

[a]Base, K_2CO_3; catalyst in mol % based on bromoarene. [b]Base, K_3PO_4·$7H_2O$. [c]This work; catalyst in mol % based on bromoarene.

Scheme 3. Plausible Mechanism for the Formation of Coupled Product



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CONCLUSION

In summary, an expedient synthesis of thermally stable tetranuclear palladium(II) complexes containing 3-acetyl-7-methoxy-2*H*-chromen-2-one Schiff bases is reported, and the structures of the complexes (**1**−**3**) were confirmed by XRD studies. In addition, the optimized structures of all the complexes have been derived using a DFT computational study. The complexes showed good activity as catalysts in Suzuki−Miyaura coupling reactions. Moreover, the catalyst (complex **2**) is able to bring about the coupling of chloroquinolines with phenyl boronic acid. This exposes the catalytic ability of our complex not only for iodo and bromo substrates but also for chloro compounds. Further extension would be the application to various other chloroquinolines with different aryl boronic acids.

EXPERIMENTAL SECTION

General. All the reactions presented were undertaken in clean oven-dried glassware, and the solvents employed were purified and dried according to the standard methods.[49] All other chemicals obtained from commercial sources were used as received. The ligands 3-acetyl-7-methoxy-2*H*-chromene-2-one-4(*N*)-substituted thiosemicarbazones ($\mathbf{H_2L^1}$−$\mathbf{H_2L^4}$) were prepared from the reaction of equimolar mixtures of 3-acetyl-7-methoxy-2*H*-chromen-2-one and thiosemicarbazide/4(*N*)-methyl thiosemicarbazide/4(*N*)-ethyl thiosemicarbazide/4(*N*)-phenyl thiosemicarbazide by following the reported procedure.[37] The metal precursor $K_2[PdCl_4]$ was prepared from potassium chloride and palladium chloride as reported elsewhere.[50] Melting points were measured on a Lab India apparatus. FT-IR spectra were recorded as KBr pellets using a Jasco FT-IR 4100 instrument between 400 and 4000 cm^{-1}. UV−visible spectra were run on a Jasco V-630 spectrophotometer, using DMSO as a solvent in the 200−800 nm range. ^{1}H NMR spectra of the complexes and coupled products were recorded at room temperature in DMSO-d_6 and $CDCl_3$, respectively, by using a Bruker 400 MHz instrument. Chemical shifts (δ) were presented in parts per million with reference to the signal of tetramethylsilane (TMS). The mass spectrum of complex **4** was recorded with a high-resolution Q-TOF mass spectrometer. The catalytic reactions were monitored with the help of a Shimadzu GC 2010 gas chromatograph and Shimadzu GCMS-QP 2010 gas chromatograph mass spectrometer fitted with a Restek-5 capillary column.

Syntheses of the Complexes. 3-Acetyl-7-methoxy-2*H*-chromen-2-one thiosemicarbazone $\mathbf{H_2L^{1-4}}$ (29−37 mg, 0.1 mmol) in dichloromethane (10 cm^3) was slowly added to a methanolic solution (10 cm^3) of $K_2[PdCl_4]$ (33 mg, 0.1 mmol) and refluxed for 2 h. A reddish orange precipitate found to separate was collected by filtration and dried. Recrystallization of the precipitated complex (**1**−**3**) in dimethylformamide/methanol yielded dark red crystals that were suitable for X-ray crystallography.

[Pd$_4$L$^1_4$] (**1**). Yield: 27%. mp: >280 °C. Anal. Calcd for $C_{52}H_{44}N_{12}O_{12}Pd_4S_4$: C, 39.45; H, 2.80; N, 10.61; S, 8.10. Found: C, 39.39; H, 2.75; N, 10.57; S, 8.03%. FT-IR (ν, cm^{-1}) in KBr: ν(C=O lactone) 1641, ν(C=N) 1578, ν(C−S) 760. UV−vis (DMSO), λ_{max}, nm (ε, dm^3 $mol^{-1}cm^{-1}$) 263 (34,910) (Intra ligand transition), 321 (29,840) (Intra ligand transition), 419 (38,496) (MLCT). ^{1}H NMR (400 MHz, DMSO-d_6, δ ppm, *J* Hz): 9.00 (s, 1H, −CHO (DMF)), 7.95 (d, *J* = 8 Hz, 1H, $-NH_2$), 7.30 (d, *J* = 2.4 Hz, 1H, $-NH_2$), 7.18 (dd, 3H, C5−H, C6−H, and C8−H), 3.93 (s, 3H, $-OCH_3$), 2.57 (s, 3H, $-CH_3$). ESI: *m*/*z* calcd. for $C_{52}H_{44}N_{12}O_{12}Pd_4S_4$, 1582.9190; found, 1582.4091 [M^+].

[Pd$_4$L$^2_4$] (**2**). Yield: 24%. mp: >280 °C. Anal. Calcd for $C_{62}H_{66}N_{14}O_{14}Pd_4S_4$: C, 41.71; H, 3.72; N, 10.98; S, 7.18. Found: C, 41.62; H, 3.68; N, 10.91; S, 7.15%. FT-IR (ν, cm^{-1}) in KBr: ν(C=O lactone) 1642, ν(C=N) 1593, ν(C−S) 758. UV−vis (DMSO), λ_{max}, nm (ε, dm^3 $mol^{-1}cm^{-1}$) 263 (33,490) (Intra ligand transition), 324 (36,420) (Intra ligand transition), 427 (89,970) (MLCT). ^{1}H NMR (400 MHz, DMSO-d_6, δ ppm, *J* Hz): 9.05 (s, 1H, −CHO (DMF)), 7.98 (d, *J* = 8.8 Hz, 1H, C5−H), 7.63 (br s, 1H, −NH), 7.32 (d, *J* = 2.4 Hz, 1H, C8−H), 7.21 (dd, 1H, C6−H), 3.95 (s, 3H, $-OCH_3$), 2.79 (d, *J* = 4 Hz, 3H, NH−CH_3), 2.62 (s, 3H, $-CH_3$). ESI: *m*/*z* calcd. for $C_{56}H_{52}N_{12}O_{12}Pd_4S_4$, 1639.0253; found, 1639.2641 [M^+].

[Pd$_4$L$^3_4$] (**3**). Yield: 22%. mp: >280 °C. Anal. Calcd for $C_{60}H_{60}N_{12}O_{12}Pd_4S_4$: C, 42.51; H, 3.56; N, 9.91; S, 7.56. Found: C, 42.44; H, 3.50; N, 9.87; S, 7.51%. FT-IR (ν, cm^{-1}) in KBr: ν(C=O lactone) 1644, ν(C=N) 1577, ν(C−S) 763. UV−vis (DMSO), λ_{max}, nm (ε, dm^3 $mol^{-1}cm^{-1}$) 266 (10,700) (Intra ligand transition), 327 (13,490) (Intra ligand transition), 428 (31,750) (MLCT). ^{1}H NMR (400 MHz, DMSO-d_6, δ ppm, *J* Hz): 7.96 (d, *J* = 8.8 Hz, 1H, C5−H), 7.67 (br s, 1H, −NH), 7.30 (d, *J* = 2.4 Hz, 1H, C8−H), 7.18 (dd, 1H, C6−H), 3.93 (s, 3H, $-OCH_3$), 3.17−3.24 (m, 2H, $-CH_2$), 2.59 (s, 3H, $-CH_3$), 1.06−1.09 (t, *J* = 7.2 Hz, 3H, terminal $-CH_3$). ESI: *m*/*z* calcd. for $C_{60}H_{60}N_{12}O_{12}Pd_4S_4$, 1695.1316; found, 1696.2725 [M + H]$^+$.

[PdHL^{4}Cl] (**4**). Yield: 77%. mp: 259 °C. Anal. Calcd for $C_{19}H_{16}N_3O_3PdSCl$: C, 44.89; H, 3.17; N, 8.26; S, 6.30. Found: C, 44.82; H, 3.13; N, 8.19; S, 6.22%. FT-IR (ν, cm^{-1}) in KBr: ν(C=O lactone) 1643, ν(C=N) 1586, ν(C−S) 755.UV−vis (DMSO), λ_{max}, nm (ε, dm^3 $mol^{-1}cm^{-1}$) 263 (39,850) (Intra ligand transition), 329 (19,540) (Intra ligand transition), 432 (42,400) (MLCT). ^{1}H NMR (400 MHz, DMSO-d_6, δ ppm, *J* Hz): 9.90 (s, 1H, −NH), 9.17 (s, 1H, C4−H), 8.03 (d, *J* = 8.8 Hz, 1H, C5−H), 7.56 (d, *J* = 8 Hz, 2H, C6−H and C8−H), 7.23−7.35 (m, 5H, phenyl protons), 3.97 (s, 3H, $-OCH_3$), 2.71 (s, 3H, $-CH_3$). ESI: *m*/*z* calcd. for $C_{19}H_{16}N_3O_3PdSCl$, 508.2866; found, 509.2641 [M + H]$^+$.

Crystal Structure Determination. Suitable single crystals of complexes **1**−**3** were obtained by the slow evaporation from a dimethylformamide−methanol mixture. The data were collected on a Rigaku AFC12 diffractometer with a Saturn 724+CCD using a graphite monochromator with Mo Kα radiation (λ = 0.71073 Å) at 100 K for complexes **1** and **3** and at 293 K for complex **2** using a Rigaku XStream Cryostream low-temperature device. Data reduction was performed by using Rigaku Americas Corporation's Crystal Clear version 1.40.[51] The structures were solved by direct methods using SHELXT[52] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-hydrogen atoms using SHELXL-2016/6.[53] Structure analysis was aided by use of the programs PLATON98[54] and WinGX.[55]

Density Functional Theory Computational Study. The DFT calculations of the synthesized complexes have been performed using Gaussian 09.[56,57] The geometries of complexes **1**−**4** were optimized by using the B3LYP functional with LANL2DZ/6-31G* basis set.[58] The relativistic corrected effective core potential with double-ζ LANL2DZ basis set has been used for Pd(II) metal, and the 6-31G* Gaussian split valency basis set with polarization functions has been used for the C, N, O, and S atoms of the molecules. In addition, for regress energy comparison, single-point energy calculations have been performed at the M062X/LANL2DZ level of theory. The optical properties of the structures are calculated from the time-dependent density functional theory (TD-DFT) calculations with the B3LYP/lanl2dz level of theory. Single-point solvent corrections are carried out by the B3LYP/LANL2DZ level of theory. The same levels of theory were used to carry out the UV absorbance calculations in the presence of DMSO by varying the number steps to 20, 50, and 100.

Procedure for the Suzuki−Miyaura Coupling Reaction. Aryl halide (1 mmol), potassium carbonate (1.5 mmol), and catalyst (0.00125 mmol) were dissolved in a 10 cm^3 round-bottom flask with 2:1 ethanol:water mixture and stirred at 70 °C. After complete dissolution, boronic acid (1.2 mmol) [2.4 mmol of boronic acid was used while coupling with aryl dihalides] was added, and the mixture was stirred further for given times. The progress of the reaction was monitored by thin-layer chromatography. The reaction mixture was then worked up with ethyl acetate, and the organic layer was collected and dried over anhydrous sodium sulfate. The resulting crude product was purified by means of column chromatography on silica gel using hexane and ethyl acetate as eluents. The coupled product was further

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analyzed by GC/GC-MS. The catalyst was recycled by centrifugation. Regenerated catalyst from three reactions was used to check its reusability, in order to maintain a quantitative amount of catalyst (1.25×10^{-3} mmol) in every reaction.

2-Phenyl-3-formylquinoline (Table 1, Entry 17). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm, J Hz): 10.50 (s, 1H, −CHO), 8.58 (s, 1H, C4−H), 7.83−7.85 (m, 5H, phenyl protons), 7.73 (d, J = 6.8 Hz, 1H, C8−H), 7.59 (d, J = 6 Hz, 1H, C5−H), 7.40−7.43 (t, J = 7.2 Hz, 2H, C6−H and C7−H).

2-Phenyl-3-formylbenzoquinoline (Table 1, Entry 18). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm, J Hz): 10.62 (s, 1H, −CHO), 9.24 (d, J = 3.6 Hz, 1H, C7−H), 8.74 (s, 1H, C4−H), 7.88−7.95 (m, 3H, C8−H, C9−H and C10−H), 7.79−7.80 (m, 5H, phenyl protons), 7.70 (d, J = 3.2 Hz, 2H, C5−H and C6−H).

2-Phenyl-3-formyl-8-methylquinoline (Table 1, Entry 19). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm, J Hz): 10.57 (s, 1H, −CHO), 8.71 (s, 1H, C4−H), 7.81 (d, J = 8 Hz, 1H, C6−H), 7.72 (d, J = 6.8 Hz, 2H, C5−H and C7−H), 7.51−7.57 (m, 5H, phenyl protons), 2.79 (s, 3H, $-CH_3$).

2,4-Diphenyl-6-methylquinoline (Table 1, Entry 20). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm, J Hz): 8.21 (s, 2H, C3−H and C5−H), 8.08 (d, J = 8 Hz, 1H, C8−H), 8.00 (s, 1H, C7−H), 7.49−7.63 (m, 10H, phenyl protons), 2.90 (s, 3H, $-CH_3$).

C1, Catalyst Regenerated after First Cycle (Figure S38). ^{1}H NMR (400 MHz, DMSO-d_6, δ ppm, J Hz): 8.00 (d, J = 8.4 Hz, 1H, C5−H), 7.66 (br s, 1H, −NH), 7.34 (s, 1H, C8−H), 7.22 (d, J = 8.4 Hz, 1H, C6−H), 3.96 (s, 3H, $-OCH_3$), 2.80 (s, 3H, NH−CH_3), 2.64 (s, 3H, $-CH_3$).

C3, Catalyst Regenerated after Third Cycle (Figure S39). ^{1}H NMR (400 MHz, DMSO-d_6, δ ppm, J Hz): 8.00 (d, J = 8 Hz, 1H, C5−H), 7.66 (br s, 1H, −NH), 7.34 (s, 1H, C8−H), 7.23 (d, J = 8.8 Hz, 1H, C6−H), 3.96 (s, 3H, $-OCH_3$), 2.80 (d, J = 4 Hz, 3H, NH−CH_3), 2.64 (s, 3H, $-CH_3$).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.9b00794.

Additional experimental methods, Figures S1−S50, and Tables S1−S11(PDF)

Accession Codes

CCDC 1863065−1863067 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: rpnchemist@gmail.com (R. Prabhakaran).
*E-mail: kar@nitt.edu (R. Karvembu).

ORCID

Ramasamy Karvembu: 0000-0001-8966-8602
Rathinasabapathi Prabhakaran: 0000-0002-8941-3295

Notes

The authors declare no competing financial interest.

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