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Synthesis, characterization and structure of new diazoketiminato chelates of palladium(II): Potential catalyst for C–C coupling reactions

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ABSTRACT

The 1N-(*N*,*N*-diethylaminoethyl)-2-arylazoaniline, HL [where HL = ArN = $NC_6H_4N(H)\{C_2H_4N(C_2H_5)_2\}$; Ar = C_6H_5 (for HL^1), *p*-MeC_6H_4 (for HL^2) or *p*-ClC_6H_4 (for HL^3)], ligands were prepared by treating the appropriate 2-(arylazo)aniline with 2-bromo-*N*,*N*-diethylethanamine. Reactions of Na_2PdCl_4 with HL afforded the [(L)PdCl] complexes. HL binds palladium(II) in a tridentate fashion (*N*,*N*,*N*), forming a new diazoketiminato chelate. The X-ray structure of [(L^3)PdCl] was determined to confirm the characterization. The newly synthesized complex [(L^1)PdCl] was utilized to carry out Suzuki and Heck reactions for a variety of substrates.

1. Introduction

This work stems from our interest on the coordination chemistry of palladium incorporating 2-(arylazo)aniline and related ligands [1–5]. The 2-(arylazo)aniline ligands and their derivatives, **1**, have been employed recently in the development of the coordination chemistry of palladium(II). Formation of six membered diazoketiminato chelates, **2**, and orthopalladation, **3**, are two noteworthy binding modes of the ligand **1** [1–5]. Six membered diazoketiminato chelates, **2**, were obtained upon dissociation of the amino proton when R′ = 2-benzyl pyridyl and H (Chart I), whereas in the other cases orthopalladation occurred, as shown in **3** [1–5].

The plausible mechanisms addressing the origin of such diversity in the binding mode of **1** have been described earlier [2,3]. As a result, we were encouraged to design new ligands having a specific binding mode. Over the past decade, several ligands, which are sterically and electronically suitable, have been developed for highly effective Suzuki and Heck reactions [6–41]. Efforts and advances have been made to design oxygen and/or moisture-stable ligands due to the water- and/or air-sensitivity of most ligands.

Furthermore, our interest centered on Heck and Suzuki reactions, catalyzed by coordination complexes of palladium, for both practical and scientific reasons. Synthesis of new palladium chelates that are stable under the Heck and Suzuki coupling reaction conditions is important in terms of their commercial application [36–38].

Palladium(II) complexes incorporating nitrogen donor ligands have been reported to exhibit catalytic activity in Suzuki and Heck reactions (Eqs. (1) and (2), respectively) [14–25], which drew our interest to study the catalytic activities of palladium(II) chelates of nitrogen donor azo ligands in homogenous media. Palladium chelates containing imines, oximes and diazobutadiene N-heterocyclic carbene ligands were shown to be active catalysts for the iodo and/or bromo aryl substrates (Eqs. (1) and (2)) [14–25]:

$$\underset{\text{X=I or Br}}{\text{Ar-X}} + \text{PhB(OH)}_2 \rightarrow \text{Ar-Ph} \quad (1)$$

$$\underset{\text{X=I or Br}}{\text{Ar-X}} + \text{Ph-CH=CH}_2 \rightarrow \text{Ar-CH=CH-Ph} \quad (2)$$

Scientifically, the field is in the midst of a debate on the nature of the active species and the mechanism of the Heck and Suzuki coupling reactions. In particular, the mechanisms were unclear when the catalysts used were palladacycle-based complexes or other palladium(II) chelates [39–41].

Herein we describe the synthesis of some new azoamine ligands, 1N-(*N*,*N*-diethylaminoethyl)-2-arylazoaniline, HL (**4**) and the reactions of these new ligands with Na_2PdCl_4. Formation of the diazoketiminato chelate of the composition [(L)PdCl], **5**, have been authenticated on the basis of X-ray studies and ^{1}H NMR spectroscopy. Suzuki and Heck coupling reactions were carried out, in the presence of air and moisture, using [(L^1)PdCl] as a catalyst.

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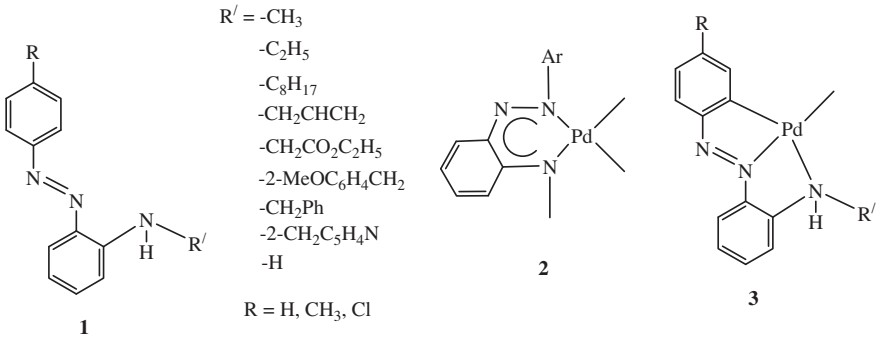


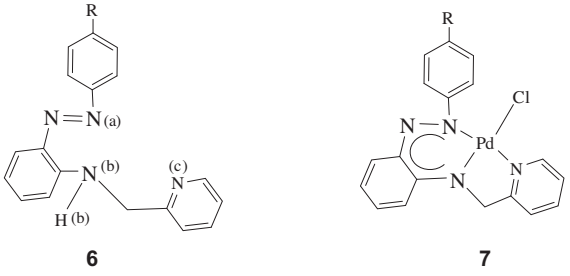
Chart I. Coordination modes of 2-(arylazo)aniline and related ligands.

The stability of the [(L)PdCl] catalysts under the reaction conditions has been verified.

2. Results and discussion

2.1. Syntheses

The new ligands 1N-(*N*,*N*-diethylaminoethyl)-2-arylazoaniline, HL (**4**), have been prepared by substituting one of the amino protons of 2-(aryazo)aniline with 2-bromo-*N*,*N*-diethylethanamine in the presence of potassium carbonate in refluxing acetonitrile (Scheme 1). The ligands were isolated as orange liquids after column chromatographic purification. Earlier it was reported, with a plausible mechanism, that tridentate (*N*,*N*,*N*) ligands of type **6** bind Pd(II) through N(a), N(b) and N(c) to form diazoketiminato chelates, **7**, dissociating the amino proton H(b).

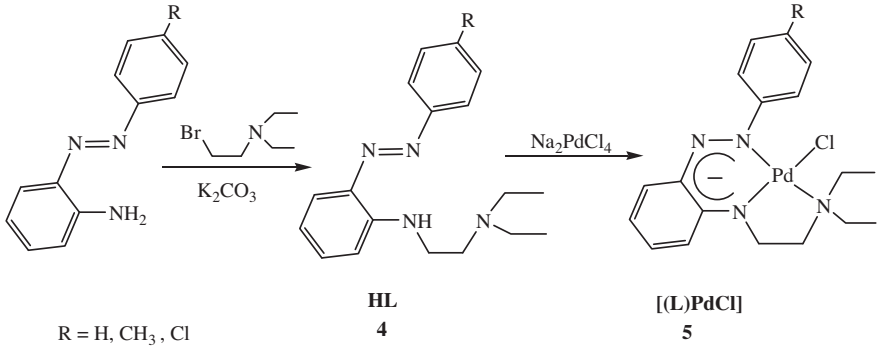


The coordinated N(*c*) is an sp^2 ring nitrogen (specifically the pyridyl nitrogen) in **6**. As a sequel, it was interesting to examine the coordination behavior of similar ligands where N(*c*) is an acyclic sp^3 amino-N, with the expectation that the HL ligands would form diazoketiminato chelates. Interestingly, the HL ligands afforded only diazoketiminato chelates of Pd(II), [(L)PdCl], **5**, upon treatment with Na_2PdCl_4 in methanol at room temperature (Scheme 1). The deprotonated HL ligand coordinated Pd(II) in a tridentate (*N*,*N*,*N*) fashion, which is consistent with our proposition reported earlier in the case of **6**.

2.2. Characterization

All the ligands displayed characteristic UV–Vis spectra with an absorption maxima near 325 nm, assigned to the n–π^* transition of azo compounds [1,42,43]. The [(L)PdCl] complexes exhibited a characteristic low energy absorption near 575 nm, which was assigned to a MLCT transition. Representative UV–Vis spectra of the ligand HL^1 and [(L^1)PdCl] are shown in Fig. 1. Relevant data are collected in Section 3. In the IR spectra, the $\nu_{N=N}$ band of the HL ligands (~1506 cm^{-1}) shifted to a lower frequency (1495 cm^{-1}) after formation of the Pd(II) chelates, [(L)PdCl], which was consistent with coordination of the azo nitrogen [1,42,43].

The compositions of the ligands HL and the corresponding palladium complexes [(L)PdCl] matched well with the C, H, N analytical data and ^{1}H NMR spectral data. The ^{1}H NMR data are given in Section 3. The ^{1}H NMR spectra of the ligands and the complexes have been described considering the atomic numbering scheme given in **8**. The HL ligands exhibited broad N–H signals with a triplet-like structure due to coupling with two 13-H protons. This N–H resonance is absent in the ^{1}H NMR spectra of the [(L)PdCl] complexes, signifying the dissociation of this proton upon complexation. As a result, the multiplet resonances (near δ 3.26 ppm) for the 13-H methylene protons of HL ligands turn into a triplet (near δ 3.71–3.44 ppm) in the spectra of the [(L)PdCl] complexes. The methyl signal of HL^2 was observed at δ 2.34 ppm. The aromatic proton resonances appeared in the region δ 7.79–6.35 ppm and are complicated due to overlapping of the signals, though the



Scheme 1. Synthesis of HL and LPdCl.

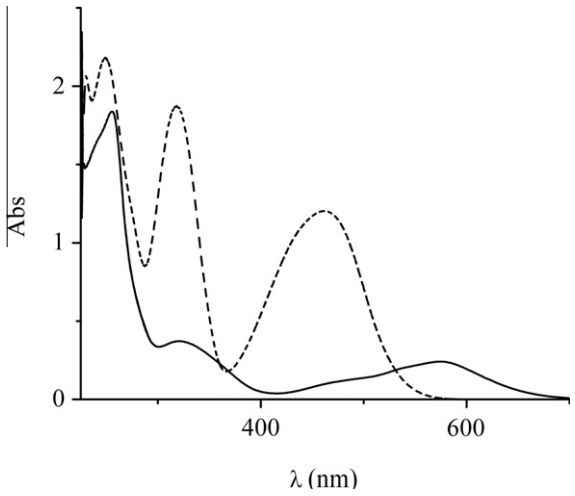


Fig. 1. UV–Vis spectra of HL^1 (---) and $[(L^1)PdCl]$ (—) in dichloromethane.

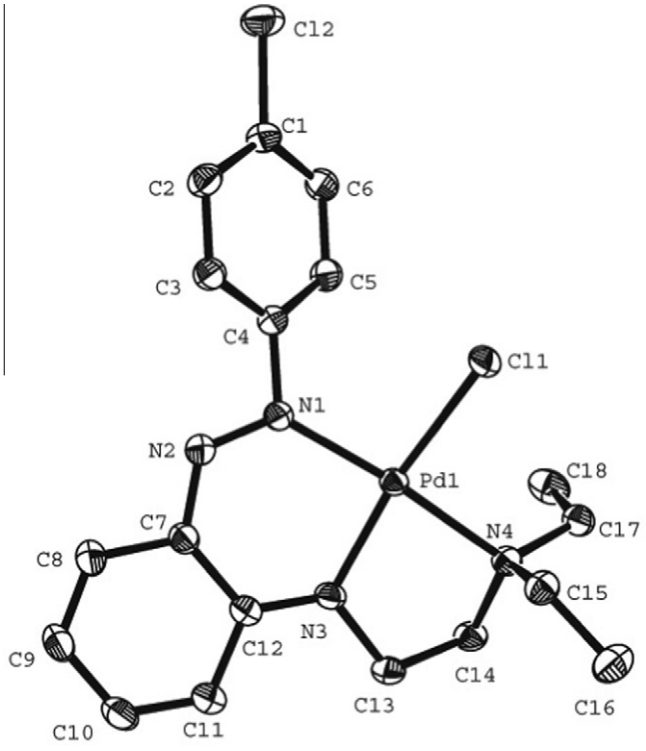
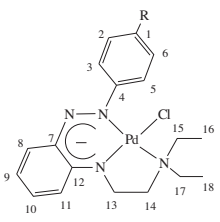


Fig. 2. Molecular structure of $[(L^3)PdCl]$ with the atomic numbering scheme. Hydrogen atoms are omitted for clarity.

integrations match well with the number of protons. Therefore the structure of the ligands and complexes in solution are very consistent with the molecular structures obtained from the X-ray studies (see below).



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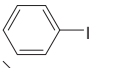
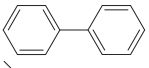
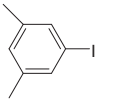
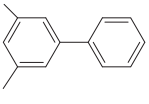
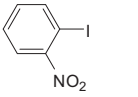
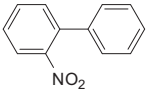
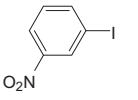
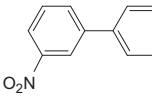
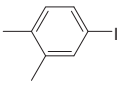
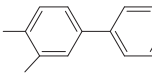
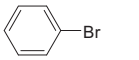
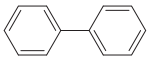
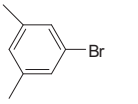
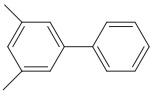
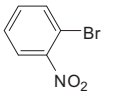
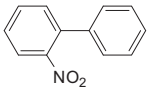
2.3. X-ray structure

Suitable crystals of $[(L^3)PdCl]$ were grown by slow diffusion of a dichloromethane solution into petroleum ether. A perspective view of the molecule is shown in Fig. 2 and selected bond distances and angles are collected in Table 1. The geometry about palladium is distorted square planar, where the mono anionic deprotonated ligand (L) binds in a tridentate (*N*,*N*,*N*) fashion. A chloride ligand satisfies the tetracoordination. The Pd(1)–N(azo), Pd(1)–N(aryl), Pd(1)–N(al-

Table 1
Selected bond distances (Å) and angles (°) for $[(L^3)PdCl]$, **3c**.

Distances			
Pd(1)–N(3)	1.9796(16)	Pd(1)–N(1)	2.0117(17)
Pd(1)–N(4)	2.1065(17)	Pd(1)–Cl(1)	2.3295(5)
N(1)–N(2)	1.285(2)	N(1)–C(4)	1.443(3)
N(2)–C(7)	1.355(3)	N(3)–C(12)	1.329(3)
N(4)–C(14)	1.486(3)	N(3)–C(13)	1.463(3)
N(4)–C(17)	1.495(3)	N(4)–C(15)	1.506(3)
C(13)–C(14)	1.495(3)	C(7)–C(8)	1.425(3)
C(7)–C(12)	1.438(3)	C(8)–C(9)	1.348(3)
C(9)–C(10)	1.402(4)	C(11)–C(12)	1.432(3)
C(10)–C(11)	1.358(3)		
Angles			
N(3)–Pd(1)–N(1)	91.14(7)	N(3)–Pd(1)–N(4)	83.61(7)
N(1)–Pd(1)–N(4)	174.38(7)	N(3)–Pd(1)–Cl(1)	166.74(5)
N(1)–Pd(1)–Cl(1)	95.41(5)	N(4)–Pd(1)–Cl(1)	90.14(5)
N(2)–N(1)–C(4)	110.18(16)	N(2)–N(1)–Pd(1)	126.45(14)
N(1)–N(2)–C(7)	124.29(18)	C(4)–N(1)–Pd(1)	123.34(13)
C(12)–N(3)–C(13)	119.20(17)	C(12)–N(3)–Pd(1)	125.42(14)
C(13)–N(3)–Pd(1)	113.85(13)	C(14)–N(4)–C(17)	109.84(16)
C(17)–N(4)–C(15)	109.71(17)	C(14)–N(4)–Pd(1)	103.04(12)
C(15)–N(4)–Pd(1)	105.38(12)	C(17)–N(4)–Pd(1)	116.64(13)

Table 2
Suzuki cross coupling reaction with the catalyst $[(L^1)PdCl]$.[x,y,z]

Aryl halide	Product	Isolated yield
		95
		90
		92
		90
		82
		78
		70
		76

[x] Solvent = THF.
[y] base = K_2CO_3.
[z] time = 2 h.

kyl) and Pd(1)–Cl(1) lengths (2.0117(17), 1.9796(16), 2.1065(17) and 2.3295(5) Å, respectively) are within the normal range [1–5,42]. The geometry about palladium is distorted square planar, justifying the oxidation state of Pd(II) and the uninegative ligand, since the complex is a non-electrolyte. The bond lengths within the ligand backbone are suitably altered due to delocalization of the negative charge [1–3]. The C(12)–N(3) length (1.329(3) Å) is shorter than the C–N single bond (N(1)–C(4), 1.443(3) Å) in the same molecule and is close to the imine (C=N) distance [1–3]. The effect of imine formation due to delocalization is reflected in the adjacent phenyl ring, which is distorted with two short (~1.35 Å) and four long (~1.42 Å) carbon–carbon bond distances. Thus the formation of an azoimine chelate could be inferred from the X-ray studies [1–3] and the structural formula of [(L^3)PdCl] has been drawn accordingly in **5** of Scheme 1 (vide supra).

2.4. Catalytic reactions

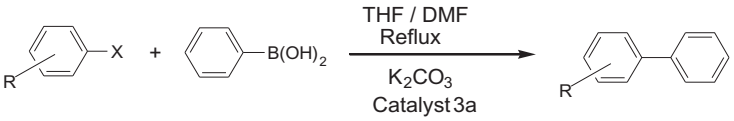
2.4.1. Suzuki cross-coupling reaction

The Suzuki cross-coupling reaction is a powerful method for C–C bond formation [6–25,36–41,43–45]. It is represented according to Eq. (1), where phenylboronic acid and aryl halides are used as substrates for C–C coupling. Synthesis of biaryl compounds exploiting the Suzuki reaction has gained importance in organic synthesis. Catalysts for Suzuki reactions are based on palladium metal, and large numbers of palladium complexes have been shown to be active catalysts for such reactions. Therefore, using the new palladium complex [(L)PdCl] as a catalyst, we carried out the Suzuki reaction (Eq. (3)) by coupling several arylhalides and phenylboronic acid in THF solvent. Temperature sensitive coupling reactions afforded the products only in low to moderate yield at room temperature (30–35 °C), whereas higher yields were obtained upon boiling whilst keeping the same reaction time. We carried out the Suzuki coupling reactions in refluxing THF (~66 °C) using K_2CO_3 as a base and keeping the reaction time constant, i.e. for 2 h in all the cases. The isolated yields of the products varied from 70% to 95% upon variation of aryl halide substrate. The results of the transformations are given in Table 2. All the reactions were carried out in contact with air:

At the end of each reaction the palladium catalyst was isolated and it was found that coupling reactions did take place reusing the isolated catalyst. This reusability of the catalyst was checked up to three times for a reaction, keeping the other conditions intact. The products were characterized by ^{1}H NMR spectroscopy. The palladium catalyst [(L)PdCl] could be separated from the products easily by column chromatography since it appears as an intense violet band with a lower R_f value than the products in the silica column. The most important and probably most controversial issue in such coupling reactions is the actual catalytic cycle. There have been discussions regarding two classes of palladium chelates that are used as catalysts for C–C coupling reactions. For one class of such catalysts, it was demonstrated that decomposition of the catalyst occurred under the reaction conditions leaving "naked" palladium as the active catalyst [43,44]. Another class of palladium complexes exhibited complete stability under the reaction conditions, indicating a mechanism may operate by a Pd(II)–Pd(IV) cycle [45]. As a result we examined the stability of the [(L^1)PdCl] catalyst under the reaction conditions. Spectrophotometrically (λ_{max} = 570 nm) we have shown that the amount of [(L)PdCl] taken for a reaction differed negligibly from the amount after it was refluxed in THF for 2 h in the presence of K_2CO_3 (Fig. S19). This observation may keep the issue of the Pd(0)–Pd(II) versus Pd(II)–Pd(IV) mechanism alive, and this may inspire the proponents of the Pd(II)–Pd(IV) cycle [45]. Quite a large number of suitable experimental data are necessary to come to a definite conclusion in this regard.

2.4.2. Heck reaction

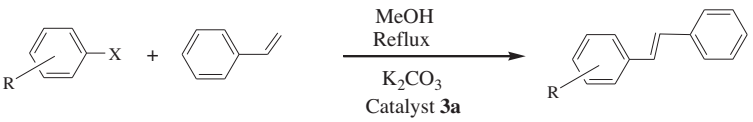
Heck coupling is another important palladium catalyzed C–C coupling reaction, where the substrates are arylhalides (bromoaryls and iodoaryls) and styrene [26–35]. We have studied the catalytic activity of [(L)PdCl] towards Heck coupling reactions. Conversions of arylhalides to the corresponding stilbene derivatives upon reaction with styrene using [(L)PdCl] as a catalyst in refluxing methanol and in presence of K_2CO_3 (Eq. (4)) have been examined. The results of the transformations are given in Table 3. All the reactions were carried out under ambient conditions. Although the catalysis occurred smoothly, at the end of each reaction the [(L)PdCl] catalyst could not be isolated, signifying the fact that the catalyst may actually be a precatalyst in these reactions.



X = I or Br

R = H, Me, NO_2

(3)

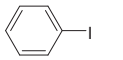
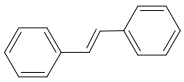
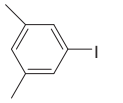
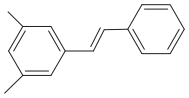
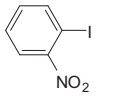
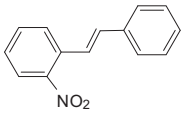
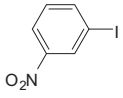
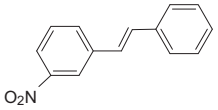
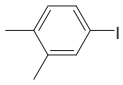
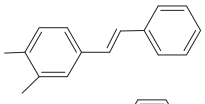
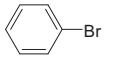
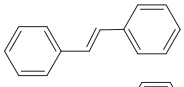
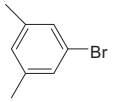
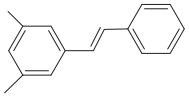
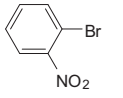
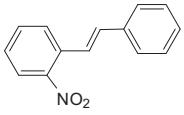


X = I or Br

R = H, Me, NO_2

(4)

Table 3
Heck reaction with the catalyst [(L^1)PdCl].[x,y,z]

Aryl halide	Product	Isolated yield
		95
		92
		90
		88
		92
		76
		80
		80

[x] Solvent = MeOH.
[y] base = K_2CO_3.
[z] time = 2 h.

Table 4
Crystallographic data for [(L^3)PdCl], **3c**.

Chemical formula	$C_{18}H_{22}Cl_2N_4Pd$
Formula weight	471.70
Crystal system	monoclinic
Space group	*P*21/*c*
a (Å)	7.6680(2)
b (Å)	10.5733(2)
c (Å)	23.1257(5)
α (°)	90
β (°)	90.6700(10)
γ (°)	90
λ (Å)	0.71073
V (Å^3)	1874.81(7)
F(000)	952
Z	4
T (K)	295(2)
D (mg m^{-3})	1.671
μ (mm^{-1})	1.283
R_1 (all data)	0.0316
wR_2 [$I > 2\sigma(I)$]	0.0590
Goodness-of-fit (GOF)on F^2	1.050

The yields of the products obtained from all the reactions were determined after isolation, and the products were characterized by ^{1}H NMR spectra:

3. Conclusion

The synthesis, characterization and structure of new diazoketiminato chelates of Pd(II) have been reported. Specifically *N*,*N*,*N* tridentate arylazo aniline derivatives are suitable for the formation of diazoketiminato chelates of Pd(II). The new [(L)PdCl] complexes have been used as catalysts for Suzuki and Heck coupling reactions. The [(L)PdCl] complexes are stable under the conditions of Suzuki coupling, indicating the catalytic activity of the molecular complex itself.

4. Experimental

4.1. Materials

The solvents used in the reactions were of reagent grade (E. Marck, Kolkata, India) and were purified and dried by reported procedures [46]. The 2-(arylazo)anilines were prepared according to the reported procedures [1,47,48]. Palladium chloride and potassium carbonate were purchased from E. Merck, Kolkata, India. 2-Bromo-*N*,*N*-diethylethanamine, phenylboronic acid, iodobenzene, bromobenzene, 1-iodo-3,5-dimethylbenzene, 1-iodo-3,4-dimethylbenzene, 1-iodo-2-nitrobenzene, 1-iodo-3-nitrobenzene, 1-bromo-3,5-dimethylbenzene, 1-bromo-2-nitrobenzene and styrene were purchased from Aldrich. Disodium tetrachloropalladate was prepared by a reported procedure [1].

4.2. Physical measurements

Microanalyses (C, H, N) was performed using a Perkin-Elmer 2400 C, H, N, S/O series II elemental analyzer. Infrared spectra were recorded on a Parkin-Elmer L120-00A FT-IR spectrometer with the samples prepared as KBr pellets. Electronic spectra were recorded on a Shimadzu UV-1800 PC spectrophotometer. ^{1}H NMR spectra were obtained on Brucker 400 spectrometers in $CDCl_3$.

4.3. Syntheses of the ligands

All the ligands, HL^1, HL^2 and HL^3, were prepared following similar procedures. A representative procedure for HL^1 is given below.

4.3.1. HL^1

A mixture of 2-(phenylazo)aniline (0.3 g, 1.52 mmol), 2-bromo-*N*,*N*-diethylethanamine (0.27 g, 1.52 mmol) and 1 g of K_2CO_3 in 30 cm^3 dry acetonitrile was refluxed for 5 h. The orange liquid mass that was obtained after evaporation of the solvent, afforded the ligand HL^1, which was isolated by column chromatography on silica gel (60–120 mesh) using the eluent petroleum ether:benzene (1:1 v/v). Upon evaporation of the solvent after chromatography, the orange-red liquid of pure HL^1 was obtained. Yield: 60%. *Anal.* Calc. for $C_{18}H_{24}N_3$ (282): C, 76.59; H, 8.51; N, 14.89. Found: C, 76.93; H, 8.36; N, 14.65%. UV–Vis λ_{max} (CH_2Cl_2, nm) (ε, M^{-1} cm^{-1}): 460 (8600), 320 (13400), 250 (15590), 230 (14740). IR (KBr pellets, cm^{-1}): 1509 (N=N). ^{1}H NMR ($CDCl_3$, ppm) δ: 8.81 (s, 1H), 7.79–7.75 (m, 3H), 7.40 (t, 2H), 7.31 (t, 1H), 7.19 (t, 1H), 6.72–6.67 (m, 2H), 3.30–3.25 (m, 2H), 2.70 (t, 2H), 2.58–2.52 (m, 4H), 0.99 (t, 6H).

4.3.2. HL^2 and HL^3

The ligands HL^2 and HL^3 were prepared using 2-(*p*-tolylazo)aniline and 2-(*p*-chlorophenylazo) aniline in place of 2-(phenylazo)aniline, respectively. Yield: HL^2, 60% and HL^3, 55%.

Anal. Calc. for $C_{19}H_{26}N_3$ (296): C, 77.02; H, 8.78; N, 14.18. Found: C, 76.73; H, 8.42; N, 14.45%. UV–Vis λ_{max} (CH_2Cl_2, nm) (ε, M^{-1} cm^{-1}): 460 (6620), 325 (10290), 250 (10850), 230 (12010). IR (KBr pellets, cm^{-1}): 1506 (N=N). ^{1}H NMR ($CDCl_3$, ppm) δ: 8.68 (s, 1H), 7.74 (d, 1H), 7.69 (d, 2H), 7.20–7.17 (m, 3H), 6.71–6.65 (m, 2H), 3.28–3.24 (m, 2H), 2.69 (t, 2H), 2.57–2.51 (m, 4H), 2.34 (s, 3H), 0.98 (t, 6H).

Anal. Calc. for $C_{18}H_{23}N_3Cl$ (316.5): C, 68.24; H, 7.26; N, 13.27. Found: C, 68.45; H, 7.12; N, 13.52%. UV–Vis λ_{max} (CH_2Cl_2, nm) (ε, $M^{-1}\,cm^{-1}$): 470 (6570), 325 (10230), 250 (10740), 210 (13010). IR (KBr pellets, cm^{-1}): 1506 (N=N). ^1H NMR ($CDCl_3$, ppm) δ: 8.86 (s, 1H), 7.75–7.71 (m, 3H), 7.35 (t, 2H), 7.23–7.18 (m, 1H), 6.72–6.67 (m, 2H), 3.29–3.25 (m, 2H), 2.69 (t, 2H), 2.57–2.52 (m, 4H), 0.98 (t, 6H).

4.4. Syntheses of the complexes

All the complexes, L^1PdCl, L^2PdCl and L^3PdCl, were prepared following similar procedures. A representative procedure for L^1PdCl is given below.

4.4.1. L^1PdCl

A solution of HL^1 (0.146 g, 0.52 mmol) in 10 cm^3 methanol was added to a solution of Na_2PdCl_4 (0.153 g, 0.52 mmol) in 5 cm^3 methanol. The mixture was stirred for 4 h. A dark solid precipitate was separated by filtration and purified by column chromatography using silica gel (60–120 mesh). The eluent was benzene:acetonitrile (95:5 v/v) mixed solvent. Upon evaporation of the solvent, a blue-violet solid of pure L^1PdCl was obtained. Yield: 60%. *Anal.* Calc. for $C_{18}H_{23}N_3PdCl$ (422.92): C, 51.07; H, 5.43; N, 9.93. Found: C, 51.18; H, 5.50; N, 10.00%. UV–Vis λ_{max} (CH_2Cl_2, nm) (ε, $M^{-1}\,cm^{-1}$): 574 (4000), 321 (6300), 255 (31000). IR (KBr pellets, cm^{-1}): 1493 (N=N). ^1H NMR ($CDCl_3$, ppm) δ: 7.64–7.62 (m, 1H), 7.43 (t, 2H), 7.30–7.16 (m, 4H), 6.76 (d, 1H), 6.51 (t, 1H), 3.59 (t, 1H), 3.24–3.16 (m, 2H), 2.86–2.77 (m, 4H), 1.45 (t, 6H).

4.4.2. L^2PdCl and L^3PdCl

The complexes L^2PdCl and L^3PdCl were prepared using HL^2 and HL^3 in place of HL^1, respectively. Yield: L^2PdCl, 60% and L^3PdCl, 55%.

Anal. Calc. for $C_{19}H_{25}N_3PdCl$ (436.92): C, 52.18; H, 5.72; N, 9.61. Found: C, 52.35; H, 5.83; N, 9.50%. UV–Vis spectrum λ_{max} (CH_2Cl_2, nm) (ε, $M^{-1}\,cm^{-1}$): 574 (3700), 325 (5800), 254 (29000). IR (KBr pellets, cm^{-1}): 1496 (N=N). ^1H NMR ($CDCl_3$, ppm) δ: 7.50–7.48 (m, 1H), 7.19 (t, 2H), 7.10–7.05 (m, 3H), 6.94 (d, 1H), 6.61 (d, 1H), 6.31 (t, 1H), 3.44 (t, 2H), 3.09–3.03 (m, 2H), 2.70–2.63 (m, 4H), 2.15 (s, 3H), 1.30 (t, 6H).

Anal. Calc. for $C_{18}H_{22}N_3PdCl_2$ (458.42): C, 47.61; H, 4.79; N, 9.16. Found: C, 47.27; H, 4.75; N, 9.25%. UV–Vis spectrum λ_{max} (CH_2Cl_2, nm) (ε, $M^{-1}\,cm^{-1}$) = 579 (4600), 324 (6900), 254 (31000). IR (KBr pellets, cm^{-1}): 1496 (N=N). ^1H NMR ($CDCl_3$, ppm) δ: 7.68 (dd, 1H), 7.46 (d, 2H), 7.34–7.28 (m, 4H), 6.85 (d, 1H), 6.59 (t, 1H), 3.69 (t, 2H), 3.51–3.24 (m, 2H), 2.94–2.86 (m, 4H), 1.54 (t, 6H).

4.5. General procedures for the Suzuki cross coupling reaction and isolation of the catalyst

A mixture containing phenyl boronic acid (0.183 g, 1.5 mmol), aryl halide (1.5 mmol), the palladium complex [(L^1)PdCl] (0.0005 mmol) and potassium carbonate (0.174 g, 3.0 mmol) in THF (10 ml) was heated to reflux for 2 h, as mentioned in Table 2. After evaporation of the solvent, the reaction mixture was extracted with diethyl ether. The ether solution was dried over Na_2SO_4 and filtered. The ether solution was passed through a 12 inch silica column (60–120 mesh) and the complex remain trapped. After extraction of the desired compound, the complex was extracted using dichloromethane. The complex remains unchanged after being reused three times. Upon evaporation of the ether, solid pure products were obtained. The yields of the products obtained from all the reactions were determined after isolation, and the products were characterized by ^1H NMR spectra.

4.6. General procedures for the Heck reaction

A mixture containing styrene (3.5 mmol), aryl halide (3.5 mmol), the palladium complex [(L^1)PdCl] (0.001 mmol) and potassium carbonate (8.0 mmol) in methanol (10 ml) were heated to reflux for 4 h, as mentioned in Table 3. After evaporation of the solvent, the product was poured into water and extracted with diethyl ether. The ether solution was dried over Na_2SO_4 and filtered. The ether solution was passed through a 12 inch silica column (60–120 mesh) and the complex remain trapped. After extraction of the desired compound, the complex was extracted using dichloromethane. Upon evaporation of the ether, solid pure products were obtained. The yields of the products obtained from all the reactions were determined after isolation, and the products were characterized by ^1H NMR spectra.

5. Crystallography

A single crystal of [(L^3)PdCl] was grown by slow diffusion of petroleum ether into a dichloromethane solution at 298 K. Data were collected by the ω-scan technique on a Bruker Smart CCD diffractometer with Mo Kα radiation monochromated by graphite crystal. The structure solution was done by direct methods with the SHELXS-97 program [49,50]. Full matrix least square refinements on F^2 were performed using the SHELXL-97 program [49,50]. All non-hydrogen atoms were refined anisotropically using reflections $I > 2\sigma(I)$. All hydrogens were included at calculated positions. The data, collection parameters and relevant crystal data are collected in Table 4.

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Appendix A. Supplementary data

CCDC 803660 contains the supplementary crystallographic data for [(L^3)PdCl]. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2011.11.026.

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