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Introduction

Palladium remains the preferred metal over less expensive metals such as iron, copper or nickel for the catalysis of carbon–carbon cross coupling reactions owing to its higher activity, facile two electron oxidative addition and reductive elimination and tolerance towards several functional groups among others.¹ The Suzuki–Miyaura cross-coupling reaction has been investigated using several palladium complexes containing a wide variety of ligand systems.² It is understood that ligands play the major role of determining the efficiency of a catalyst.³ Hence, this named reaction has been studied with

Exhibition of the Brønsted acid-base character of a Schiff base in palladium(II) complex formation: lithium complexation, fluxional properties and catalysis of Suzuki reactions in water†

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The reaction of the dialdehyde N,N-di(α -formylpyrrolyl- α -methyl)-N-methylamine **1** with two equiv. of 2,6-diisopropylaniline yielded two Schiff bases: bis(iminopyrrolylmethyl)amine (H₂L) and its hydrolyzed monoimino compound (H_2L') after column separation. The dimeric lithium complex [(HL)Li]₂ (2) containing the monoanionic form of H_2L was obtained by treating H_2L with "BuLi. The presence of both proton donors and acceptors causes the diimino compound H_2L to undergo tautomerization to exhibit an amine-azafulvene structure, though the central amine nitrogen competes for a proton. As a result, in the presence of Pd^{2+} ions, the cationic complex $[Pd(Cl)(H_2L)][Cl]$ (3) containing one pendant amine-azafulvene arm and the protonated central amine nitrogen was obtained. Its X-ray structure showed that the bond distances are reversed for the imino-pyrrole moiety relative to those in the structure of H_2L . However, the reaction of H_2L with $[Pd(OAc)_2]$ afforded the neutral complex [PdL] (4) containing the dianionic form of the ligand. The reaction of H2L' with [PdCl2(PhCN)2] yielded a zwitterionic complex $[PdCl_2(H_2L')]$ (5) owing to the presence of the central amine nitrogen. The formation of these palladium complexes with the features mentioned above can be explained by invoking the Brønsted acid-base character of the Schiff base. Complex 4 is fluxional owing to the up and down movements of the palladium square plane formed by two 5-membered palladacycles, which causes the interconversion of its enantiomers and is studied by the variable temperature ¹H NMR method. Furthermore, both complexes **3** and 4 are precatalysts for the Suzuki-Miyaura cross-coupling reaction in water. Sterically encumbered and electronically different substrates including activated aryl chlorides and benzyl halides gave the coupled products in very good yields. The reaction proceeds even at room temperature and in the presence of a large excess amount of mercury.

palladium complexes bearing ligands such as phosphines,⁴ N-heterocyclic carbenes,⁵ imines,^{6,7} pincer ligands,⁸ and oxazolines.⁹ These efforts have led to several impressive catalytic systems being developed that promote coupling even with difficult substrates such as aryl chlorides¹⁰ and hindered substrates¹¹ and coupling with various organoboron species¹² and nonaryl halide substrates.¹³ Furthermore, catalysis reactions involving very low catalyst loading,¹⁴ mild conditions,¹⁵ aqueous medium,¹⁶ an immobilized catalyst,¹⁷ 'ligandless' systems¹⁸ and room temperature¹⁹ have been reported. Despite enormous progress, the reaction still continues to be an active area of research in search of a better catalyst as well as because of its applications in pharmaceutical, agro- and fine-chemical industries,²⁰ which require an economical method.

We became interested in Schiff base ligands because of their easy synthesis and tendency to coordinate to several metals in various oxidation states.²¹ In addition, Schiff base metal complexes have been reported as catalysts for a wide

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variety of organic reactions.²² We recently reported the dipyrrole-dialdehyde compound **1** and its condensations with diamines/triamines to give macrocycles and macrobicycles for anion binding studies.²³ Herein, we report two new multidentate Schiff base ligands synthesized by condensation with a monoamine containing two bulky substituents. In addition, we report the coordination chemistry of these ligands with lithium and palladium metals, in which the Schiff base shows an amine-azafulvene tautomeric structure among others in support of the Brønsted acid-base character of the ligand. The fluxional properties and the catalytic activity for Suzuki-Miyaura reactions in water are also described.

Results and discussion

Synthesis of Schiff base ligands

The condensation reaction between dipyrrole-dialdehdye 1 and 2,6-diisopropylaniline in the presence of concentrated nitric acid in the 1:2:2 molar ratio gave two Schiff bases, H_2L and H_2L' , in 53% and 24% yields, respectively, after silica gel column chromatography separation (Scheme 1). The yield of the [1 + 2] Schiff base H_2L could not be improved even with an excess amount of the amine or acid, indicating that H_2L might have undergone partial hydrolysis in the silica gel column to give the [1 + 1] Schiff base H_2L' .

Both compounds have the imino-pyrrole moiety and are expected to show an amine–azafulvene tautomeric structure as presented in Chart 1. If the rate of exchange of protons between the pyrrole and imine nitrogen is rapid enough, it will not appear in the ¹H NMR spectrum. Consistently with this, the ¹H NMR spectrum of H_2L in CDCl₃ does not show the pyrrolic NH resonance. The imine CH resonance appears as a sharp singlet at δ = 7.81 ppm, which is closer to the resonance (7.09 ppm) of the aromatic protons. In contrast to this, the ¹H NMR spectrum of H_2L in toluene- d_8 shows a broad singlet at δ = 11.58 ppm for the pyrrolic NH proton, probably because of the slowdown of the rate of exchange of protons. The ¹H NMR spectrum of H_2L' in CDCl₃ features a broad singlet at



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Chart 1 The tautomerization of bis(iminopyrrolylmethyl)amine H_2L to an amine–azafulvene structure.

 δ = 10.53 ppm which is assigned to the NH of the pyrrole ring carrying the formyl group; the other pyrrolic NH resonance does not appear, probably because of the amine–azafulvene tautomerism. The aldehydic and the imine CH protons appear as singlets at δ = 9.47 ppm and 7.88 ppm, respectively. In addition, their integrated intensities are in accord with the structure. In the ¹³C NMR spectrum, the resonance of the carbonyl group appears at δ = 179.3 ppm, which is only slightly shifted upfield relative to the dialdehyde **1** (δ = 179.4 ppm).

The structures of H₂L and H₂L' were confirmed by single crystal X-ray diffraction analysis and are given in ESI (Fig. S23[†]). The X-ray structure of H_2L (ESI, Fig. S23(a)[†]) showed that the pyrrolic NH protons point towards the water molecule present in the cavity formed by the molecule. The pyrrolic NH and water hydrogens were located from the Fourier difference map. The water molecule is hydrogen bonded to the pyrrolic NH and the imine nitrogen atoms. The diisopropylphenyl ring planes face each other and are almost perpendicular to the imino-pyrrole ring planes on both sides of the molecule, which facilitates the bending of the molecule to form hydrogen bonds with the cavity water molecule. In contrast, the X-ray structure of H₂L' revealed no water molecules, probably because of one carbonyl group in the molecule (ESI, Fig. S23(b)[†]). The presence of the carbonyl group induces dimerization in the crystal lattice by the intermolecular hydrogen bonding between the aldehyde oxygen and the pyrrolic NH groups of the other molecule.

Synthesis and characterization of the lithium and palladium complexes

Treatment of H_2L with three equiv. of ^{*n*}BuLi in THF at -78 °C afforded the dimeric lithium complex 2, which contains the



Scheme 1 Synthesis of bis(iminopyrrolylmethyl)amine, H₂L and its hydrolyzed monoimino compound H₂L'.



monodeprotonated form of the ligand (Scheme 2). Its structure was determined by the X-ray diffraction method and is given in Fig. 1. The X-ray structure shows that the dinuclear lithium complex is formed by the coordination of one portion of the



Fig. 1 The X-ray structure of the dimeric lithium complex 2. Most hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: N3-Li1 2.141(6), N4-Li1 2.126(6), N4-Li2 2.069(6), N5-Li2 2.040(6), N6-Li2 2.017(6), N7-Li2 2.097(6), N7-Li1 2.100(6), N8-Li1 2.139(6), Li1...Li2 2.645(8), N7-Li1-N4 100.8(2), N7-Li1-N8 92.0(2), N4-Li1-N8 125.8(3), N7-Li1-N3 126.8(3), N4-Li1-N3 92.3(2), N8-Li1-N3 120.8(3), N6-Li2-N5 126.3(3), N6-Li2-N4 134.0(3), N5-Li2-N4 86.0(2), N6-Li2-N7 86.2(2), N5-Li2-N7 123.6(3), N4-Li2-N7 102.8(3).

ligand which consists of the imine, pyrrolic, and the central amine nitrogen atoms; the other imino-pyrrole moiety remains uncoordinated. Both the amine or imine nitrogens are bonded to the same lithium atom rather than being in a *trans* fashion, resulting in the same side orientation of the uncoordinated portion of the ligand. In the structure, the two imino-pyrroleamine moieties are twisted and bonded, which gives a distorted tetrahedral geometry around each lithium atom. The pyrrolide nitrogen atom of each ligand is bridge-bonded to both lithium atoms with an Li1-N-Li2 angle of 78.1(2)°. The imine N-Li distances (2.017(6) Å and 2.040(6) Å) are shorter than the amine N-Li distances (2.139(6) Å and 2.141(6) Å). The Li…Li distance of 2.645(8) Å is longer than those $(2.395(5) \text{ Å},^{24})$ 2.444(15) Å²⁵ and 2.495(8) Å²⁶) found in similar dimeric lithium complexes.

The cationic palladium(II) complex 3 was obtained in 97% yield from the reaction between H_2L and $[Pd(PhCN)_2Cl_2]$ or $[Pd(COD)Cl_2]$. Conversely, the neutral palladium(II) complex 4 was obtained in 95% yield when H₂L was treated with Pd- $(OAc)_2$ (Scheme 2). Complex 3 is formed by the abstraction of the pyrrolic NH proton by the central amine nitrogen followed by the partial tautomerization of the ligand to the amine-azafulvene. For complex 4, the acetate group of [Pd(OAc)₂] removes the pyrrolic NH proton with concomitant formation of two molecules of acetic acid. This NH group can be either from the imine-pyrrole or amine-azafulvene structure because both can give the same structure owing to the double bond conjugation. In addition, the ¹H NMR spectrum of the crystals

obtained from the reaction between 3 and two equiv. of K_2CO_3 in MeOH/H₂O under reflux conditions showed the formation of the neutral complex 4 which is formed by removing two HCl molecules from complex 3 by the base.

Complex 3 is well soluble in MeOH or DMSO but is only sparingly soluble in solvents such as CHCl₃, DCM, and EtOH, indicating the ionic nature of the complex. In contrast to this, complex 4 is soluble in all these solvents. The ¹H NMR spectrum of 3 in CDCl₃ features signals in support of an amineazafulvene tautomeric structure, suggesting the presence of an unsymmetrically bound ligand. The NH proton of the amineazafulvene structure appears at δ = 11.65 ppm as a doublet with coupling constant J = 17.2 Hz, while the azafulvene C==CH proton gives a doublet at δ = 9.01 ppm with *J* = 15.6 Hz. This magnitude of the coupling constant indicates the anticonformation of the azafulvene C=CH and NH protons, which is consistent with its solid state structure (vide infra). In addition, this is consistent with the coupling constant value (16.2 Hz) of an amine-azafulvene structure reported by Love and co-workers.²⁷ Furthermore, the presence of an ammonium hydrogen in the structure is supported by the broad resonance at δ = 8.39 ppm and the NMe resonance is observed at δ = 2.69 ppm as a broad signal. Furthermore, the spectrum shows a few unassignable multiplets and broad signals, which are probably due to decomposition of 3 in CDCl₃ (see ESI, Fig. S10[†]). Nevertheless, the HRMS(ES+) spectrum shows a molecular ion peak at m/z 704.2709 which corresponds to the mass of the $[M - Cl^{-}]^{+}$ ion (704.2706).

The X-ray structure of **3** shown in Fig. 2 revealed that the palladium atom is coordinated by two pyrrolic nitrogens, one imine nitrogen and one chlorine atom, and the complex is ionic. This set of ligating atoms indicates that a partial amine-azafulvene tautomerization has occurred, which is then coordinated to the metal atom. This partial tautomerization is comparable to metal complexes containing an amine-azaful-

vene tautameric structure reported by Sessler,^{28b} Love^{28a,c,d} and Fout.²⁹ In addition to this, a similar tautomeric structure has been reported for other ligands containing the pyrrole³⁰ and oxazoline³¹ rings. The pyrrolic nitrogen which forms the five-membered NN chelate ring can be treated as the anion part. Interestingly, the C-C single and double bond distances in the anionic-part pyrrole ring are reversed relative to those in the free ligand structure. For example, the double bond (C14-C15 = 1.377(5) Å) and the single bond (C15-C16 = 1.392(5))Å) distances in the free ligand are changed more to a single bond (1.398(10) Å) and a double bond (1.378(10) Å) distance, respectively, in complex 3. This is probably because of π -back bonding from the metal to the pyrrole ring which has been reported for a few metal complexes that show the reversed pyrrole ring bond distances.³² Conversely, as compared to those in the free ligand structure H₂L, the alternating shortlong-short bond distances (1.384(10), 1.397(10), and 1.361(11) Å) in the other pyrrole ring of the pendant arm are attributed to an amine-azafulvene structure, as shown in Fig. 3. The middle amine nitrogen is protonated and the resulting cationic complex is charge balanced by the outside chloride anion. Consistently with the protonation, the bond distances around the ammonium nitrogen atom are increased, C18-N3 = 1.514(11) Å, C20-N3 1.522(11) Å relative to those found in the free ligand structure (Fig. 3). In addition, the outside chlorine atom assists in the formation of the intermolecular hydrogen bonding involving the NH of the amine-azafulvene and the ammonium NH⁺ hydrogens (Fig. 2b).

The geometry around the palladium atom is a distorted square planar. The anionic pyrrole ring and the imine moiety (-CH==N-), along with the 'Pd-Cl' unit, form a mean plane, and the ammonium cation (MeNH⁺) group lies above this plane. This arrangement gives the N1_(imine)-Pd-N4_(pyrrole) angle of 175.8°. The bond distance of the pyrrolic nitrogen *trans* to the imine nitrogen atom, N4-Pd1, is 2.008(6) Å, and that of the



Fig. 2 (a) The X-ray structure of $3 \cdot 0.5(H_2O)$. Most hydrogen atoms, the outside chlorine atom and the water molecule are omitted for clarity. Selected bond lengths [Å] and angles [°]: N1-Pd1 2.024(5), N2-Pd1 2.035(5), N4-Pd1 2.008(6), Pd1-Cl1 2.301(2), C13-N1 1.321(8), C13-C14 1.407(9), C14-C15 1.398(10), C15-C16 1.378(10), C16-C17 1.396(10), C14-N2 1.350(8), C17-N2 1.376(8), N1-Pd1-N4 175.8(2), N2-Pd1-Cl1 173.42(15), N4-Pd1-N2 96.9(2), N1-Pd1-N2 80.8(2), N4-Pd1-Cl1 88.87(17), N1-Pd1-Cl1 93.62(16); (b) the intermolecular hydrogen bondings formed *via* the outside chlorine atoms in the crystal lattice. N3…Cl2ⁱ 3.006(7), H1N3…Cl2ⁱ 2.13(2), N3-H1N3…Cl2ⁱ 173(8), N5…Cl2 3.096(6), H1N5…Cl2 2.24(3), N5-H1N5…Cl2 167(7). The symmetry operation used to generate equivalent atoms: -x + 1, -y + 1, -z.



Fig. 3 Bond length (Å) comparison between the imino-pyrrole and amino-azafulvene tautomers: (a) bond lengths found in the free ligand structure H_2L and (b) those found in the cationic complex 3.

imine N1–Pd1 is 2.024(5) Å, which are slightly shorter than those (2.042(5) Å and 2.073(5) Å) reported for a Pd(II) complex containing a similar arrangement of ligating atoms of a hybrid macrocycle,³³ whereas the bond distance of the pyrrolic N which is *trans* to the chlorine atom, N2–Pd1 = 2.035(5) Å, is slightly longer than that (1.950(5) Å) reported for the aforementioned complex. Furthermore, the N2–Pd1 bond distance remains very much $closer^{34}$ as well as longer than those (1.995(3) Å and 2.022(4) Å)³⁵ reported for Pd(II) complexes containing the pyrrole ring nitrogen atom *trans* to the chlorine atom which include the case of the Pd(II) complex in which there is a back bonding from a metal to the pyrrole ring.^{32a}

The ¹H NMR spectrum of 4 in CDCl₃ at room temperature shows four well separated sets of isopropyl methyl, two sets of isopropyl CH and two sets of methylene resonances. All these resonances, among others, are broad and indicate a dynamic process in solution. This prompted us to carry out the variable temperature ¹H NMR study (Fig. 4). Spectra were recorded for every 10 °C intervals from 23 °C to -30 °C and the same sample was used for recording spectra from 23 °C to 55 °C. When the temperature is lowered, the broad room temperature resonances begin to resolve into multiplets from 10 °C onwards, which remain the same till -30 °C. The two diastereotopic methylene protons display an AB pattern with J = 12.8 Hz at low temperatures. Each of the four sets of methyl and two sets of CH resonances appear as doublets and multiplets, respectively, with J = 6.4 Hz. This indicates that the isopropyl groups are oriented in different directions and settle into two sets of methine and four sets of methyl groups. When the temperature is raised, the methylene resonances are broadened and merged into a single broad resonance at 40 °C. In addition, the isopropyl CH resonances almost vanished at high temperatures.

As shown by the X-ray structure of **4** (see below), the two diisopropylphenyl rings lie above and below the distorted palladium square plane by which the isopropyl groups split into sets. At high temperatures, there could be fast up and down movements of the two five-membered palladacycles, owing to



Fig. 4 Variable temperature ¹H NMR spectra of complex 4 in CDCl₃. At 10 °C, $k_c = \pi \Delta \nu / \sqrt{2} \text{ s}^{-1}$, $\Delta G^{\ddagger} = 2.303 RT_c$ (10.319 + log $T_c - \log k_c$) kJ mol⁻¹, $\Delta \nu = 103.2 \text{ Hz}$, $k_c = 229.2 \text{ s}^{-1}$, $T_c = 313 \text{ K}$, $\Delta G^{\ddagger} = 62.6 \text{ kJ mol}^{-1}$.



Fig. 5 Up and down movements of the two palladacycles in complex 4 cause the interconversion of the enantiomers with their methylene protons to become the equivalent at 40 °C, which is arrested at 10 °C to give an AB pattern.

the presence of two heavy diisopropylphenyl groups hanging on both ends of the plane, by which one enantiomer is converted to another with their methylene groups shifted up and down, as shown in Fig. 5. This interconversion gives a broad resonance for the diastereotopic methylene protons. At low temperature, the interconversion is arrested to give a resolved AB spectrum. The coalescence temperature is 40 °C and the Gibbs free energy of activation ΔG^{\ddagger} for this process is calculated to be 62.6 kJ mol⁻¹.³⁶ Furthermore, at low temperature, the two imine CH protons appear as a sharp singlet at δ = 7.03 ppm, with an upfield shift of 0.8 ppm owing to the imine nitrogen coordination.

Complex 4 crystallizes in the triclinic $P\bar{1}$ space group, and two molecules constitute the asymmetric unit. One of the molecules is shown in Fig. 6 and the other molecule is like the one shown in Fig. 5. The X-ray structure showed that the palladium atom is coordinated by two pyrrolic and two imine nitrogen atoms, indicating the flexibility of the ligand. The palladium atom is in the +2 oxidation state and has a distorted square planar geometry formed by the two five-membered palladacycles which are twisted with a N4–N5–N1–N2 torsion angle value of -20.3° . The two diisopropylphenyl ring planes



Fig. 6 The X-ray structure of complex **4**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: N1–Pd1 2.076(4), N2–Pd1 1.995(4), N4–Pd1 2.000(4), N5–Pd1 2.078(4), N2–Pd1–N5 166.05(16), N4–Pd1–N1 165.85(17), N4–Pd1–N2 98.28(17), N4–Pd1–N5 80.38(17), N5–Pd1–N1 104.36(16).

are perpendicular to, and lie above and below, the distorted palladium square plane. Consistent with the conjugation of the pyrrole double bonds with the imine double bonds and the back bonding from the palladium atom, the pyrrole ring C–C, and the $C_{(imine CH)}$ – $C_{(\alpha-pyrrole)}$ bond distances show changes relative to those found in the free ligand H₂L, as were the case in complex 3. The N(pyrrole)-Pd bond distances are slightly shorter than that of complex 3. In addition, both the N_(pyrrole)-Pd bond distances are slightly longer than those reported for similar palladium(II) complexes containing the pyrrolic and imine nitrogen coordinations, whereas the N(imine)-Pd bond distances are slightly shorter than most of those found in these reported complexes.³⁷ The N5_(imine)-Pd1-N1_(imine) angle of 104.4° is larger than the N4_(pyrrole)-Pd1-N2_(pyrrole) angle, 98.3°. Furthermore, this N5(imine)-Pd1-N(imine) angle is lower than all those found in the reported palladium complexes.³⁷ This lower angle could be because of the parallel orientation of the diisopropylphenyl rings and the flexibility of the three-atom chain connecting the two pyrrole rings in the ligand H_2L .

Having synthesized two different palladium complexes of H_2L , we became interested in synthesizing a palladium complex of H_2L' because it contains only one iminopyrrole moiety. When H_2L' was treated with one equiv. of $[Pd(PhCN)_2Cl_2]$ in dichloromethane, the zwitterionic palladium(π) complex 5 was obtained in 97% yield as an orange solid (Scheme 3). Complex 5 is soluble in MeOH and DMSO and sparingly soluble in CHCl₃ and CH₂Cl₂. The ¹H NMR spectrum of 5 in CDCl₃ features resonances corresponding to the pyrrolic NH, aldehyde, and ammonium NH groups at $\delta = 11.06$ (br s), 9.48(s), 8.49(br s) ppm, respectively, and two sets of resonances for the methylene protons among other resonances. This pattern of signals is consistent with its solid state structure.



Scheme 3 Synthesis of the zwitterionic palladium(11) complex 5 of the monoaldehyde Schiff base H_2L' .

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The structure of 5 was confirmed by single crystal X-ray diffraction study (Fig. 7a). The asymmetric unit contains one molecule of 5 and one benzonitrile in the crystal lattice. The X-ray structure revealed that the deprotonated imino-pyrrole moiety is coordinated to the palladium(II) atom containing two chlorine atoms. As a result, the palladium atom carries an anionic charge which is balanced by the internal ammonium cation formed by the abstraction of the pyrrole NH proton by the central amine nitrogen, giving a zwitterionic complex. Interestingly, this ammonium hydrogen is hydrogen bonded to one of the chloride atoms. As a result, the hydrogen bonded chloride atom bond distance Cl2-Pd1 is slightly longer (2.3005(17) Å) than the other Cl1-Pd1 distance (2.2968(15) Å). This is comparable to palladium complexes having this structural feature, which have been reported by us³⁸ and others.³⁹ Furthermore, because of this hydrogen bonding the unbound pyrrole-aldehyde moiety is pointed to the other side of the hydrogen bonding so that they form an intermolecular hydrogen bonding with the same groups from an adjacent molecule in the crystal lattice (Fig. 7b). In addition, the structure shows that the diisopropylphenyl ring plane remains perpendicular to the square plane of the palladium atom, probably because of the steric demand of the isopropyl group. The Cl1-Pd1-Cl2 angle value of 91.3° is larger than that (81.2°) of the N2-Pd1-N1 angle. The Pd1-N(pyrrole) distance of 2.015(5) Å is longer than those found in the reported palladium complexes containing the imino-pyrrole coordination mode³⁷ and those found in the cationic 3 and the neutral 4 complexes, whereas its Pd1-N_(imine) distance remains shorter than those reported for similar palladium complexes³⁷ and those found in complexes 3 and 4. As observed in 3 and 4, the coordinated pyrrole ring shows bond distances which are a reverse of those found in the free ligand structure H₂L and are attributed to the possible back bonding from the metal atom.³²

Catalysis of Suzuki-Miyaura cross coupling reactions

Complexes 3 and 4 were investigated for the Suzuki–Miyuara cross coupling reaction in water. Initially, the reaction between *p*-bromoacetophenone and phenylboronic acid in the presence

of K₂CO₃ was carried out in water under different conditions. From this, it was found that the yield of the product changed with the catalyst loading, temperature, reaction time and the amount of solvent water used, and the best conditions are 0.005 mol% of 3 or 4 in 1 mL of water around 100 °C for about 20 h for a maximum yield of the product. With these optimized conditions, different coupling reactions involving substrates having different electronic and steric factors were carried out and the results are summarized in Table 1. In particular, the sterically encumbered, 2,6-dimethylbromobenzene and the heteroaryl, 2-bromopyridine, substrates (entries 5 and 6) were found to give their coupled products in good yields. Remarkably, the *p*-bromoacetophenone reaction proceeds well even at a room temperature ~25 °C and gave the product in a nearly quantitative yield with 0.1 mol% of catalyst 3 in 1 mL of water for 90 h. In addition, the coupling of aryl chlorides was also achieved in DMF at 110 °C for 20 h reaction time in good yields (entries 7 & 8). Moreover, both complexes catalyze coupling of benzyl halides including benzyl chloride with phenylboronic acid in water to give diarylmethanes in good yields (entries 9–11). These $C(sp^3)-C(sp^2)$ coupling reactions show the versatile nature of the catalysts.

As shown in Scheme 2, the formation of the neutral complex 4 from the ionic complex 3 by K₂CO₃ treatment indicates that the catalysis reaction proceeds via the neutral complex 4 in all catalysis reactions in which complex 3 was used, because the same base was used in all the Suzuki reactions carried out here and complex 4 also catalyzes the reaction. In addition, a preliminary mechanistic investigation was also carried out. The coupling between *p*-bromoacetophenone and phenylboronic acid in the presence of K₂CO₃, 0.005 mol% of complex 3 and 500 equiv. of mercury⁴⁰ in water at 100 °C for 20 h was carried out and nearly quantitative formation of the coupled product was observed. Similarly, when the same reaction was carried out in toluene, the same result was observed. Besides, the reaction proceeds at room temperature in the presence of an excess amount of mercury to give 43% yield of the product after 90 h. In addition, there is no induction period observed in the plot of time versus yield (see ESI,



Fig. 7 (a) The X-ray structure of complex 5·PhCN. The co-crystallized benzonitrile and most hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: N1–Pd1 2.014(5), N2–Pd1 2.015(5), Pd1–Cl1 2.2968(15), Pd1–Cl2 2.3005(17), N1–Pd1–Cl2 176.46(14), N2–Pd1–Cl1 172.95(15), N1–Pd1–N2 81.2(2), Cl1–Pd1–Cl2 91.26(6); (b) the intermolecular hydrogen bonding formed by the pyrrolic NH and the aldehyde oxygen with the same groups from an adjacent molecule in the crystal lattice. N3…Cl2 3.157(5), H3…Cl2 2.40(7), N3–H3…Cl2 147(6), N4…O1ⁱ 2.789(10), H4…O1ⁱ 1.97, N4–H4…O1ⁱ 159.8. The symmetry operation was used to generate equivalent atoms: -x, -y + 1, -z + 2.

Table 1 Suzuki-Miyaura cross coupling reactions of aryl halides and phenylboronic acid in water catalyzed by complexes 3 and 4

				Complex 3 or 4 (mol%)					
		+ B(0	$(1)_2 + K_2 C O_3$	H ₂ O o	r DMF (1 r	mL)	/—Ar		
	X = Br and Cl				100 - 110 ℃, 20 h				
Entry	Ar–X	Product	Catalyst (mol%)	Yield ^a (%)	TON	Catalyst (mol%)	Yield ^a (%)	TON	
1	Br	Ph-	3 (0.005)	>99	>19 800	4 (0.005)	99	19 800	
2	Br	Ph-	3 (0.005) 3 (0.01)	79 >99	15 800 >9900	-4(0.01)	 92	18 400	
3	Br	Ph-NO ₂	3 (0.005)	99	19 800	4 (0.005)	99	19 800	
4	Br	Ph-	3 (0.005)	75	15 000	4 (0.005)	73	14600	
5	Br	Ph	3 (0.005)	68	13 600	4 (0.005)	61	12 200	
6	Br	Ph	3 (0.005)	57	11 400	4 (0.005)	52	10 400	
7	ci-	Ph-	3 (1)	73 ^b	73	4 (1)	63 ^{<i>b</i>}	63	
8	CI	Ph-	3 (1)	75 ^b	75	4 (1)	65 ^{<i>b</i>}	65	
9	Br	Ph	3 (0.005)	33	6600	4 (0.005)	33	6600	
10	Br NO ₂	Ph NO ₂	3 (0.005)	79	15 800	4 (0.005)	74	14 800	
11		Ph	3 (1)	78 ^b	78	4 (1)	72 ^b	72	

^a All are isolated yields. ^b 1 mL of DMF was used, instead of water at 110 °C.

Fig. S22†). While, from these observations, it is difficult to claim a mechanism involving palladium(π) species,⁴¹ further studies are required to establish actual catalytic species.

Conclusions

Ligands H_2L and H_2L' can be regarded as having both a proton donor (the pyrrolic NH) and an acceptor (the middle amine and the imine N). As a result, in the palladium complex formation, the imine, amine or both nitrogens accept protons, a Brønsted base, from the acidic pyrrolic NH protons, a Brønsted acid, resulting in the formation of the cationic 3 and the zwitterionic 5 complexes. In addition, there can be competition between the imine and the middle nitrogen atoms for protons. In the absence of a metal ion, the imine nitrogen wins the abstraction of the proton owing to its stronger basicity to give the amine-azafulvene tautomer. Thus, the ligands H_2L and H_2L' form a self conjugate acid which is the amine group of the amine-azafulvene structure or the ammonium cation and a self conjugate base which is the pyrrole nitrogen in the amine–azafulvene structure. This demonstrates the Brønsted acid–base character of the Schiff base ligands synthesized here, which facilitates the formation of different types of metal complexes. The ligand H_2L framework is flexible and versatile. In the structure of the dimeric lithium complex, it acts as a monoanionic ligand with the central amine nitrogen coordination, which was isolated and structurally characterized. Complex 4 is fluxional owing to the interconversion between the enantiomers and is studied by the variable temperature NMR method.

Both complexes 3 and 4 generate a very active catalyst for the Suzuki–Miyaura cross coupling reactions of various substrates in water. Although the catalytic activity is moderate with isolated yields, these results gain significance from an industrial point of view because an imine ligand was used as compared to the toxic and relatively expensive phosphine ligands. In particular, the relatively cheap aryl chloride coupling with 1 mol% of catalyst loading can have an impact as compared to several cases of the same coupling effected with greater than 1 mol% of phosphine ligands together with palladium complexes.^{10,42} Synthesis of other metal complexes and study of their catalytic properties are underway.

Experimental section

General procedures

Petroleum ether (bp 40-60 °C) and other solvents were distilled according to standard procedures. Pyrrole-2-carbaldehyde,43 [Pd(COD)Cl₂]⁴⁴ and [Pd(PhCN)₂Cl₂]⁴⁵ were prepared as reported. [Pd(OAc)₂], pyrrole, methylamine hydrochloride, and CDCl₃ were purchased from Aldrich and used without further purification except pyrrole, which was distilled, and methylamine hydrochloride, which was dried under vacuum with warm water. Other chemicals were obtained from commercial sources and used without further purification. ¹H NMR (200 MHz or 400 MHz) and ¹³C NMR (50.3 or 100.6 MHz) spectra were recorded on a Bruker ACF200 or AV400 spectrometer. Chemical shifts are referenced with respect to the chemical shift of the residual protons present in the deuterated solvents. FTIR spectra were recorded using a Perkin Elmer Spectrum Rx. High resolution mass spectra (ESI) were recorded using a Xevo G2 Tof mass spectrometer (Waters). Elemental analyses were carried out using a Perkin-Elmer 2400 CHN analyzer.

Synthesis of the Schiff base ligands H₂L and H₂L'

2,6-Diisopropylaniline (9.70 mL, 51.37 mmol) was added to a warmed methanol solution (150 mL) of the dialdehyde 1 (6.00 g, 24.46 mmol). After 5 minutes, concentrated HNO₃ (3.21 mL, 51.37 mmol, in MeOH, 10 mL) was added dropwise, giving a dark red clear solution. After stirring the solution at room temperature for 22 h, NaOH (2.05 g, 51.37 mmol) was added and stirring was continued for another 30 minutes, resulting in the formation of a precipitate. The solvent was removed under reduced pressure and the residue was extracted with dichloromethane $(2 \times 25 \text{ mL})$. The combined dichloromethane solution was dried over Na2SO4. The solution was filtered and the solvent was removed under vacuum. The resulting residue was loaded onto a column filled with silica gel. Elution using a mixture of ethyl acetate-petroleum ether (1:5 v/v) gave the first fraction from which the solvent was removed under vacuum to give the [1 + 2] Schiff base H₂L (7.54 g, 12.96 mmol, 53%) as viscous oil. This oil was dissolved in dichloromethane-petroleum ether (1:3 v/v) and allowed to evaporate slowly to give colorless crystals of H₂L. Further elution using ethyl acetate-petroleum ether (1:3 v/v) gave the [1 + 1] Schiff base H₂L' (2.38 g, 5.88 mmol, 24%) as a colorless solid after removal of the solvents under vacuum.

For H₂L: ¹H NMR (200 MHz, CDCl₃, 25 °C, ppm): δ = 7.81 (s, 2H, *HC*=N), 7.09 (s, 6H, aromatic *CH*), 6.59 (d, 2H, ³*J*(H,H) = 2.0 Hz, pyrrole β -C*H*), 6.16 (d, 2H, ³*J*(H,H) = 4.0 Hz, pyrrole β -C*H*), 3.74 (s, 4H, *CH*₂N), 3.00 (q, 4H, ³*J*(H,H) = 6.0 Hz, CH₃CHCH₃), 2.35 (s, 3H, NCH₃), 1.07 (d, 24H, *J*(H,H) = 8.0 Hz, CH₃CHCH₃). ¹H NMR (200 MHz, toluene-*d*₈, 25 °C, ppm): δ =

11.58 (br s, 2H, N*H*), 7.69 (s, 2H, *H*C=N), 7.00 (s, 6H, aromatic C*H*), 6.47 (d, 2H, ${}^{3}J(H,H) = 3.6$ Hz, pyrrole β -C*H*), 5.98 (d, 2H, ${}^{3}J(H,H) = 3.6$ Hz, pyrrole β -C*H*), 3.21 (s, 4H, CH₂N), 3.16 (q, 4H, ${}^{3}J(H,H) = 6.8$ Hz, CH₃CHCH₃), 1.94 (s, 3H, NCH₃), 1.07 (d, 24H, *J*(H,H) = 7.0 Hz, CH₃CHCH₃). ${}^{13}C{}^{1}H$ NMR (50.3 MHz, CDCl₃, 25 °C, ppm): $\delta = 153.5$, 148.8, 139.2, 136.8, 129.5, 124.5, 123.3, 118.3, 108.7, 54.9, 42.8, 28.0, 23.8. DEPT-135{}^{1}H NMR (50.3 MHz, CDCl₃, 25 °C, ppm): $\delta = 153.5$, 124.5, 123.3, 118.3, 108.7, 55.0, 42.8, 28.0, 23.8. FT-IR (KBr, cm⁻¹): $\nu = 3277$ (s), 3061(w), 2961(vs), 2868(m), 2790(w), 1622(vs), 1586(m), 1566 (m), 1493(w), 1457(m), 1361(s), 1333(m), 1306(m), 1256(m), 1167(m), 1100(w), 1036(s), 932(w), 864(m), 781(m), 759(m), 729 (w), 554(w). HRMS(+ESI): *m*/z calcd for [M + H⁺] C₃₇H₅₀N₅ 564.4061, found 564.4063.

For H_2L' : ¹H NMR (200 MHz, CDCl₃, 25 °C, ppm): δ = 10.53 (br s, 1H, pyrrole NH), 9.47 (s, 1H, CHO), 7.88 (s, 1H, HC=N), 7.10–7.14 (m, 3H, aromatic CH), 6.86 (d, 1H, ${}^{3}J(H,H) = 3.6$ Hz, pyrrole β-*CH*), 6.55 (d, 1H, ${}^{3}J$ (H,H) = 3.6 Hz, pyrrole β-*CH*), 6.19 (d, 1H, ${}^{3}J(H,H) = 3.8$ Hz, pyrrole β -CH), 6.16 (d, 1H, ${}^{3}J(H,H) =$ 3.6 Hz, pyrrole β-CH), 3.64 (s, 2H, CH₂N), 3.61 (s, 2H, CH₂N), 3.03 (q, 2H, ${}^{3}J(H,H) = 6.8$ Hz, CH₃CHCH₃), 2.27 (s, 3H, NCH₃), 1.15 (d, 24H, ${}^{3}J(H,H) = 7.0$ Hz, $CH_{3}CHCH_{3}$). ${}^{13}C{}^{1}H{}$ NMR (50.3 MHz, CDCl₃, 25 °C, ppm): δ = 179.3, 152.1, 149.1, 140.1, 138.7, 135.2, 132.7, 130.4, 124.2, 123.2, 116.5, 110.6, 109.5, 54.6, 54.1, 42.7, 28.0, 23.8. DEPT-135{¹H} NMR (50.3 MHz, CDCl₃, 25 °C, ppm): *δ* = 179.3, 152.0, 124.2, 123.2, 116.4, 110.6, 109.6, 54.6, 54.0, 42.7, 28.0, 23.8. FT-IR (KBr, cm⁻¹): ν = 3319 (vs), 2959(s), 2865(w), 2772(w), 1645(vs), 1588(w), 1571(w), 1493(w), 1445(w), 1362(w), 1336(w), 1242(s), 1218(w), 1203(w), 1175(s), 1131(w), 1099(w), 1044(w), 1010(w), 932(w), 858(w), 795(m), 777(s), 756(m), 730(w), 711(w). HRMS(+ESI): m/z calcd for $[M + H^+] C_{25}H_{33}N_4O$ 405.2649, found 405.2654.

Synthesis of the lithium complex [(HL)Li]₂, 2

To a solution of H_2L (0.45 g, 0.78 mmol) in THF (35 mL) under a nitrogen atmosphere was added dropwise ^{*n*}BuLi solution (1.6 M in hexane, 1.60 mL, 2.49 mmol) at -78 °C. The solution was stirred for 22 h. The volatiles were removed to give a colorless solid. The solid was dissolved in petroleum ether (~30 mL) and filtered. Colorless crystals of 2 were formed over a period of 15 days at room temperature, which were separated and dried under vacuum. Yield: 0.14 g, 0.12 mmol, 31%. FT-IR (nujol, cm⁻¹): ν = 3378(vs), 3266(s), 3059(s), 2920(vs), 2168(w), 2028(w), 1916(w), 1862(w), 1714(m), 1619(vs), 1566(vs), 1456(s), 1376(s), 1258(s), 1164(s), 1033(s), 973(s), 932(s), 859(s), 792(s), 668(m), 629(w), 603(m), 573(m), 507(w), 460(w).

Synthesis of the ionic palladium complex [Pd(Cl)(H₂L)][Cl], 3

To a solution of $[Pd(PhCN)_2Cl_2]$ (0.10 g, 0.26 mmol) in dichloromethane (10 mL) was added the crystals of H_2L (0.15 g, 0.26 mmol). The color of the solution immediately changed to orange. The solution was stirred at room temperature for 24 hours and a yellow precipitate was formed slowly. The solution was filtered, and the precipitate was washed with dichloromethane and then dried under vacuum to give compound 3 as a yellow solid (0.19 g, 0.25 mmol, 97%). ¹H NMR (400 MHz, $CDCl_3$, 25 °C, ppm): δ = 11.64 (d, 1H, ${}^{3}J(H,H)$ = 17.2 Hz, amine NH of the tautomerized arm), 9.00 (d, 1H, ${}^{3}J(H,H) = 15.6$ Hz, imine CH of the tautomerized arm), 8.39 (s, 1H, N^+H), 6.95-7.48 (m, 6H, aromatic CH), 6.73-7.81 (m, 2H, pyrrole β-CH), 6.20-6.26 (m, 2H, pyrrole β-CH), 4.45-4.99 (m, 4H, CH₂N), 3.17-3.91 (m, 4H, CH₃CHCH₃), 2.69 (s, 3H, NCH₃), 0.60-1.42 (m, 24H, CH₃CHCH₃). ¹³C{¹H} NMR (100.6 MHz, CD₃OD, 25 °C, ppm): δ = 165.7, 162.4, 145.8, 143.7, 143.6, 136.1, 131.4, 128.5, 125.5, 124.2, 123.8, 119.5, 39.7, 30.1, 29.9, 29.6, 24.8, 24.8, 24.4, 23.8, 23.7, 22.3. FT-IR (KBr, cm⁻¹): ν = 3432(w), 3084(w), 2962(m), 2594(w), 1628(vs), 1578(s), 1461(w), 1412(w), 1323(vs), 1240(w), 1178(w), 1110(w), 1069(m), 998(w), 940(w), 802(w), 774(w), 740(w). HRMS(+ESI): m/z calcd for $[M - Cl^{-}]^{+} C_{37}H_{49}ClN_5Pd$ 704.2706, found 704.2709; $[M - 2Cl^{-}]^{-}$ $-H^{+}]^{+}C_{37}H_{48}N_{5}Pd$ 668.2939, found 668.2924. Anal. Calcd for C37H51N5OCl2Pd: C, 58.54; H, 6.77; N, 9.23. Found: C, 56.81; H, 7.06; N, 9.15.

Synthesis of the neutral complex [PdL], 4

To a solution of [Pd(OAc)₂] (0.11 g, 0.49 mmol) in dichloromethane (15 mL) was added the crystals of H_2L (0.29 g, 0.49 mmol). The color of the solution immediately changed to orange. The solution was stirred at room temperature for 24 h and washed with water twice. The combined organic layer solution was dried over Na₂SO₄ and then filtered. The solvent was removed under vacuum to give complex 4 as a brown solid (0.31 g, 0.46 mmol, 95%). ¹H NMR (400 MHz, CDCl₃, 25 °C, ppm): δ = 7.06–7.09 (m, 4H, aromatic CH), 7.03 (s, 2H, HC=N), 6.79 (d, 2H, ${}^{3}J$ (H,H) = 3.6 Hz, pyrrole β -CH), 6.72 (br s, 2H, aromatic CH), 6.32 (d, 2H, ${}^{3}J(H,H) = 3.6$ Hz, pyrrole β -CH), 4.35 (br s, 2H, CH₃CHCH₃), 3.67 (br s, 2H, CH₂N), 3.44 (br s, 2H, CH₂N), 2.54 (s, 3H, NCH₃), 2.30 (br s, 2H, CH₃CHCH₃), 1.43 (br s, 6H, CH₃CHCH₃), 1.14 (br s, 6H, CH₃CHCH₃), 0.78 (br s, 6H, CH₃CHCH₃), 0.50 (br s, 6H, CH₃CHCH₃). ¹H NMR (400 MHz, $CDCl_3$, 0 °C, ppm): δ = 7.08–7.15 (m, 4H, aromatic CH), 7.05 (s, 2H, *H*C==N), 6.79 (d, 2H, ${}^{3}J(H,H) = 3.6$ Hz, pyrrole β -C*H*), 6.69 (d, 2H, ${}^{3}J(H,H) = 7.2$ Hz, aromatic CH), 6.35 (d, 2H, ${}^{3}J(H,H) =$ 4.0 Hz, pyrrole β-CH), 4.28 (m, 2H, CH₃CHCH₃), 3.46-3.75 (AB quartet, 4H, CH2N), 2.58 (s, 3H, NCH3), 2.26 (m, 2H, CH_3CHCH_3 , 1.41 (d, 6H, ${}^{3}J(H,H) = 6.8$ Hz, CH_3CHCH_3), 1.13 (d, 6H, ${}^{3}J(H,H) = 6.8$ Hz, $CH_{3}CHCH_{3}$), 0.75 (d, 6H, ${}^{3}J(H,H) =$ 6.8 Hz, CH_3CHCH_3 , 0.48 (d, 6H, ${}^{3}J(H,H) = 6.8$ Hz, CH₃CHCH₃). ¹³C{¹H} NMR (100.6 MHz, CDCl₃, 25 °C, ppm): δ = 164.1, 147.1, 146.0, 142.8, 139.4, 127.2, 124.4, 123.0, 118.5, 114.6, 51.7, 42.1, 29.9, 28.2, 25.9, 22.6. FT-IR (KBr, cm⁻¹): ν = 2960(s), 1575(vs), 1465(m), 1406(w), 1322(m), 1277(m), 1174(m), 1111(m), 1054(m), 893(w), 733(w). HRMS(+ESI): m/z calcd for $[M + H^+] C_{37}H_{48}N_5Pd$ 668.2939, found 668.2924. Anal. Calcd for C₃₇H₄₇N₅Pd: C, 66.50; H, 7.09; N, 10.48. Found: C, 66.51; H, 7.20; N, 9.81.

Synthesis of the zwitterionic palladium complex [PdCl₂(H₂L')], 5

To a solution of $[Pd(PhCN)_2Cl_2]$ (0.19 g, 0.50 mmol) in dichloromethane (15 mL) was added the crystals of H_2L' (0.20 g, 0.50 mmol). The color of the solution changed to orange. The solution was stirred at room temperature for 24 h and an orange precipitate was formed. The solution was filtered, and the precipitate was washed with dichloromethane. The precipitate was dried under vacuum to give complex 5 as an orange solid (0.28 g, 0.48 mmol, 97%). ¹H NMR (400 MHz, CDCl₃, 25 °C, ppm): δ = 11.06 (br s, 1H, NH pyrrole), 9.48 (s, 1H, CHO), 8.49 (br s, 1H, N⁺H), 7.26 (s, 1H, HC=N), 7.06-7.24 (m, 3H, aromatic CH), 6.90 (s, 1H, pyrrole β -CH), 6.71 (d, 1H, ${}^{3}J$ (H, H) = 3.2 Hz, pyrrole β -CH), 6.46 (s, 1H, pyrrole β -CH), 6.22 (d, 1H, ${}^{3}J(H,H) = 3.2$ Hz, pyrrole β -CH), 4.08–4.86 (m, 4H, CH₂N), 3.43 (m, 2H, CH₃CHCH₃), 2.90 (s, 3H, NCH₃), 1.07-1.29 (m, 12H, CH₃CHCH₃). ¹³C{¹H} NMR (100.6 MHz, DMSO-*d*₆, 25 °C, ppm): δ = 180.0, 163.4, 144.7, 142.1, 141.9, 138.2, 133.8, 128.5, 126.6, 122.4, 117.8, 115.4, 114.3, 79.2, 52.8, 50.4, 38.4, 27.8, 24.3, 24.2, 22.7. FT-IR (KBr, cm^{-1}): $\nu = 3357(w)$, 2961(s), 1659(vs), 1580(vs), 1460(m), 1321(s), 1180(m), 1109(w), 1056(m), 898(w), 798(w), 759(m). HRMS(+ESI): m/z calcd for [M + H⁺] C₂₅H₃₃N₄OCl₂Pd 581.1055, found 581.1916. Anal. Calcd for C₂₅H₃₆N₄O₃Cl₂Pd: C, 48.59; H, 5.87; N, 9.07. Found: C, 48.23; H, 5.17; N, 8.98.

General method for the Suzuki-Miyaura coupling reaction

Aryl halide (1 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2 mmol) and complex 3 or 4 (0.005 mol% or 1 mol%) were taken in a 10 mL round bottom flask. The solvent (1 mL, water or DMF) was added and the mixture was heated at 100–110 °C for 20 h. After cooling to room temperature, water (10 mL) was added and the mixture was extracted with dichloromethane (3 × 5 mL). The combined dichloromethane solution was dried over Na₂SO₄ for 20 minutes and then filtered. The solvent was removed under vacuum and the resulting residue was loaded onto a silica gel column. Elution using ethyl acetate–petroleum ether afforded the product, which was identified by the NMR method.

X-Ray crystallography

Single crystal X-ray diffraction data collections for all the compounds were performed using a Bruker-APEX-II CCD diffractometer with graphite monochromated MoK α radiation (λ = 0.71073 Å). The structures were solved by SIR-9246 or SHELXS-9747 available in WinGX, which successfully located most of the non-hydrogen atoms. Subsequently, least squares refinements were carried out on F^2 using SHELXL-97 (WinGX version) to locate the remaining non-hydrogen atoms. Suitable single crystals of 2 were obtained from a petroleum ether solution at -15 °C. Single crystals of H₂L, H₂L' and 4 suitable for X-ray analysis were obtained by the slow evaporation of the dichloromethane-petroleum ether solution (1:3 v/v). The slow evaporation of a solution of 3 in MeOH-EtOH (1:4 v/v) gave suitable single crystals for 3. Suitable single crystals of 5 were obtained by the slow evaporation of the filtrate of the reaction mixture in DCM-MeOH (2:1, v/v).

All non-hydrogen atoms were refined anisotropically and most of the hydrogen atoms were refined isotropically at calculated positions using a riding model. All the pyrrolic NH hydrogens except that in structure 5 and the water hydrogens were located from the difference Fourier map and refined iso-

Table 2 Crystallographic data for 2, 3.0.5(H₂O), 4 and 5.PhCN

	2	3.0.5(H ₂ O)	4	5·PhCN
Empirical formula	C ₇₄ H ₉₆ Li ₂ N ₁₀	C ₃₇ H ₅₀ Cl ₂ N ₅ O _{0.5} Pd	C ₃₇ H ₄₇ N ₅ Pd	C ₃₂ H ₃₇ Cl ₂ N ₅ OPd
Formula weight	1139.49	750.12	668.20	684.97
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Temperature (K)	100(2)	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$Par{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	10.0134(10)	9.898(6)	10.340(5)	9.7397(10)
b/Å	18.3400(19)	10.527(7)	15.075(8)	10.5677(10)
c/Å	36.980(4)	20.359(12)	22.169(11)	17.2217(17)
$\alpha/^{\circ}$	90	82.68(2)	88.651(16)	77.782(3)
β/\circ	94.521(3)	87.07(2)	82.564(17)	78.771(3)
γ/\circ	90	72.53(2)	86.454(16)	84.951(3)
Volume (Å ³)	6770.1(12)	2007(2)	3149(3)	1697.2(3)
Z	4	2	4	2
$D_{\rm calcd}/{\rm g}~{\rm cm}^{-3}$	1.118	1.241	1.298	1.340
μ/mm^{-1}	0.066	0.627	0.575	0.735
F(000)	2464	782	1400	704
θ range (°)	1.10 to 25.00	1.01 to 24.99	0.93 to 25.00	1.23 to 25.00
Limiting indices	$-11 \le h \le 11$,	$-11 \le h \le 11$,	$-12 \le h \le 12$,	$-11 \le h \le 11$,
0	$-21 \le k \le 21$,	$-12 \le k \le 11$,	$-17 \le k \le 17$,	$-12 \le k \le 12$,
	$-43 \le l \le 43$	$-24 \le l \le 24$	$-26 \le l \le 26$	$-20 \le l \le 20^{1}$
Total/unique no. of reflns.	76 909/11 901	20 021/6877	40 581/11 837	20 285/5946
Rint	0.1442	0.0848	0.0782	0.0883
Data/restr./params.	11 901/0/781	6877/2/421	11 837/0/775	5946/0/373
$GOF(F^2)$	1.038	1.023	1.012	0.998
R_1, WR_2	0.0708, 0.1679	0.0683. 0.1604	0.0495, 0.0954	0.0534.0.1086
R indices (all data) R_1 , w R_2	0.1417. 0.2096	0.1220. 0.1890	0.1091. 0.1170	0.1160, 0.1405
Largest different peak and hole (e $Å^{-3}$)	0.607 and -0.598	0.784 and -0.881	0.629 and -0.611	0.378 and -0.501

tropically with restraints DFIX or SADI, and their thermal parameters were set equivalent to 1.2 times the value of the parent atom to which the hydrogen atoms are bonded. The water molecule in the structure of **3** was refined with half occupancy, and its hydrogen atoms could not be located. The refinement data for all the structures are summarized in Table 2. CCDC 1045797–1045802.

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