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Palladium(II) 9,10-phenanthrenequinone N-substituted thiosemicarbazone/semicarbazone complexes as efficient catalysts for N-arylation of imidazole

PANNEERSELVAM ANITHA, RAJENDRAN MANIKANDAN[1] and PERIASAMY VISWANATHAMURTHI*

Department of Chemistry, Periyar University, Salem, India

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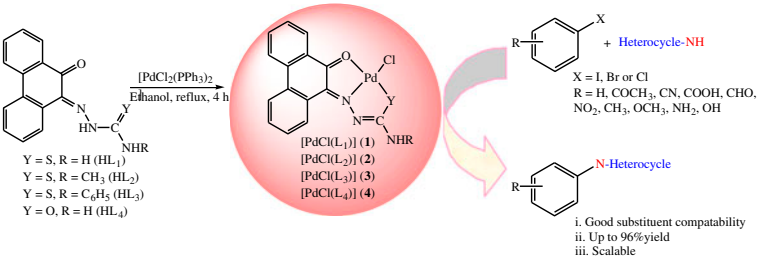


Palladium(II) 9,10-phenanthrenequinone N-substituted thiosemicarbazone/semicarbazone complexes as efficient catalysts for N-arylation of imidazole

A series of palladium complexes, [PdCl(L_{1-4})] (**1–4**) (L_1 = 9,10-phenanthrenequinone thiosemicarbazone, L_2 = 9,10-phenanthrenequinone methylthiosemicarbazone, L_3 = 9,10-phenanthrenequinone phenylthiosemicarbazone, and L_4 = 9,10-phenanthrenequinone semicarbazone), have been synthesized and characterized by elemental analyses, UV–vis, FT-IR, ^{1}H and ^{13}C NMR, and ESI-Mass spectroscopic methods. The catalytic efficiency of the synthesized complexes was examined against N-arylation of imidazole. The system works well with the electron-rich, -neutral, and -deficient aryl halides to afford the products in good to excellent yields. Sterically congested aryl halides and heteroaryl halides have also been used as substrates to provide N-arylated heterocycles. In addition, this methodology can be applicable to other substrates with N-containing heterocycles.

Keywords: ONS/ONO donor ligands; Pd-catalyzed; N-arylation; Imidazole; Aryl halides

1. Introduction

Organic molecules containing C(aryl)–N(heterocycle) linkages are found in numerous natural products and biologically active pharmaceuticals [1]. Therefore, extensive efforts

*Corresponding author. Email: viswanathamurthi72@gmail.com
[1]Present address: Department of Chemistry, KSR College of Arts and Science, Tiruchengode 637 215, India

are made to develop new and efficient synthetic transformations to make these linkages [2]. Among the synthetic transformations, transition metal complex catalyzed cross-coupling is an attractive tool for the synthesis of compounds containing C–N bond. Since Ohta and co-workers were the first to report the direct arylation of several heteroaromatics with aryl halides using $Pd(PPh_3)_4$ as the catalyst in 1990 [3], development of this coupling has proved to be a very powerful method for synthesis of a wide variety of arylated heterocycles [4]. This cross-coupling reaction provides cost-effective and environmentally attractive access to the target molecules because it can eliminate the need for the organometallic starting materials required in traditional cross-coupling methods, such as Stille, Suzuki or Negishi couplings. Moreover, the major wastes of the reaction are base associated with HX and the solvent, instead of metallic salts produced under classical cross-coupling procedures [5].

On the other hand, the environment around the coordination center is an important aspect in catalytic activity exhibited by metal complexes. The catalytic activity of complexes can be tuned by the coordinated ligands, either by altering the redox properties of metal or by impacting specific activity of ligand to the complexes [6–8]. Hence, selecting ligands in the coordination sphere of a metal is an interesting part of coordination chemistry and catalysis research. Chemistry of thiosemicarbazones has gained importance because of their simple preparation, unpredictable complexation properties and variety of applications [9]. The coordinating ability of thiosemicarbazones is attributed to extended delocalization of electron density over the –NH–C(S)–NH–N= system, which is enhanced by substitution on the terminal nitrogen. Variation in the substituent on the azomethine carbon of the thiosemicarbazone ligands influences the mode of their binding. On introduction of nitrogen or oxygen-containing substituents on azomethine carbon, it is anticipated that the binding ability of thiosemicarbazone becomes more capricious. The versatility of the thiosemicarbazone ligands for binding to the metal ion has been well documented. Besides the enormous structural diversity exhibited by the thiosemicarbazone complexes [10], they possess a wide range of applications in biology [11] and catalysis [12]. For the past few years, our group has been actively engaged in the synthesis and characterization of N-substituted thiosemicarbazone complexes with various transition metals [13]. In continuation of our efforts in understanding the coordination propensities of thiosemicarbazones, in this work, we have carried out the synthesis and structural characterization of palladium(II) complexes containing 9,10-phenanthrenequinone appended with derivatives of thiosemicarbazones/semicarbazone. In addition, the catalytic performance of the synthesized complexes was explored for arylation of nitrogen-containing heterocycles with aryl halides.

2. Experimental

2.1. *Materials and methods*

All reagents used were chemically pure and AR grade. The solvents were purified and dried according to standard procedures. The ligands HL_{1-4} and $[PdCl_2(PPh_3)_2]$ were prepared based on literature procedures [14, 15]. Microanalyses of carbon, hydrogen, nitrogen, and sulfur were carried out using a Vario EL III Elemental analyzer at SAIF – Cochin India. IR spectra of the ligands and their complexes were recorded as KBr pellets on a Nicolet Avatar model spectrophotometer from 4000 to 400 cm^{-1}. Electronic spectra of the complexes have

been obtained in dichloromethane using a Shimadzu UV-1650 PC spectrophotometer from 800 to 200 nm. ^{1}H and ^{13}C NMR spectra were measured on a Jeol GSX-400 instrument using $CDCl_3$ as the solvent at room temperature with TMS as the internal standard. The ESI-MS spectra were performed with a LC-MS Q-ToF Micro Analyzer (Shimadzu) in the SAIF, Panjab University, Chandigarh. Melting points were checked on a Technico micro heating table and are uncorrected.

2.2. *Synthesis of palladium(II) complexes*

An ethanol solution (10 mL) containing $HL_{1–4}$ (0.1 mmol) was added to $[PdCl_2(PPh_3)_2]$ (0.1 mmol) in ethanol (10 mL) and the resulting green solution was refluxed for 4 h. After cooling to room temperature, the green complex separated out, was filtered off and recrystallized from ethanol. Our efforts to obtain single crystals of the complexes were unsuccessful.

2.2.1. [PdCl(L_1)] (1). Yield 88%, m.p. 220 °C. Anal. calcd. for $C_{15}H_{10}ClN_3OPdS$ (%): C, 42.67; H, 2.39; N, 9.95; S, 7.59. Found: C, 42.34; H, 2.23; N, 9.67; S, 7.43. FT-IR (KBr, cm^{-1}): 1611 (quinone C=O), 1550 (C=N), 753 (C–S). UV–vis (λ_{max}, nm; ε_{max}, $dm^3\ mol^{-1}\ cm^{-1}$): 424 (5932), 398 (7677), 311 (9896), 250 (14325). ^{1}H NMR ($CDCl_3$, ppm): 9.90 (s, 1H, NH_2), 10.06 (s, 1H, NH_2), 7.18–7.98 (m, 8H, Ar–H). ^{13}C NMR ($CDCl_3$, ppm): 181.83 (quinone C=O), 169.97 (C–S), 161.18 (C=N), 124.03–136.81 (Ar–C). ESI-MS (m/z) = 422.6 [M^+].

2.2.2. [PdCl(L_2)] (2). Yield 85%, m.p. 214 °C. Anal. calcd. for $C_{16}H_{12}ClN_3OPdS$ (%): C, 44.05; H, 2.77; N, 9.63; S, 7.35. Found: C, 44.35; H, 2.51; N, 9.49; S, 7.71. FT-IR (KBr, cm^{-1}): 1618 (quinone C=O), 1551 (C=N), 761 (C–S).UV–vis (λ_{max}, nm; ε_{max}, $dm^3\ mol^{-1}\ cm^{-1}$): 446 (6325), 394 (7981), 334 (10112), 253 (16742). ^{1}H NMR ($CDCl_3$, ppm): 8.92 (s, 1H, NH–CH_3), 7.19–7.71 (m, 8H, Ar–H), 3.28 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, ppm): 180.01 (quinone C=O), 171.23 (C–S), 161.87 (C=N), 124.77–136.61 (Ar–C), 29.92 (CH_3). ESI-MS (m/z) = 436.1 [M^+].

2.2.3. [PdCl(L_3)] (3). Yield 87%, m.p. 225 °C. Anal. calcd. for $C_{21}H_{14}ClN_3OPdS$ (%): C, 50.62; H, 2.83; N, 8.43; S, 6.43. Found: C, 50.77; H, 2.50; N, 8.61; S, 6.21. FT-IR (KBr, cm^{-1}): 1619 (quinone C=O), 1521 (C=N), 758 (C–S). UV–vis (λ_{max}, nm; ε_{max}, $dm^3\ mol^{-1}\ cm^{-1}$): 426 (4739), 393 (6326), 320 (8467), 267 (12348). ^{1}H NMR ($CDCl_3$, ppm): 11.83 (s, 1H, NH–C_6H_5), 7.18–8.05 (m, 13H, Ar–H). ^{13}C NMR ($CDCl_3$, ppm): 179.91 (quinone C=O), 170.04 (C–S), 160.87 (C=N), 125.23–136.97 (Ar–C). ESI-MS (m/z) = 498.1 [M^+].

2.2.4. [PdCl(L_4)] (4). Yield 82%, m.p. 211 °C. Anal. calcd. for $C_{15}H_{10}ClN_3O_2Pd$ (%): C, 44.36; H, 2.48; N, 10.35. Found: C, 44.15; H, 2.60; N, 10.12. FT-IR (KBr, cm^{-1}): 1627 (quinone C=O), 1558 (C=N), 1180 (C–O). UV–vis (λ_{max}, nm; ε_{max}, $dm^3\ mol^{-1}\ cm^{-1}$): 445 (5012), 381 (6946), 330 (9322), 272 (13746). ^{1}H NMR ($CDCl_3$, ppm): 8.84, 8.98 (s, 2H, NH_2), 7.18–7.97 (m, 8H, Ar–H). ^{13}C NMR ($CDCl_3$, ppm): 180.01 (quinone C=O), 167.53 (C–O), 159.93 (C=N), 124.83–137.94 (Ar–C). ESI-MS (m/z) = 406.2 [M^+].

2.3. *Catalytic arylation of nitrogen-containing heterocycles with aryl halides*

Arylhalide (1.0 mM), nitrogen-containing heterocycle (1.2 mM), KOH (2 mM), and the catalyst (0.75 M%) were stirred in dimethyl sulfoxide (DMSO) (4 mL) at 110 °C for 10 h. After completion of the reaction, the mixture was cooled to room temperature, diluted with ethyl acetate (10 mL) and filtered. The filtrate was concentrated and the residue was purified by column chromatography on silica gel using hexane/ethyl acetate (70 : 30) as eluent to afford the desired product. The products have been characterized by ^{1}H NMR spectroscopy.

1-Phenyl-1H-imidazole. ^{1}H NMR ($CDCl_3$, ppm): 7.90 (s, 1H), 7.38–7.56 (m, 5H), 7.18 (s, 1H), 7.08 (s, 1H).

1-(4-Formylphenyl)-1H-imidazole. ^{1}H NMR ($CDCl_3$, ppm): 10.01 (s, 1H), 7.82–8.04 (m, 4H), 7.70 (s, 1H), 7.27 (s, 1H), 7.21 (s, 1H).

1-(4-Nitrophenyl)-1H-imidazole. ^{1}H NMR ($CDCl_3$, ppm): 8.18–8.32 (m, 4H), 7.93 (s, 1H), 7.34 (s, 1H), 7.20 (s, 1H).

1-(4-Cyanophenyl)-1H-imidazole. ^{1}H NMR ($CDCl_3$, ppm): 8.02 (s, 1H), 7.61–7.78 (m, 4H), 7.29 (s, 1H), 7.21 (s, 1H).

1-(4-Acetylphenyl)-1H-imidazole. ^{1}H NMR ($CDCl_3$, ppm): 8.10 (s, 1H), 7.58–7.80 (m, 4H), 7.26 (d, J = 6.8 Hz, 1H), 7.18 (d, J = 7.2 Hz, 1H), 2.68 (s, 3H).

4-(1H-Imidazol-1-yl)-benzoic acid. ^{1}H NMR ($CDCl_3$, ppm): 10.98 (s, 1H), 8.20 (s, 1H), 7.75–7.98 (m, 4H), 7.30 (d, J = 7.0 Hz, 1H), 7.22 (d, J = 7.2 Hz, 1H).

1-(4-Methoxyphenyl)-1H-imidazole. ^{1}H NMR ($CDCl_3$, ppm): 7.73 (s, 1H), 7.42–7.69 (m, 4H), 7.30 (s, 1H), 7.22 (s, 1H), 3.79 (s, 3H).

1-(4-Methylphenyl)-1H-imidazole. ^{1}H NMR ($CDCl_3$, ppm): 7.70 (s, 1H), 7.22–7.37 (m, 4H), 7.11 (s, 1H), 6.99 (s, 1H), 2.37 (s, 3H).

4-(1H-Imidazol-1-yl)-phenol. ^{1}H NMR ($CDCl_3$, ppm): 10.74 (s, 1H), 8.26 (s, 1H), 7.78–8.02 (m, 4H), 7.31 (d, J = 6.0 Hz, 1H), 7.22 (d, J = 6.2 Hz, 1H).

4-(1H-Imidazol-1-yl)-aniline. ^{1}H NMR ($CDCl_3$, ppm): 8.24 (s, 1H), 7.73–7.96 (m, 4H), 7.46 (d, J = 6.8 Hz, 1H), 7.28 (d, J = 7.2 Hz, 1H), 3.88 (s, 1H).

1-(2-Methoxyphenyl)-1H-imidazole. ^{1}H NMR ($CDCl_3$, ppm): 7.86 (s, 1H), 7.50–7.73 (m, 4H), 7.36 (d, J = 4.4 Hz, 1H), 7.23 (d, J = 5.0 Hz, 1H), 3.87 (s, 3H).

1-(2-Methylphenyl)-1H-imidazole. ^{1}H NMR ($CDCl_3$, ppm): 8.12 (s, 1H), 7.74–7.88 (m, 4H), 7.44 (d, J = 5.2 Hz, 1H), 7.28 (d, J = 5.0 Hz, 1H), 2.32 (s, 3H).

2-(1H-Imidazol-1-yl)-pyridine. ^{1}H NMR ($CDCl_3$, ppm): 8.23 (s, 1H), 7.78–8.02 (m, 4H), 7.48 (d, J = 4.8 Hz, 1H), 7.30 (d, J = 4.2 Hz, 1H).

2-(1H-Imidazol-1-yl)-pyrimidine. ^{1}H NMR ($CDCl_3$, ppm): 8.18 (s, 1H), 7.80–7.94 (m, 3H), 7.52 (d, J = 4.6 Hz, 1H), 7.41 (d, J = 5.2 Hz, 1H).

1-Phenyl-1H-pyrazole. ^{1}H NMR ($CDCl_3$, ppm): 7.78 (d, J = 3.8 Hz, 2H), 7.12–7.53 (m, 5H), 6.86 (t, J = 3.6 Hz, 1H).

1-Phenyl-1H-pyrrole. ^{1}H NMR ($CDCl_3$, ppm): 7.41–7.68 (m, 4H), 6.91–7.15 (m, 5H).

1-Phenyl-1H-indole. ^{1}H NMR ($CDCl_3$, ppm): 7.83 (d, J = 5.8 Hz, 1H), 7.69 (d, J = 6.0 Hz, 1H), 7.33–7.46 (m, 4H), 6.98–7.18 (m, 5H).

1-Phenyl-1H-benzimidazole. ^{1}H NMR ($CDCl_3$, ppm): 8.08 (s, 1H), 7.57–7.73 (m, 4H), 7.13–7.38 (m, 5H).

3. Results and discussion

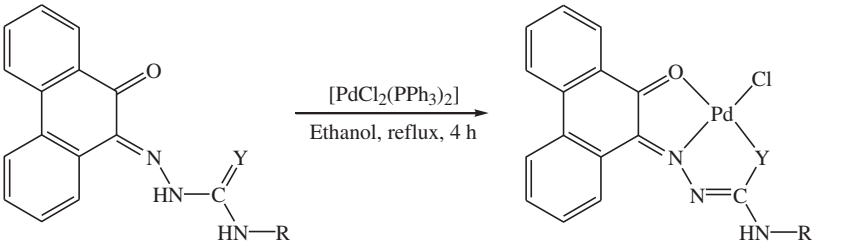
Reactions of $HL_{1–4}$ and $[PdCl_2(PPh_3)_2]$ in 1 : 1 molar ratio (scheme 1) were carried out in ethanol to obtain four-coordinate complexes (**1–4**). Complex **1** was already reported by the reaction of K_2PdCl_4 with HL_1 in ethanol [16]. The isolated complexes are stable in air, soluble in common solvents such as dichloromethane, chloroform, benzene, acetonitrile, ethanol, methanol, DMF, and DMSO. All the complexes were characterized by elemental analyses, IR, electronic, NMR, and ESI-mass spectra.

3.1. *FT-IR spectra*

The FT-IR spectra of the ligands and the corresponding palladium(II) complexes provided information about the metal–ligand bonding. Strong vibrations at 1593–1598 and 1630–1634 cm^{-1} in the ligands corresponding to azomethine ν(C=N) and quinone carbonyl ν(C=O) were shifted to lower wavenumbers, 1521–1558 and 1611–1627 cm^{-1}, respectively, in the complexes indicating participation of azomethine nitrogen and quinone oxygen in bonding [17]. A sharp band at 807–843/1674 cm^{-1} ascribed to ν(C=S)/ν(C=O) in the ligands disappeared in spectra of the palladium complexes and a new band at 753–761/1180 cm^{-1} due to ν(C–S)/ν(C–O) indicated coordination of the sulfur/oxygen after thio/keto enolization followed by deprotonation [18]. Further, the hydrazinic ν(N–H) band at 3111–3148 cm^{-1} in the free ligands disappears in all the complexes, suggesting deprotonation of the –NH group [19].

3.2. *Electronic spectra*

The electronic spectra of the palladium(II) complexes showed four bands from 250 to 451 nm. The appearance of bands below 470 nm suggests a square planar geometry around



Y = S, R = H (HL_1)
Y = S, R = CH_3 (HL_2)
Y = S, R = C_6H_5 (HL_3)
Y = O, R = H (HL_4)

[$PdCl(L_1)$] (**1**), Y = S, R = H
[$PdCl(L_2)$] (**2**), Y = S, R = CH_3
[$PdCl(L_3)$] (**3**), Y = S, R = C_6H_5
[$PdCl(L_4)$] (**4**), Y = O, R = H

Scheme 1. Synthetic route of palladium(II) complexes.

palladium(II) in the complexes [20, 21]. Bands in the ultraviolet region at 250–334 nm have been assigned to intra ligand transitions. The bands at 381–398 nm have been assigned to ligand to metal charge transfer transitions and the bands at 424–451 nm are due to metal to ligand charge transfer transitions [22, 23].

3.3. *NMR spectra*

^{1}H NMR spectra of the ligands and their complexes show signals in the expected regions. The singlets for the hydrazinic *ν*(N–H) proton of the free ligands at 13.82–14.81 ppm are absent in the complexes, supporting the enolization and coordination of the thiolate sulfur/enolate oxygen to palladium(II). The terminal NH_2 protons of HL_1 and HL_4 and their corresponding complexes show two singlets at 8.35–10.06 ppm. HL_2, HL_3, and their corresponding complexes show one singlet at 8.35–11.83 ppm assigned to NH methyl and NH phenyl protons. In spectra of all the complexes, the multiplet at 7.18–8.05 ppm is assigned to aromatic protons of ligands. Methyl protons are at 2.98–3.28 ppm (figures S1–S4, see online supplemental material at http://dx.doi.org/10.1080/00958972.2015.1071484).

^{13}C NMR spectra (figures S5–S8) of the complexes show a peak at 179.91–181.83 ppm assigned to quinone carbonyl (C=O). The azomethine (C=N) carbon has a resonance at 159.93–161.87 ppm. A sharp peak at 29.92 ppm is expected to be methyl carbon. Peaks at 169.97–171.23 and at 167.53 ppm are assigned to thiosemicarbazone C–S and semicarbazone C–O, respectively. The aromatic carbons are at 124.03–137.94 ppm.

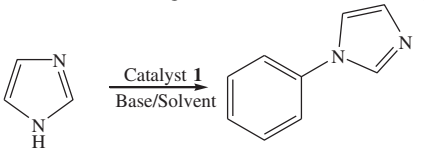
3.4. *Mass spectra*

ESI-Mass spectral analysis of the complexes (figures S9–S12) confirms the molecular masses of the complexes. The *m*/*z* values of the molecular ion peaks for **1–4** were obtained at 422.6, 436.1, 498.1, and 406.2 [M^+], respectively. The calculated molecular masses of these complexes are 422.2, 436.2, 498.2, and 406.1, in good agreement with calculated molecular masses.

3.5. *Catalysis*

3.5.1. Screening reaction conditions for N-arylation of imidazole with iodobenzene. In order to optimize the reaction conditions including solvent, bases, catalyst concentration, and time, a model reaction was carried out with iodobenzene and imidazole as the substrates and **1** as catalyst in the presence of Cs_2CO_3 at 110 °C for 10 h in different solvents (table 1). Among the solvents used, DMSO was the most beneficial to the catalysis, giving the desired product in 60% isolated yield (entry 6). Observation of the different bases indicated that KOH is the most favorable base for the model reaction (entry 8). To study the effect of amount of catalyst, the reactions were carried out at different concentrations of catalyst. An excellent yield was obtained for 0.75 M% of catalyst (entry 11) and it can be observed that even at very low catalyst loading of 0.25 M% (entry 10), moderate yield was obtained. No coupling product was observed without catalyst under similar reaction conditions (entry 15). To optimize the reaction time, different time intervals (6–14 h) were employed. Reaction time of 10 h gave a higher yield (entry 11). Finally, to choose the best catalyst among the synthesized complexes, the model reaction was carried out using **1–4** under the above-optimized conditions (table 2). From the results, **2** was the best catalyst

Table 1. Screening reaction conditions for N-arylation of imidazole with iodobenzene[a].



Entry	Solvent	Base	Catalyst (M%)	Time (h)	Yield (%)[b]
1	MeCN	Cs_2CO_3	0.5	10	27
2	Toluene	Cs_2CO_3	0.5	10	04
3	MeOH	Cs_2CO_3	0.5	10	16
4	DMAc	Cs_2CO_3	0.5	10	55
5	DMF	Cs_2CO_3	0.5	10	51
6	DMSO	Cs_2CO_3	0.5	10	60
7	DMSO	K_2CO_3	0.5	10	68
8	DMSO	KOH	0.5	10	75
9	DMSO	K_3PO_4	0.5	10	65
10	DMSO	KOH	0.25	10	52
11	DMSO	KOH	0.75	10	87
12	DMSO	KOH	1.0	10	87
13	DMSO	KOH	1.5	10	87
14	DMSO	KOH	2.0	10	88
15	DMSO	KOH	–	10	–
16	DMSO	KOH	0.75	6	49
17	DMSO	KOH	0.75	8	72
18	DMSO	KOH	0.75	12	87
19	DMSO	KOH	0.75	14	88

[a]Reaction conditions: iodobenzene (1.0 mM), imidazole (1.2 mM), base (2 mM), solvent (4 mL) at 110 °C.
[b]Isolated yield by the column chromatography.

Table 2. Selection of favorable catalyst for N-arylation of imidazole[a].

Complex	Yield (%)[b]
1	87
2	95
3	78
4	83

[a]Reaction conditions: iodobenzene (1.0 mM), imidazole (1.2 mM), KOH (2 mM), complexes **1–4** (0.75 M%) in 4 mL of DMSO were stirred for 10 h at 110 °C.
[b]Isolated yield by the column chromatography.

and showed yield of 95%. The order of reactivity of complexes with respect to different substituent on the thiosemicarbazone fragment of the ligands is **2** > **1** > **4** > **3**. Thus, **2** proved to be the most efficient complex for N-arylation of imidazole with iodobenzene in terms of yield and selectivity, 0.75 M% of catalyst loading was chosen, given the high yields and shorter reaction time to complete the process in presence of KOH in DMSO at 110 °C (10 h).

3.5.2. N-Arylation of imidazole with various aryl halides. With the optimized reaction conditions in hand, a number of aryl halides were screened to demonstrate the general applicability and efficacy of this protocol and the results are summarized in table 3. We

Table 3. N-Arylation of imidazole with various aryl halides.[a]

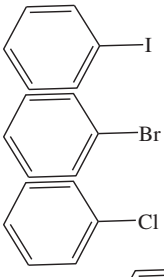
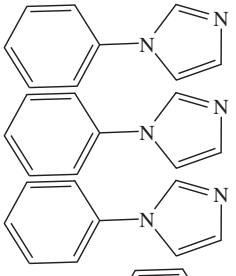
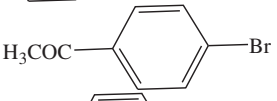
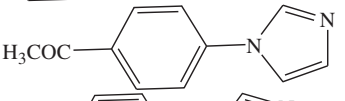
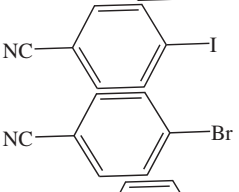
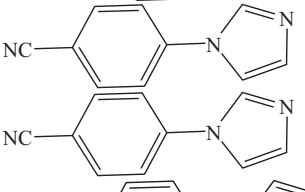
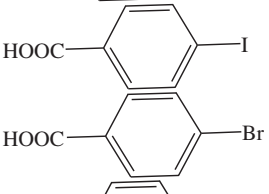
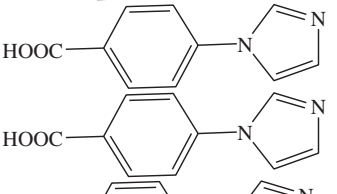
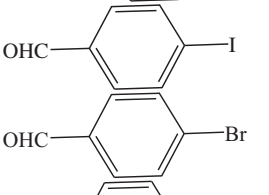
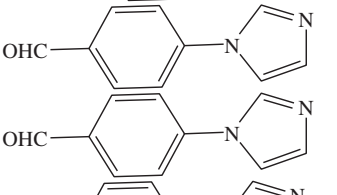
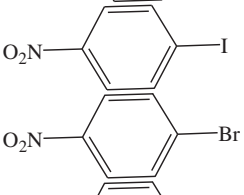
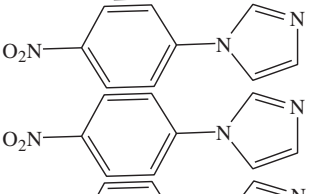
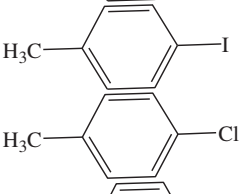
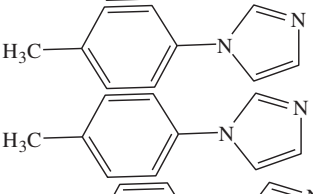
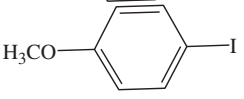
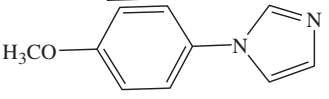
Arylhalide	Product	Conversion (%)[b]
		95 91 85
		87
		96 92
		93 87
		90 85
		95 90
		84 75
		82

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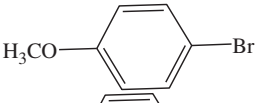
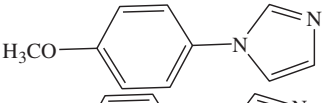
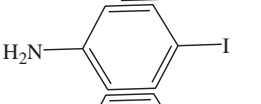
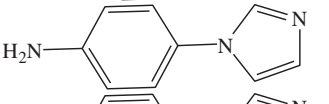
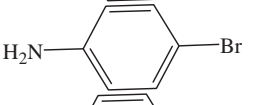
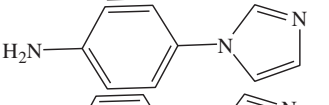
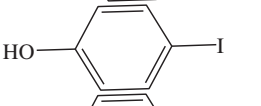
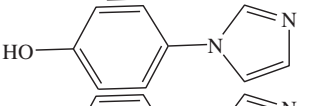
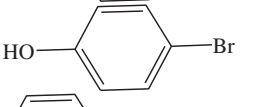
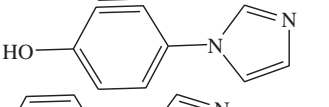
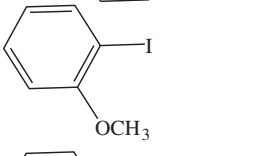
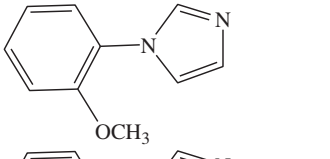
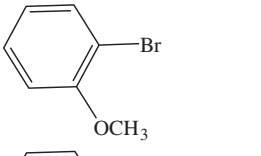
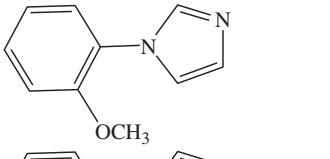
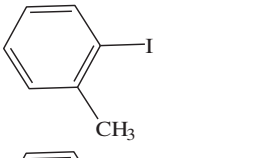
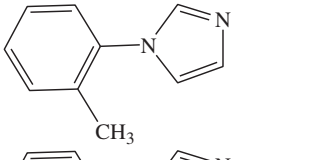
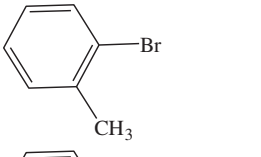
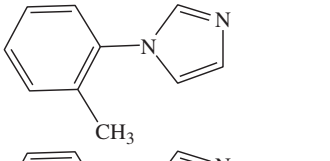
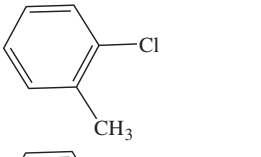
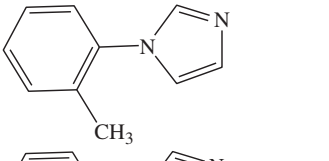
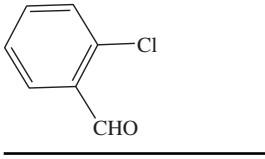
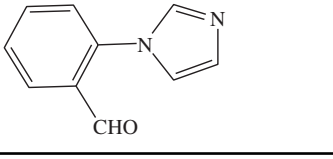
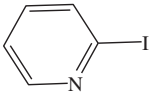
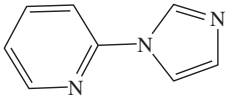
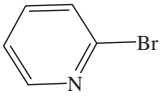
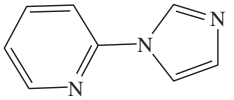
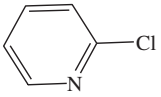
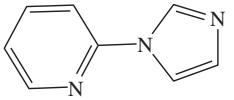
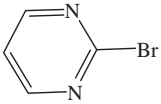
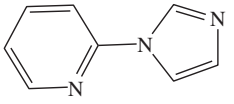
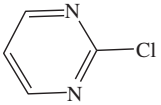
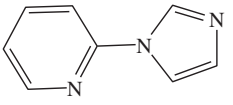
Table 3. (*Continued*).

Arylhalide	Product	Conversion (%)[b]
		77
		80
		75
		81
		73
		90
		84
		87
		85
		81
		80

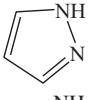
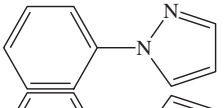
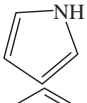
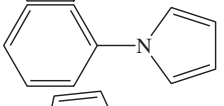
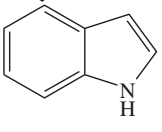
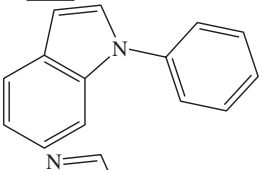
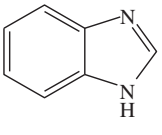
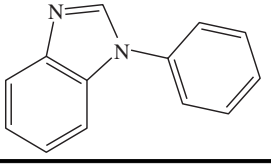
(*Continued*)

Table 3. (*Continued*).

Arylhalide	Product	Conversion (%)[b]
		89
		85
		82
		86
		84

[a]Reaction conditions: Aryl halide (1.0 mM), imidazole (1.2 mM), KOH (2 mM), complex **2** (0.75 M%) in 4 mL of DMSO was stirred for 10 h at 110 °C.
[b]Isolated yield by the column chromatography.

Table 4. N-Arylation of nitrogen-containing heterocycles with iodobenzene.[a]

N-Heterocycle	Product	Conversion (%)[b]
		81
		85
		78
		80

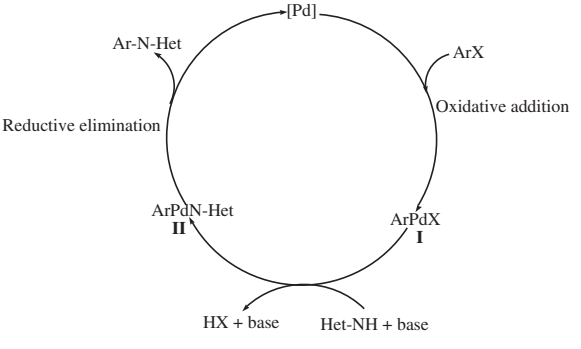
[a]Reaction conditions: Iodobenzene (1.0 mM), N-heterocycle (1.5 mM), KOH (2 mM), complex **2** (0.75 M%) in 4 mL of DMSO was stirred for 10 h at 110 °C.
[b]Isolated yield by the column chromatography.

were pleased to see that all the reactions proceeded smoothly and afforded the desired products in moderate to excellent yields upon isolation. For example, unsubstituted aryl halides and electron-deficient groups on the aryl halides afford coupling products in excellent yield whereas substrates with electron-rich groups gave moderate to good yields. This reaction was less sensitive to steric factors and gave good to excellent yields for *ortho* substituted aryl halides. Among them, the coupling proceeds readily with aryl iodides giving excellent yield of the corresponding N-aryl derivative. Heteroaryl halides also react smoothly giving an excellent yield.

3.5.3. N-Arylation of nitrogen-containing heterocycles with iodobenzene. In order to check the versatility of our catalyst, we decided to study the expanded substrates scope with various nitrogen-containing heterocycles such as pyrrole, pyrazole, indole, and benzimidazole (table 4). All the heterocyclic systems gave yields from 78 to 85% (entries 1–4) under optimized conditions. The present catalytic system works at mild reaction conditions with low reaction time, low catalyst loading, and the efficiency in terms of yield of products without side products is higher than the existing catalytic systems [24].

3.5.4. Mechanism. The exact mechanism for the catalytic N-arylation reactions is still under investigation. However, a proposed mechanism based on the literature [25] is provided in scheme 2. Pd(II) catalyst undergoes an oxidative addition reaction with aryl halide across C–X in the first step and forms an intermediate **I**. The palladium ion is Pd (IV) in **I** and reacts with heterocyclic amine in the presence of base to form **II**. In this step, heterocyclic amine simply replaces the halide ligand from **I**. In the final step, reductive elimination of intermediate **II** results in the formation of N-arylated product followed by the regeneration of Pd(II) catalyst. The oxidative addition and formation of intermediate **I** is more feasible in more polar solvents by polarization of the C–X bond of aryl halides (table 1).

Apart from this proposed mechanism, Pd(0)/(II) mechanism can also be suggested [26], on which the Pd(II) catalyst undergoes a reduction to Pd(0) by the solvent in the initial step, followed by oxidative addition as explained in previous mechanism. However, the reduction of Pd(II) is not favorable in DMSO. Therefore, we believe that the Pd(II)/(IV) mechanism is preferable.



Scheme 2. Possible mechanistic pathway for palladium(II) catalyzed N-arylation of imidazole.

4. Conclusion

Four-coordinate palladium(II) complexes, $[PdCl(L_{1–4})]$, have been synthesized by reacting 9,10-phenanthrenequinone N-substituted thiosemicarbazone/semicarbazone Schiff base ligands with $[PdCl_2(PPh_3)_2]$. Analytical and spectral (FT-IR, UV–vis, NMR, ESI-Mass) studies revealed that the ligand is coordinated to palladium(II) through quinone oxygen, imine nitrogen, and thiolate sulfur/enolate oxygen. The synthesized complexes show good catalytic activity in N-arylation of imidazole with aryl halides and give the corresponding N-arylimidazoles. The choice of the base and solvent is crucial to form these products in high yields. Using KOH as the base, DMSO as the solvent and 0.75 mol% of the catalyst, the target products were obtained in moderate to good yields with a wide variety of aryl halides. Complex **2** was the most active and hence was used for probing the scope of possible substrates. Substituents such as methyl, methoxyl, hydroxyl, formyl, acetyl, carboxyl, nitrile, amino or nitro group on the aryl halide are tolerated. Hindered aryl halides or heteroaryl halides were also suitable substrates using the conditions reported herein. In addition, the optimized catalyst efficiently catalyzes the cross-coupling reactions of other N-containing heterocycles with iodobenzene, affording the corresponding products in good yields. In the present catalyst system, no organometallic reagent is required, reducing the number of steps and therefore the mass of waste products. The major waste is relatively nontoxic base/HX instead of metal salts obtained in classical metal-catalyzed coupling reactions. For these reasons, the methodology developed here is very promising for the sustainable synthesis of N-aryl heterocycle.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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