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A strategy of Pd(II) assisted C–H activation in 2-alkylamino azobenzene ligands: Syntheses, characterisation and structure of a new family of orthopalladated complexes

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Abstract

Several 2-(arylazo)-*N*-alkyl aniline ligands, **1a**–**11a**, have been prepared by the reaction between 2-(arylazo) aniline and the appropriate alkyl halide in the presence of K_2CO_3. Treatment of sodium tetrachloropalladate with **1a**–**11a** in methanol afforded the orthopalladated complexes **1b**–**11b**, where the ligand is tridentate (C,N,N). The ligands and complexes were characterised from spectroscopic data and confirmed by X-ray studies. The X-ray structure of **9b** displayed an unsupported Pd(II)···Pd(II) interaction (3.301 Å).

Keywords: 2-Alkylamino azobenzene; Sodiumtetrachloropalladate; Orthopalladation; C–H activation

1. Introduction

Currently there is considerable interest in the exploitation of transition metal mediated C–H activation for bringing about interesting organic transformations [1]. These reactions involve the formation of reactive organometallic complexes, from which the desired products are yielded. This work reports the results of palladation reactions of several new azoamine substrates. The reasons for choosing the azoamine target molecule are manifold. Due to the basic interest and potential applications of aromatic azo compounds, it is an active area of chemical research. The notable features of their interests include photochromism [2] redox activity [3] and liquid crystal properties [4]. Syntheses of organometallic or coordination compounds of azo ligands with enhanced performance are still required. On the other hand, thermotropic mesogens bearing an appropriate functional group can be relevant for electro-optical devices [5]. Therefore, specific functionalisation of new azo systems via C–H activation would increase the scope of research in this area.

With this background in mind, we are concerned with synthesising new azoamine molecules since there are only a few examples where these were utilized [6] as ligands. The reaction of 2-(arylazo) aniline, **A** (Chart 1), one of the simplest azoamine ligands, with platinum metals has been described only recently [6]. Nevertheless, the C–H activation in 2-(arylazo) aniline did not occur as a result of unsuitable electronic criteria and mismatch in appropriate geometry due to the formation of a six membered azoimine chelate **B** (Chart 1) upon dissociation of the amino proton. These results drew our interest in synthesising modified 2-(arylazo) aniline ligands and examining their reactions with Na_2PdCl_4. Herein, we describe the syntheses of several such ligands and the corresponding orthopalladated complexes of type **C** (Chart 1). The ligands and complexes have been characterized from the spectroscopic data. The crystal

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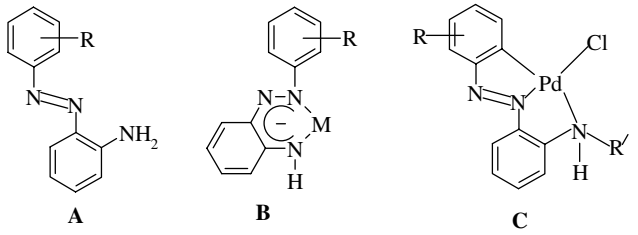


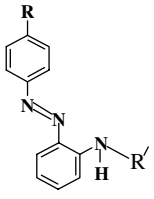
Chart 1.

structure of one of the complexes has been determined to confirm the molecular structure. Weak unsupported dimers have been recognized in the crystal lattice.

2. Results and discussion

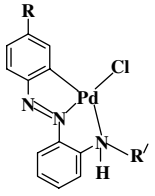
2.1. Syntheses

The orange coloured 2-arylazo-1*N*-alkyl aniline, **1a**–**11a** (Chart 2) ligands were prepared by refluxing 2-(arylazo) anilines with the appropriate alkyl halide in ethanol or DMF in the presence of potassium carbonate (Scheme 1). The product formations were monitored on a TLC plate. Eleven ligands were prepared by modifying R′ and R as given in Chart 2. The R′ substituents were chosen on the basis of increasing chain length (H_3C–, H_5C_2–, $H_{17}C_8$–,) and varying the probable binding sites (CH_2=CH–CH_2–, 2-$MeOC_6H_4CH_2$–, $C_6H_5CH_2$–, EtO_2CCH_2–). Reaction of **1a**–**11a** with sodium tetrachloropalladate in methanol at room temperature afforded brown coloured complexes of composition **1b**–**11b** (Scheme 1) as shown in (Chart 1). The orthopalladated complexes are formed upon substitution of the *ortho* aryl proton from the azobenzene fragment of the ligand precursors **1a**–**11a**. Eleven orthopalladated complexes were prepared, where the binding modes (C,N,N) of the ligands were identical (^{1}H NMR and X-ray, see below), unlike 2-(arylazo) aniline [6]. One of the important observations is the coordination of the secondary amino nitrogen without dissociating the proton. In the case of other azoamine ligands, the secondary amino groups bind the metals only when the amino proton gets dissociated [7]. Thus the complexes, **1b**–**11b**, are the first family of orthopalladated azoamine molecules. The formation of a metal–carbon bond has been presumed to occur as a result of prior binding with a suitable hetero donor atom fulfilling the electronic criteria and appropriate geometry about the metal with respect to the *ortho* carbon atom.



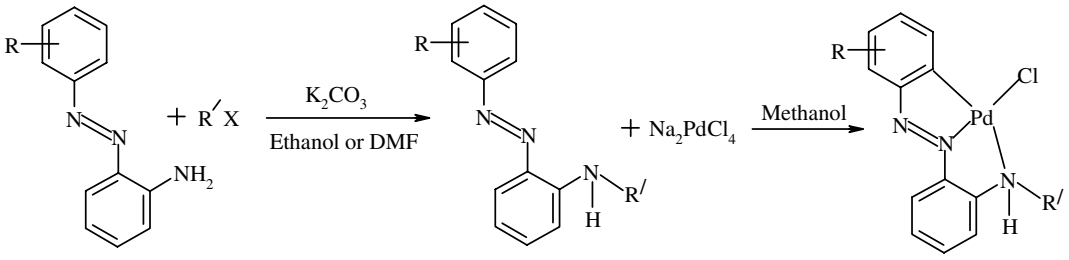
Ligand

Ligand	R	R′	Complex
1a	H	CH_3	**1b**
2a	CH_3	CH_3	**2b**
3a	H	C_2H_5	**3b**
4a	CH_3	C_2H_5	**4b**
5a	CH_3	C_8H_{17}	**5b**
6a	CH_3	CH_2CHCH_2	**6b**
7a	CH_3	2-$MeOC_6H_4CH_2$	**7b**
8a	H	CH_2Ph	**8b**
9a	CH_3	CH_2Ph	**9b**
10a	Cl	CH_2Ph	**10b**
11a	CH_3	$CH_2CO_2C_2H_5$	**11b**



Complex

Chart 2.



Scheme 1.

2.2. Characterisation

The ligands, **1a**–**11a**, and the corresponding orthopalladated complexes, **1b**–**11b**, exhibit characteristic UV–Vis spectra. Representative spectra for **9a** and **9b** have been shown in Fig. 1. It is interesting to observe that the UV–Vis spectra of all the brown orthopalladated complexes are similar, with a low energy split band in the range 490–470 nm and a structured band within the range 410–360 nm. The spectral data for all the ligands and complexes are collected in Table 1.

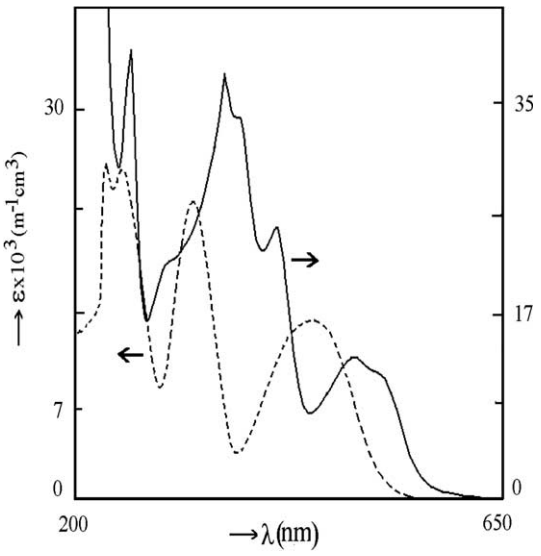


Fig. 1. UV–Vis spectra of **9a** (---) and **9b** (—). The arrows indicate scales of the corresponding spectra.

The ligands, **1a**–**11a**, displayed a ν_{N-H} absorption as a single band in the range of 3488–3413 cm^{-1}, whereas for the complexes **1b**–**11b**, the ν_{N-H} band appeared within the range 3283–3071 cm^{-1} in the IR spectra. The $\nu_{N=N}$ band (1518–1506 cm^{-1}) of all the ligands shifted to lower frequency (1394–1383 cm^{-1}) in the complexes, consistent with coordination of the azo nitrogen. The ν_{Pd-Cl} absorption of the palladium complexes was observed in the range 296–288 cm^{-1}. The spectral data for all the ligands and complexes are collected in Table 1.

The ^1H NMR spectra of all the ligands and complexes were recorded. The spectra are consistent with the composition and structure. However, to avoid unnecessary inclusion, we have tabulated only the data for the complexes in Table 2. The ^1H NMR data of the ligands are given in Table 3.

Some important features of the ^1H NMR spectra that occur upon palladation are as follows: (i) The N–H resonance of the ligands (δ 9.58–8.60) is shifted to upfield (δ 8.12–6.38) in the complexes; (ii) The aromatic proton count of the complexes is one less than that of the ligands indicating orthometallation. Further, the complexes where R is Me display a singlet within the range (δ 7.29–6.61) in the aromatic region, consistent with the orthometallation. (iii) The equivalent methylene protons

Table 1
UV–Vis[a] and IR[b] spectral data

Compound	λ_{max}/nm (ε/M^{-1} cm^{-1})	ν/cm^{-1}		
		ν_{N-H}	$\nu_{N=N}$	ν_{Pd-Cl}
1a	450 (9500), 315 (18050), 250 (23840), 230 (21500)	3426	1517	
1b	490 (6300), 400 (14600), 370 (27700), 360 (28750), 248 (25540), 230 (29600)	3238	1391	293
2a	450 (31400), 325 (53950), 250 (51620), 230 (56100)	3427	1517	
2b	490 (16100), 410 (29700), 370 (42900), 360 (44500), 260 (42800), 230(51300)	3236	1386	294
3a	460 (9800), 320 (16000), 250 (16700), 230 (17500)	3414	1514	
3b	490 (6500), 410 (15300), 370 (29830), 360 (30700), 250 (27050), 230 (38100)	3225	1388	296
4a	460 (13500), 325 (20900), 250 (20200), 230 (22000)	3413	1514	
4b	490 (8800), 410 (16850), 370 (24650), 360 (25500), 260 (23820), 230 (28800)	3229	1383	294
5a	465 (27300), 315 (40300), 250 (59300), 230 (60800)	3417	1514	
5b	490 (13150), 410 (24900), 375 (36550), 360 (37300), 260 (36500), 230 (47650)	3099	1391	290
6a	455 (18700), 320 (30650), 245 (35300), 230 (38200)	3420	1513	
6b	490 (12400), 410 (23500), 375 (33900), 360 (35000), 260 (34400), 230 (44200)	3097	1394	290
7a	450 (8450), 320 (25400), 270 (31600), 230 (57200)	3420	1510	
7b	490 (6500), 410 (12700), 375 (18200), 360 (18000), 260 (20300), 230 (33400)	3283	1387	289
8a	460 (6500), 315 (17600), 230(16600)	3421	1506	
8b	490 (2050), 406 (4800), 375 (8600), 360 (9100), 250 (8560), 230 (12000)	3231	1384	289
9a	450 (12270), 325 (20503), 250 (22770), 230 (23000)	3415	1510	
9b	490 (11400), 410 (21811), 375 (30500), 360 (34200), 260 (36500)	3205	1393	293
10a	450 (8614), 320 (14570), 250 (17000), 230 (16700)	3421	1508	
10b	480 (5237), 415 (11734), 375 (11800), 360 (16000), 260 (14200), 230 (23250)	3219	1386	290
11a	430 (29600), 320 (52000), 245 (48050), 230 (50600)	3488	1518	
11b	490 (7500), 410 (14000), 370 (20200), 360 (20600), 260 (20000), 230 (25600)	3071	1390	296

[a] In dichloromethane.
[b] KBr disc.

Table 2
^{1}H NMR spectra of the complexes, **1b**–**11b**

Compound	δ[a] (X, *n*H)[b]			
	Aromatic protons	Non-aromatic protons	R (CH_3)	N–H
1b[d]	6.72(t, 1H), 6.87(d, 1H), 7.01(t, 1H), 7.22(t, 1H), 7.44(d, 1H), 7.52(m, 3H)	3.16(d, 3H)		6.38(b, 1H)
2b[d]	6.65(s, 1H), 6.80(d, 1H), 7.16(t, 1H), 7.37(d, 1H), 7.45(d, 1H), 7.49(t, 1H), 7.55(d, 1H)	3.14(d, 3H)	2.00(s, 3H)	6.47(s, 1H)
3b[d]	6.71(t, 1H), 6.85(d, 1H), 6.99(t, 1H), 7.15–7.22(m, 1H), 7.42(d, 1H), 7.53(d, 2H), 7.58(d, 1H)	1.25(t, 3H), 3.52(m, 1H), 3.65(m, 1H)		6.69(s, 1H)
4b[d]	6.68(s, 1H), 6.81(d, 1H), 7.16(t, 1H), 7.40(d, 1H), 7.47(d, 1H), 7.52(m, 2H)	1.24(t, 3H), 3.53(m, 1H), 3.65(m, 1H)	2.03(s, 3H)	6.73(b, 1H)
5b[d]	6.61(s, 1H), 6.78(d, 1H), 7.11(t, 1H), 7.33(d, 1H), 7.44(d, 1H), 7.48(t, 1H), 7.52(d, 1H)	0.81(t, 3H), 1.16–1.40(m, 12H), 3.40(b, 1H), 3.54(b, 1H),	1.99(s, 3H)	6.82(s, 1H)
6b[d]	6.81(m, 2H), 7.15(t, 1H), 7.38(d, 1H), 7.46(d, 1H), 7.48(t, 1H), 7.54(d, 1H)	4.05(b, 1H), 4.24(b, 1H), 5.08(d, 1H), 5.14(d, 1H), 6.13–6.19(m, 1H)	2.02(s, 3H)	6.68(s, 1H)
7b[d]	6.78(s, 1H), 6.81–6.86(m, 3H), 6.89(d, 1H), 7.10(t, 1H), 7.21(t, 1H), 7.27–7.32(m, 2H), 7.44(d, 1H), 7.50(d, 1H)	3.91(s, 3H), 4.17(b, 1H), 5.14(b, 1H)	2.10(s, 3H)	6.65(t, 1H)
8b[c]	7.15–7.29(m, 5H), 7.44(t, 2H), 7.54(t, 3H), 7.74(t, 2H), 7.91(t, 1H)	4.51(s, 2H)		7.93(s, 1H)
9b[c]	7.02(d, 1H), 7.09–7.13(m, 3H), 7.29(s, 1H), 7.36(d, 1H), 7.53(d, 2H), 7.61(t, 1H), 7.68(d, 1H), 7.74(d, 1H), 7.80(s, 1H)	4.52(s, 2H)	2.30(s, 3H)	7.93(s, 1H)
10b[c]	7.16(t, 3H), 7.31(d, 1H), 7.41(t, 2H), 7.52(t, 2H), 7.69(t, 1H), 7.78(d, 1H), 7.84(d, 2H)	4.54(s, 2H)		8.12(s, 1H)
11b[d]	6.82(s, 1H), 6.83(d, 1H), 7.23(t, 1H), 7.45–7.51(m, 3H) 7.55(d, 1H)	1.22(t, 3H), 4.20(m, 2H), 4.22(d, 1H), 4.40(d, 1H)	2.06(s, 3H)	6.73(b, 1H)

[a] In ppm.
[b] X = multiplicity (m = multiplet, s = singlet, d = doublet, t = triplet, b = broad), *n* = proton count.
[c] In DMSO-d_6.
[d] In $CDCl_3$.

(N–CH_2–) of R′ in the ligands become inequivalent in the complexes (excepting R′ = CH_2Ph), diagnostic for binding of the amino nitrogen. All of these features have been shown in Fig. 2, in representative spectra for **6a** and **6b**. (iv) The N–H proton resonance of the metal complexes vanishes upon shaking with D_2O, confirming its non-dissociation upon coordination.

2.3. X-ray structure

The suitable crystals of **9b** were grown by slow diffusion of hexane into a dichloromethane solution. The crystals are triclinic and the space group is $P\bar{1}$. A perspective view with the atom numbering scheme is given in Fig. 3. Selected bond distances and angles are collected in Table 4.

The asymmetric unit of **9b** contains two molecules, which are held as a weak dimer with a non-covalent Pd···Pd interaction. The geometry and bond parameters are similar in the two molecules. The molecular structure of each monomer molecule exhibits a distorted square planar geometry about the palladium, where the anionic ligand (**9a**)$^-$ binds the metal in a tridentate (C,N,N) fashion. A chloride ligand completes the tetracoordination about Pd(II). The Pd–Cl and Pd–N(azo) distances (2.312(2) and 1.943(4) Å, respectively), are within the normal range [7b]. The Pd–C bond length (1.986(5) Å) is also matched well with the Pd–C lengths

Table 3
^{1}H NMR spectra of the ligands, **1a**–**11a**

Compound	δ[a] (X, *n*H)[b]			
	Aromatic protons	Non-aromatic protons	*p*-CH_3	N–H
1a[c]	6.72–6.80(m, 2H), 7.20–7.54(m, 9H), 7.79(d, 2H), 7.81(d, 1H)	4.54(s, 2H)		9.24(s, 1H)
2a[c]	6.74–6.84(m, 2H), 7.22–7.39(m, 8H), 7.68(d, 2H), 7.84(d, 1H)	4.54(s, 2H)	2.41(s, 3H)	9.20(s, 1H)
3a[c]	6.87(t, 2H), 7.22–7.44(m, 8H), 7.72(d, 2H), 7.84(d, 1H)	4.54(s, 2H)		9.58(s, 1H)
4a[c]	6.77–6.84(m, 2H), 7.25–7.52(m, 4H), 7.80–7.87(m, 3H)	3.01(s, 3H)		8.60(s, 1H)
5a[c]	6.77(t, 2H), 7.29(t, 4H), 7.81(d, 2H), 8.10(d, 1H)	2.99(s, 3H)	2.46(s, 3H)	8.60(s, 1H)
6a[c]	6.76(t, 2H), 7.34–7.56(m, 4H), 7.77–7.94(m, 3H)	3.33–3.35(m, 2H), 1.37(t, 3H)		8.80(s, 1H)
7a[c]	6.77–6.87(m, 2H), 7.23–7.31(m, 3H), 7.75(d, 2H) 7.82(d, 1H)	3.30–3.40(m, 2H), 1.38(t, 3H)	2.43(s, 3H)	8.70(s, 1H)
8a[c]	6.74–6.79(m, 2H), 7.23–7.30(m, 3H), 7.71(d, 2H), 7.83(d, 1H)	3.94(s, 2H), 5.22(d, 1H), 5.35(d, 1H), 5.97–6.01(m, 1H),	2.41(s, 3H)	8.72(s, 1H)
9a[c]	6.79(t, 1H), 6.86(d, 2H), 6.94(t, 2H), 7.17(t, 1H), 7.18(t, 1H), 7.21(m, 3H), 7.38(d, 1H), 7.70(d, 1H)	3.79(s, 3H), 4.55(s, 2H)	2.43(s, 3H)	9.04(s, 1H)
10a[c]	6.73–6.78(m, 2H), 7.24–7.30(m, 3H), 7.70(d, 2H), 7.82(d, 1H)	3.27(d, 2H), 1.69–1.75(m, 2H) 1.44–1.50(m, 2H), 1.25–1.39(m, 8H), 0.88(t, 3H)	2.41(s, 3H)	8.85(s, 1H)
11a[c]	6.63(d, 1H), 6.86(t, 1H), 7.28(m, 3H), 7.81–7.90(m, 3H)	1.25–1.36(m, 3H), 4.08(s, 2H), 4.28–4.32(m, 2H)	2.42(s, 3H)	8.93(b, 1H)

[a] In ppm.
[b] X = multiplicity (m = multiplet, s = singlet, d = doublet, t = triplet, b = broad), *n* = proton count.
[c] In $CDCl_3$.

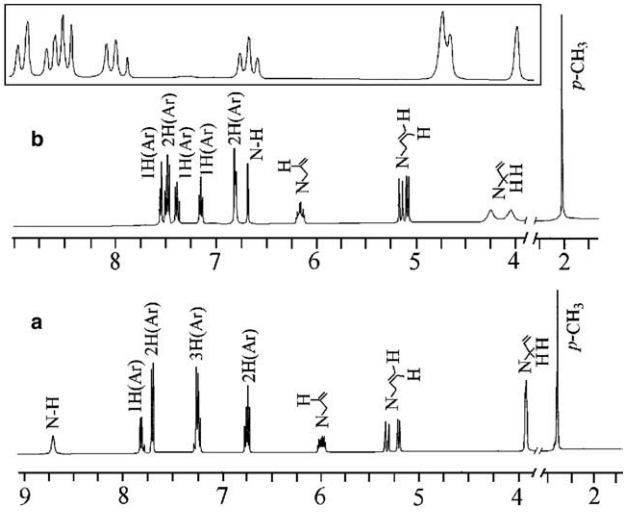


Fig. 2. The ^{1}H NMR spectra of (a) **6a** and (b) **6b** in $CDCl_3$, where *n* of *n*H(Ar) stands for the proton count. The expansion of the aromatic region (δ 6.81–7.54) of **6b** has been shown in the inset.

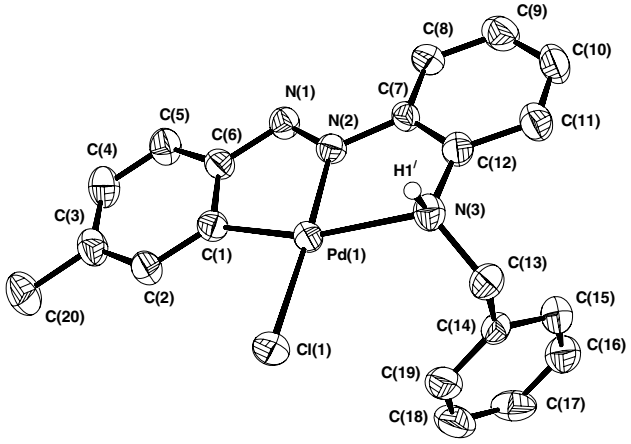


Fig. 3. Perspective view of **9b** with the atom numbering scheme. Hydrogen atoms excepting on N3 are omitted for clarity.

in other orthopalladated azo benzene complexes [8]. The Pd–N(amine) bond length (2.194(1) Å) is much longer than the Pd–N(azo) distance, presumably as a consequence of the stronger *trans* influence of the aryl carbon [9]. The N(3)–Pd–C(1) (161.17(19)°) and N(2)–Pd–Cl (177.06(13)°) bond angles deviate a little from linearity. The chelate ring bite angles are also considerably smaller [N(2)–Pd–N(3), 81.75(17)°; N(2)–Pd–C(1), 79.5(2)°] than the ideal values (90°) of a square geometry, although the atoms within the coordination sphere lie on a plane (mean deviation 0.01 Å). In fact the whole molecule, excepting the benzyl group, is planar (mean deviation 0.05 Å).

Table 4
Selected bond distances (Å) and angles (°) for **9b**

Pd(1)–C(1)	1.986(1)
Pd(1)–N(2)	1.942(1)
Pd(1)–N(3)	2.194(1)
Pd(1)–Cl(1)	2.312(2)
N(1)–C(6)	1.399(1)
N(1)–N(2)	1.266(1)
N(2)–C(7)	1.431(1)
C(7)–C(12)	1.391(1)
C(1)–C(6)	1.413(1)
N(3)–C(12)	1.465(1)
N(2)–Pd(1)–C(1)	79.5(2)
N(2)–Pd(1)–N(3)	81.7(2)
C(1)–Pd(1)–N(3)	161.1(2)
N(2)–Pd(1)–Cl(1)	177.0(1)
C(1)–Pd(1)–Cl(1)	97.9(2)
N(3)–Pd(1)–Cl(1)	100.7(1)
C(12)–N(3)–Pd(1)	106.2(3)

The dimer contained in the asymmetric unit, is held in a staggered conformation (dihedral angle is 60°) with three non-bonding inter-monomeric interactions, Pd···Pd, 3.301 Å; N(amine)···Cl, 3.256 Å and N(amine)···Pd, 3.635 Å. The dimeric unit with the non-bonding interactions is shown in Fig. 4.

However, in the packing of the molecule, no infinite stacking has been observed, where the discrete dimers are arranged in a regular pattern in the crystal lattice. A partial packing diagram has been shown in Fig. 5.

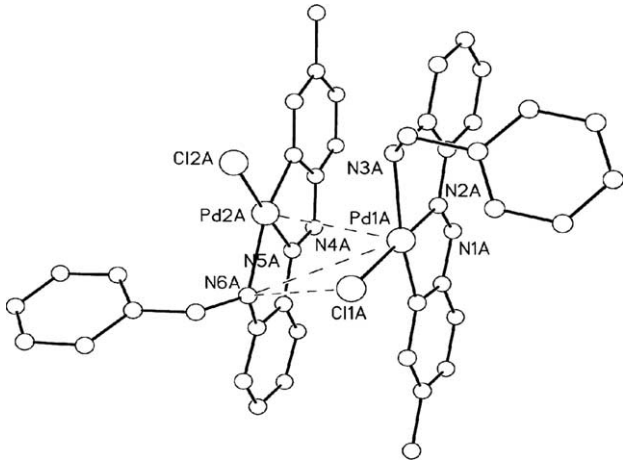


Fig. 4. A view of the dimeric unit of **9b**. The broken lines indicate the weak interactions.

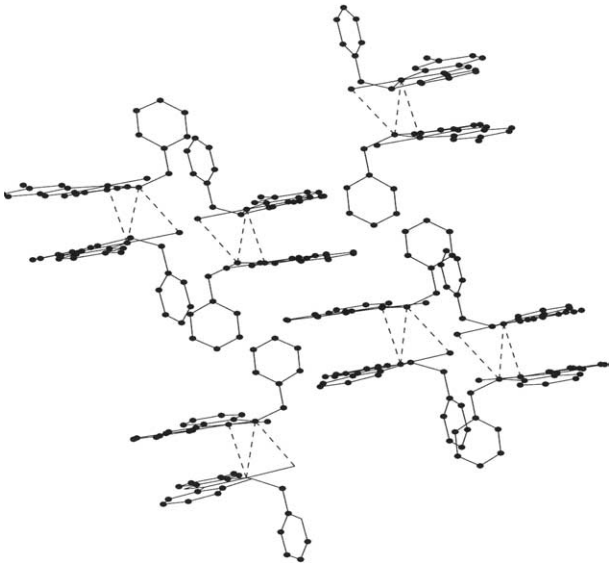


Fig. 5. Partial packing diagram of complex **9b** along the *c*-axis.

3. Experimental

3.1. Materials

The solvents used in the reactions were of reagent grade obtained from E. Merck, Kolkata, India, and were purified and dried by reported procedures [6]. The 2-(arylazo) anilines were prepared according to a reported procedure [6]. Palladium chloride, benzyl chloride, methyl iodide, ethyl bromide and potassium carbonate were purchased from E. Merck, Kolkata, India. Allyl chloride, ethyl chloroacetate, *n*-bromooctane and *o*-cresol were purchased from SRL, Mumbay, India. Disodium tetrachloropalladate was prepared by a reported procedure [6].

3.2. Syntheses of ligands

3.2.1. *1a* and *2a*

To prepare the ligands **1a** and **2a**, methyl iodide (0.095 cm^3, 1.52 mmol) was refluxed for 2 h with 2-(phenylazo) aniline (0.3 g, 1.52 mmol) and 2-(*p*-tolylazo) aniline (0.32 g, 1.52 mmol), respectively, in 30 cm^3 ethanol in the presence of 1 g of K_2CO_3. From the orange solid mass that was obtained after evaporation of ethanol, the ligands **1a** and **2a** were isolated by column chromatography on silica gel (60–120 mesh). The eluent was petroleum ether. Upon evaporation of the solvent, the orange-red semi-solid of pure ligand was obtained. Yield: **1a**, 65%; **2a**, 70%. *Anal*. Calc. for $C_{13}H_{13}N_3$, **1a**: C, 73.93; H, 6.16; N, 19.90. Found: C, 73.90; H, 6.10; N, 19.85%. Calc. for $C_{14}H_{15}N_3$, **2a**: C, 74.66; H, 6.66; N, 18.66. Found: C, 74.61; H, 6.68; N, 18.62%.

3.2.2. *3a* and *4a*

The ligands **3a** and **4a** were prepared following the same procedure as described in the case of **1a** and **2a** using ethyl bromide (0.114 cm^3, 1.52 mmol) in place of methyl iodide. The refluxing time was 4 h. Yield **3a**, 50%; **4a**, 65%. *Anal*. Calc. for $C_{14}H_{15}N_3$, **3a**: C, 74.66; H, 6.66; N, 18.66. Found: C, 74.63; H, 6.65; N, 17.05%. *Anal*. Calc. for $C_{15}H_{17}N_3$, **4a**: C, 75.31; H, 7.11; N, 17.57. Found: C, 75.27; H, 7.10; N, 17.53%.

3.2.3. *5a, 6a and 7a*

5a, **6a** and **7a** were prepared by refluxing 2-(*p*-tolylazo) aniline (0.32 g, 1.52 mmol) with *n*-bromooctane (0.264 cm^3, 1.52 mmol), allyl chloride (0.125 cm^3, 1.52 mmol) and 2-bromomethyl anisole (0.305 g, 1.52 mmol), respectively, in 30 cm^3 ethanol in the presence of 1 g of $K_2CO_3$for 4 h. The ligands were purified by the same procedure as described above. Yield: **5a**, 65%; **6a**, 65%; **7a**, 65%. *Anal.* Calc. for $C_{21}H_{29}N_3$, **5a**: C, 78.01; H, 8.97; N, 13.00. Found: C, 78.00; H, 8.91; N, 13.07%. *Anal*. Calc. for $C_{16}H_{17}N_3$, **6a**: C, 76.49; H, 6.77; N, 16.73. Found: C, 76.45; H, 6.75; N, 16.75%. *Anal*. Calc. for $C_{21}H_{21}N_3O$, **7a**: C, 76.13; H, 6.34; N, 12.69. Found: C, 76.10; H, 6.30; N, 12.70%.

3.2.4. *8a, 9a and 10a*

8a, **9a** and **10a** ligands were prepared by refluxing benzyl chloride (0.193 cm^3, 1.52 mmol) with 2-(phenylazo) aniline (0.3 g, 1.52 mmol), 2-(*p*-tolylazo) aniline (0.32 g, 1.52 mmol) and 2-(*p*-chlorophenylazo) aniline (0.352 g, 1.52 mmol), respectively, in 30 cm^3 ethanol and 1 g of K_2CO_3 for 4 h. The ligands were purified by the same procedure as described above. Yield: **8a**, 50%; **9a**, 65%; **10a**, 50%. *Anal*. Calc. for $C_{19}H_{17}N_3$, **8a**: C, 79.44; H, 5.97; N, 14.63. Found: C, 79.70; H, 6.10; N, 14.55%. *Anal*. Calc. for $C_{20}H_{19}N_3$, **9a**: C, 79.69; H, 6.36; N, 13.95. Found: C, 79.70; H, 6.40; N, 13.97%. *Anal*. Calc. for $C_{19}H_{16}N_3Cl$, **10a**: C, 70.90; H, 5.00; N, 13.00. Found: C, 70.70; H, 5.30; N, 13.40%.

3.2.5. *11a*

2-(*p*-Tolylazo) aniline (0.32 g, 1.52 mmol) was mixed with ethyl chloroacetate (0.185 cm^3, 1.52 mmol) in 30 cm^3 DMF. 1 g of K_2CO_3 was added to this mixture and which was then refluxed for 4 h. From the orange solid mass that was obtained after evaporation of DMF, the ligand **11a** was isolated by column chromatography on silica gel (60–120 mesh). The eluent was petroleum ether. Upon evaporation of solvent the orange-red semi-solid of pure ligand was obtained. Yield: 65%. *Anal.* Calc. for $C_{17}H_{19}N_3O_2$, **11a**: C, 68.68; H, 6.39; N, 14.14. Found: C, 68.65; H, 6.40; N, 14.10%.

3.3. Syntheses of complexes

3.3.1. *1b*

A solution of **1a** (0.110 g, 0.52 mmol) in 10 cm^3 methanol was added to a solution of Na_2PdCl_4 (0.150 g, 0.52 mmol) in 5 cm^3 methanol. The mixture was stirred for 8 h. The dark solid precipitate was separated by filtration and purified by column chromatography using silica gel (60–120 mesh). The eluent was toluene-acetonitrile mixed solvent (90/10 v/v) and upon evaporation of the solvent, dark red solid **1b** was obtained. Yield: 55%. *Anal*. Calc. for $C_{13}H_{12}N_3PdCl$: C, 44.32; H, 3.40; N, 11.93. Found: C, 44.29; H, 3.35; N, 11.40%.

3.3.2. *2b–11b*

The complexes **2b**–**11b** were prepared following a similar procedure as described in the case of **1b**, but the durations of the reactions were different. These are 8 h for **2b**–**4b**, 6 h for **5b**, 7 h for **6b**, 15 h for **7b**, 5 h for **8b**–**10b** and 15 h for **11b**.

Yield: **2b**, 60%; **3b**, 40%; **4b**, 60%; **5b**, 60%; **6b**, 50%; **7b**, 45%; **8b**, 60%; **9b**, 70%; **10b**, 30%; **11b**, 30%. *Anal*. Calc. for $C_{14}H_{14}N_3PdCl$, **2b**: C, 45.91; H, 3.82; N, 11.47. Found: C, 45.90; H, 3.85; N, 11.95%. *Anal*. Calc. for $C_{14}H_{14}N_3PdCl$, **3b**: C, 45.91; H, 3.82; N, 11.47. Found: C, 45.87; H, 3.80; N, 11.45%. *Anal*. Calc. for $C_{15}H_{16}N_3PdCl$, **4b**: C, 47.37; H, 4.21; N, 11.05. Found: C, 47.35; H, 4.15; N, 11.00%. *Anal*. Calc. for $C_{21}H_{28}N_3PdCl$, **5b**: C, 54.31; H, 6.03; N, 9.05. Found: C, 54.35; H, 6.07; N; 9.00%. *Anal*. Calc. for $C_{16}H_{16}N_3PdCl$, **6b**: C, 48.98; H, 4.08; N, 10.71. Found: C, 48.95; H, 4.05; N, 10.70%. *Anal*. Calc. for $C_{21}H_{20}N_3OPdCl$, **7b**: C, 53.39; H, 4.23; N, 8.89. Found: C, 53.40; H, 4.25; N, 8.85%. *Anal*. Calc. for $C_{19}H_{16}N_3PdCl$, **8b**: C, 53.28; H, 3.77; N, 9.80. Found: C, 53.50; H, 4.00; N, 9.70%. *Anal*. Calc. for $C_{20}H_{18}N_3PdCl$, **9b**: C, 54.27; H, 4.07; N, 9.49. Found: C, 54.30; H, 4.10; N, 9.51%. *Anal*. Calc. for $C_{19}H_{15}N_3PdCl_2$, **10b**: C, 49.30; H, 3.27; N, 9.00. Found: C, 49.70; H, 3.40; N, 9.31%. *Anal*. Calc. for $C_{17}H_{18}N_3O_2PdCl$, **11b**: C, 46.58; H, 4.11; N, 9.59. Found: C, 46.55; H, 4.05; N, 9.56%.

3.4. Physical measurements

Microanalyses (C,H,N) were performed using a Perkin–Elmer 240C elemental analyzer. Infrared spectra were recorded on a Perkin–Elmer L120-00A FT-IR spectrometer with the samples prepared in KBr pellets. Electronic spectra were recorded on a Shimadzu UV-2401 PC spectrophotometer. ^1H NMR spectra were obtained on Brucker AC-200, Brucker Avance DPX 300, Brucker Avance DPX 400 and Brucker Avance RPX 500 NMR spectrometers in $CDCl_3$, DMSO-d_6, D_2O using TMS as the internal standard.

3.5. Crystallography

Data of **9b** was collected by the ω-scan technique on a Nicolet R3m/v diffractometer with Mo Kα radiation monochromated by a graphite crystal. The structure solution was done by direct methods with the SHELXS-97 program. Full-matrix least-squares refinements were performed using the SHELX-97 program (PC version). All non-hydrogen atoms were refined anisotropically using reflections $I > 2\sigma(I)$. Hydrogen atoms were included at calculated positions. The crystal data and data collection parameters are listed in Table 5.

Table 5
Crystallographic data for **9b**

Chemical formula	$C_{20}H_{18}ClN_3Pd$
Formula weight	442.22
Space group	$P\bar{1}$
Crystal system	triclinic
a (Å)	10.802(5)
b (Å)	13.159(5)
c (Å)	14.397(8)
α (°)	102.17(3)
β (°)	110.25(4)
γ (°)	98.65(4)
λ (Å)	0.71073
V (Å^3)	1820.2(15)
Z	4
Temperature (K)	293(2)
ρ_{cald} (Mg/m^3)	1.614
μ (mm^{-1})	1.173
$F(000)$	888
R(all data)	$R_1 = 0.0730$, $wR_2 = 0.1080$
Unique reflections/$[I > 2\sigma(I)]$	6770/6400 [$R_{int} = 0.0277$]
R_1[a]/GOF[b]	0.0419/1.065
wR_2[c] $[I > 2\sigma(I)]$	0.0969

[a] Observation criterion: $I > 2\sigma(I)$. $R_1 = \sum \|F_o| - |F_o\| / \sum |F_o|$.
[b] GOF $= [\sum [w(F_o^2 - F_c^2)^2]/(n-p)]^{1/2}$.
[c] $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$, where $w = 1/\sigma^2(F_o^2) + (aP)^2 + bP$, $P = (F_o^2 + 2F_c^2)/3$.

4. Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Reference Number 212758. Copies of this information may be obtained free from the Director, CCDC, 12 Union Road, Cambridge CB2 1EW, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.com.ac.uk).

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