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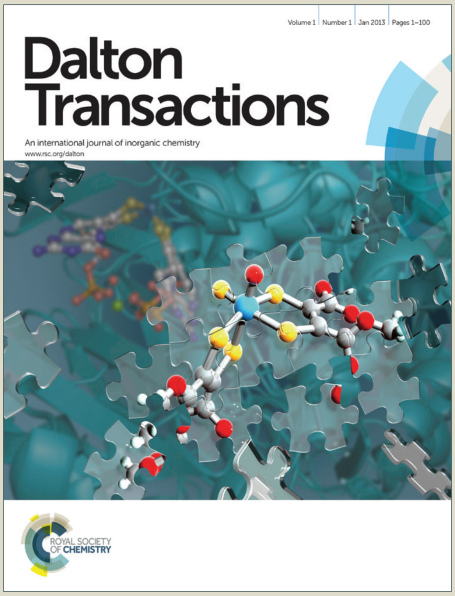

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PAPER

An Exhibition of the Brønsted Acid-Base Character by a Schiff Base in Palladium(II) Complex Formation: Lithium Complex, Fluxional Property 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–diisopropylanilline yielded two Schiff bases: bis(iminopyrrolylmethyl)amine (**H_2L**) 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 ^{n}BuLi. The presence of both proton donors and acceptors causes the diimino compound **H_2L** to undergo tautomerization to give an amine-azafulvene structure, though the central amine nitrogen competes for a proton. As a result, in the presence of Pd^{2+} ion, 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 ligand. The reaction of **H_2L'** with $[PdCl_2(PhCN)_2]$ 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 ^{1}H NMR method. Further, both complexes **3** and **4** are precatalysts for the Suzuki-Miyaura cross-coupling reaction in water. A sterically encumbered and electronically different substrates including activated aryl chlorides and benzyl halides gave the coupled products in very good yields. The reaction goes even at room temperature and in the presence of a large excess amount of mercury.

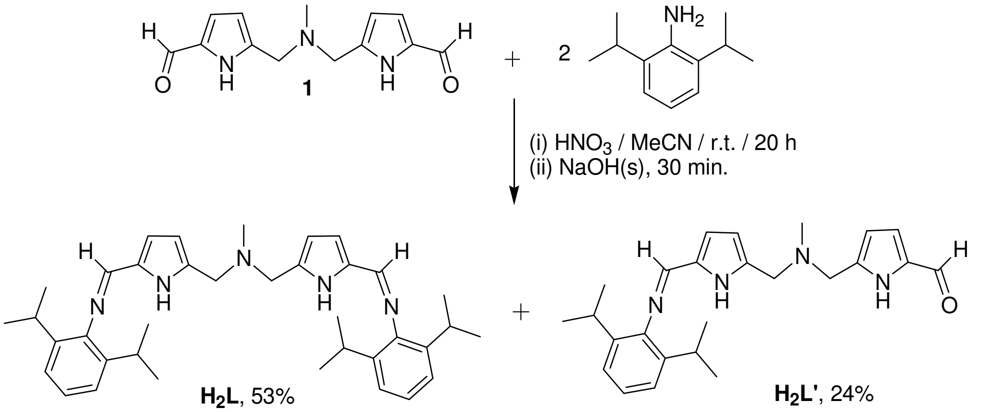
Introduction

Palladium remains the preferred metal over less expensive metals such as iron, copper or nickel for catalysis of carbon–carbon cross coupling reactions owing to higher activity, facile two electrons 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 naming reaction has been studied with 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 developed that promote coupling even with difficult substrates such as aryl chlorides[10] hindered substrates[11] and coupling with various organoboron species[12] and nonaryl halide substrates.[13] Further, catalysis reactions involving a very low catalyst loading,[14] mild conditions,[15] aqueous medium,[16] immobilized catalyst,[17] ‘ligandless’ systems[18] and room temperature[19] 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 of coordination to several metals in various oxidation states.[21] In addition, Schiff base metal complexes have been reported as catalysts for a wide variety of organic reactions.[22] We recently reported the dipyrrole-dialdehye compound **1** and its condensations with diamines/triamine to give the macrocycles and macrobicycles for anion binding studies.[23] Herein, we report two new multidentate Schiff base ligands synthesized by the 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 ligand. The fluxional property and the catalytic activity for Suzuki-Miyaura reactions in water are also described.

Results and discussion

Synthesis of Schiff Base Ligands



Scheme 1 Synthesis of bis(iminopyrrolylmethyl)amine, **H_2L** and its hydrolyzed monoimino compound **H_2L'**.

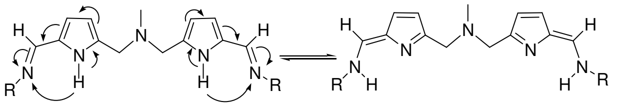


Chart 1 The tautomerization of bis(iminopyrrolylmethyl)amine **H_2L** to an amine-azafulvene structure.

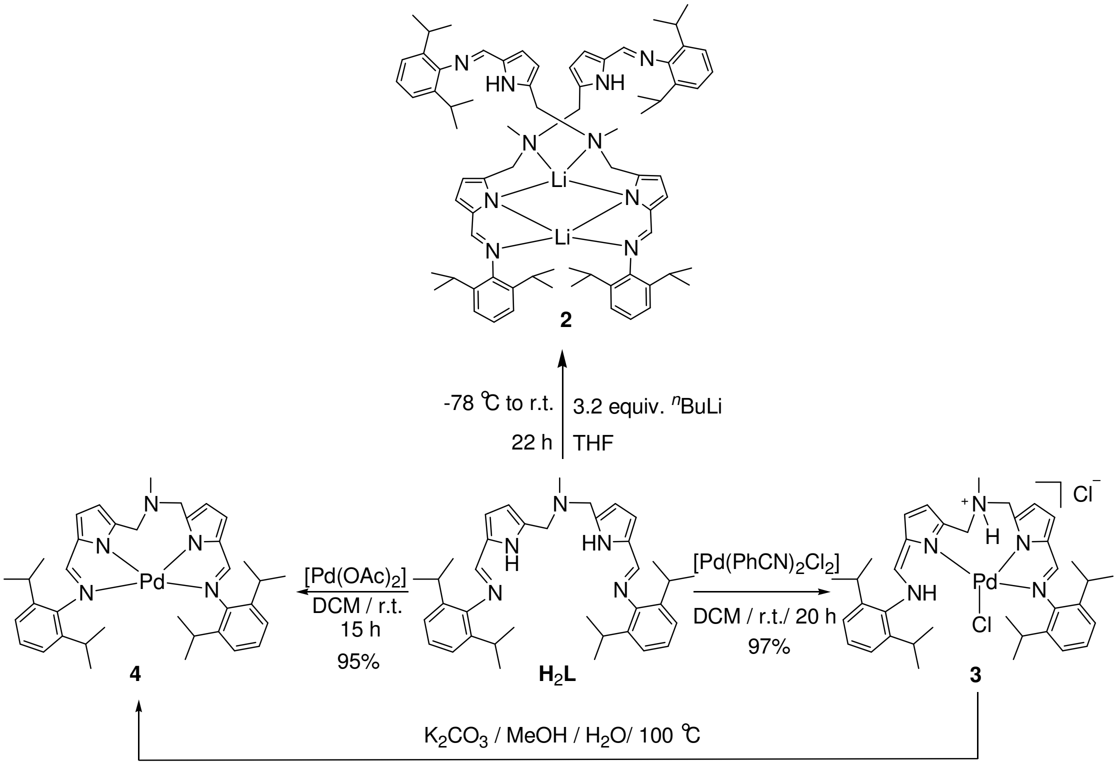
The condensation reaction between dipyrrole-dialdehdye **1** and 2,6-diisopropylaniline in the presence of concentrated nitric acid in the 1 : 2 : 2 molar ratio gave two Schiff bases, **H_2L** and **H_2L'**, in 53% and 24% yields after silica gel column chromatography separation, respectively (Scheme 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 shown in Chart 1. If the rate of exchange of proton between the pyrrole and imine nitrogen is rapid enough, it would not appear in ^{1}H NMR spectrum. In consistent with this, the ^{1}H NMR spectrum of **H_2L** in $CDCl_3$ does not show the pyrrolic NH resonance. The 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, ^{1}H 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 ^{1}H NMR spectrum of **H_2L'** in $CDCl_3$ features a broad singlet at 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 ^{13}C NMR spectrum, the resonance of the carbonyl group appears at δ = 179.3 ppm which is only slightly shifted up field relative to the dialdehyde **1** (δ = 179.4 ppm).

The structures of **H_2L** and **H_2L'** were confirmed by the single 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 are pointing 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 are facing 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 have hydrogen bonds with the cavity water molecule. On the contrary, the X-ray structure of **H_2L'** revealed no water molecule probably because of one carbonyl group in the molecule (ESI, Fig. S23(b)). The presence of carbonyl group induces dimerization in the crystal lattice by the intermolecular hydrogen bonding between the aldehyde oxygen and the pyrrolic NH groups of 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 monodeprotonated form of ligand (Scheme 2). Its structure was determined by 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 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 in a trans fashion, resulting in the same side orientation of the uncoordinated portion of the ligand. In the structure, the two imino-pyrrole-amine 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 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) Å[24], 2.444(15) Å[25] and 2.495(8) Å[26]) found in similar dimeric lithium complexes.



Scheme 2 Synthesis of the dimeric lithium and palladium(II) complexes of **H$_2$L**.

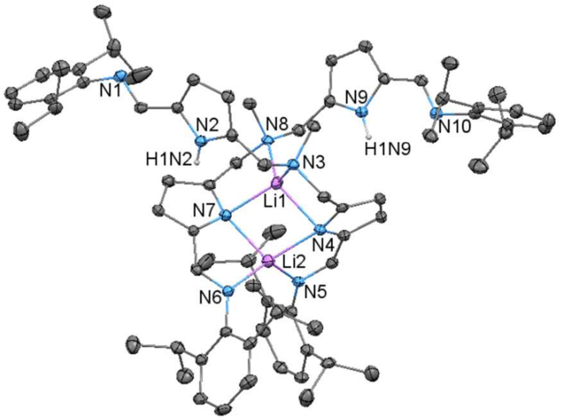


Fig. 1 The X-ray **s**tructure of the dimeric lithium complex **2**. Most hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: N3–Li1 2.141(6), N4–Li1 2.126(6), N4–Li2 2.069(6), N5–Li2 2.040(6), N6–Li2 2.017(6), N7–Li2 2.097(6), N7–Li1 2.100(6), N8–Li1 2.139(6), Li1···Li2 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).

The cationic palladium(II) complex **3** was obtained in 97% yield from the reaction between **H$_2$L** and [Pd(PhCN)$_2$Cl$_2$] or [Pd(COD)Cl$_2$]. Conversely, the neutral palladium(II) complex **4** was obtained in 95% yield when **H$_2$L** 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 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 ^{1}H NMR spectrum of the crystals obtained from the reaction between **3** and two equiv of K$_2$CO$_3$ in MeOH/H$_2$O 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 CHCl$_3$, DCM, and EtOH, indicating the ionic nature of the complex. In contrast to this, complex **4** is soluble in all these solvents. The ^{1}H NMR spectrum of **3** in CDCl$_3$ features signals in support of an amine azafulvene tautomeric structure, suggesting the presence of an unsymmetrically bound ligand. The NH proton of the amine–azafulvene structure appears at $\delta = 11.65$ ppm as a doublet with coupling constant $J = 17.2$ Hz, while the azafulvene C=CH proton gives a doublet at $\delta = 9.01$ ppm with $J = 15.6$ Hz. This magnitude of the coupling constant indicates that 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] Further, the presence of an ammonium hydrogen in the structure is supported by the broad resonance at $\delta = 8.39$ ppm and the NMe resonance is observed at $\delta = 2.69$ 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 CDCl$_3$ (See Supporting Information, Fig. S10). Nevertheless, the HRMS(ES+) spectrum shows a molecular ion peak at *m/z*

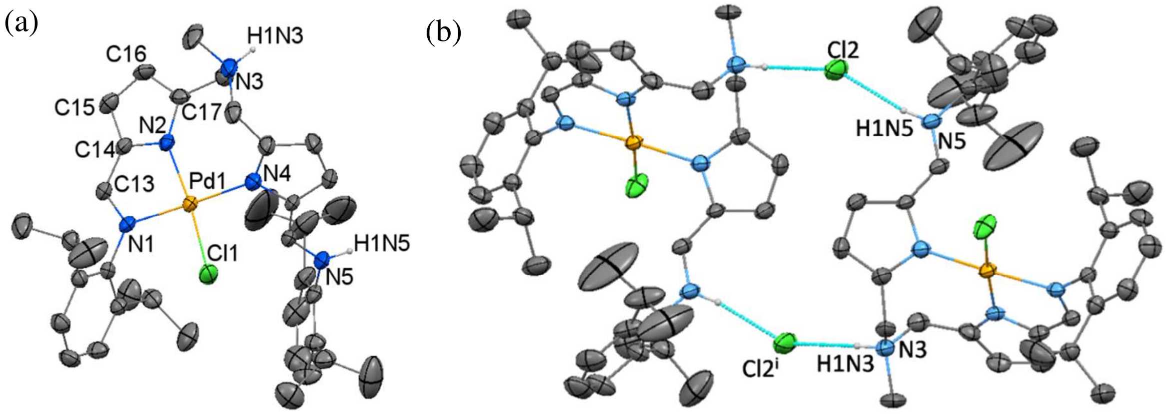


Fig. 2 (a) The X-ray structure of **3**·0.5(H_2O). Most hydrogen atoms, the outside chlorine atom and the water molecule are omitted for clarity. Selected bond lengths [Å] and angles [°]: N1–Pd1 2.024(5), N2–Pd1 2.035(5), N4–Pd1 2.008(6), Pd1–Cl1 2.301(2), C13–N1 1.321(8), C13–C14 1.407(9), C14–C15 1.398(10), 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) shows the intermolecular hydrogen bondings formed via the outside chloride atoms in the crystal lattice. N3···Cl2^i 3.006(7), H1N3···Cl2^i 2.13(2), N3–H1N3···Cl2^i 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.

704.2709 which corresponds to the mass of the $[M - Cl^-]^+$ ion (704.2706).

The X-ray structure of **3** given in Fig. 2 revealed that the palladium atom is coordinated by two pyrrolic nitrogens, one imine nitrogen and one chlorine atoms 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-azafulvene tautameric structure reported by Sessler,[28b] Love[28a,c,d] and Flout[29]. In addition to this, similar tautomeric structure has been reported for other ligands containing the pyrrole[30] and oxazoline[31] 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) distances, respectively, in the 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 **H_2L**, the alternating short-long-short bond distances (1.384(10), 1.397(10), and 1.361(11) Å) in the other pyrrole ring of the pendant arm is 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. In consistent 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 forming the intermolecular hydrogen bonding involving the NH of the amine-azafulvene and the ammonium NH^+ hydrogens (Fig. 2b).

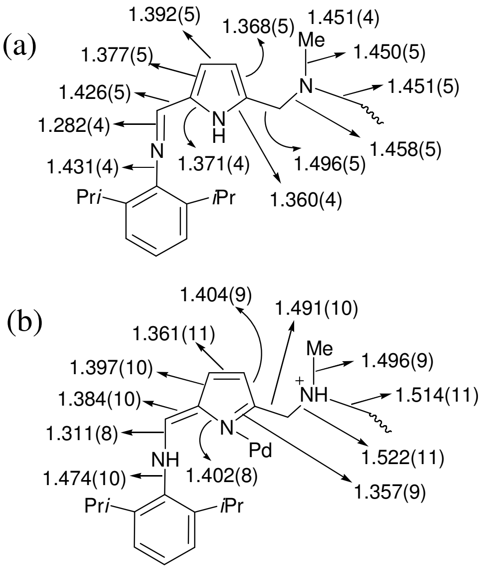


Fig. 3 Bond length (Å) comparison between the imino-pyrrole and amino-azafulvene tautomers: (a) shows bond lengths found in the free ligand structure **H_2L** and (b) shows those found in the cationic complex **3**.

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 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 similar arrangement of ligating atoms of a hydrid 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. Further, the N2–Pd1 bond distance remains very 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

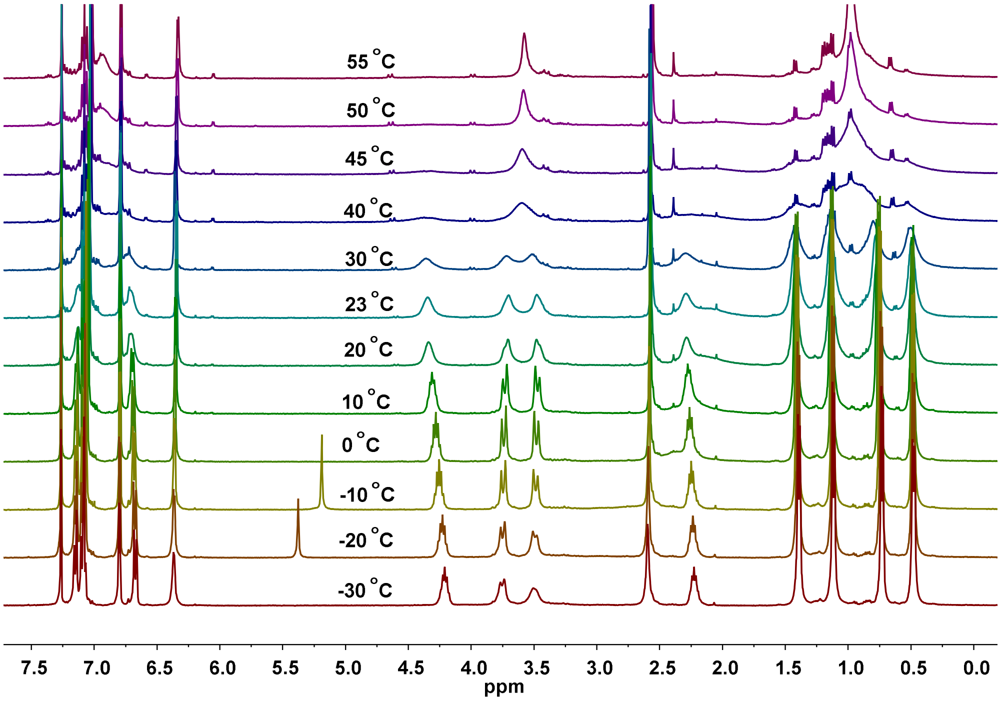


Fig. 4 Variable temperature ^{1}H NMR spectra of complex **4** in CDCl$_3$. At 10 °C, $k_c = \pi\Delta\nu/\sqrt{2}\ s^{-1}$, $\Delta G^\ddagger = 2.303RT_c(10.319 + \log T_c {}^{-} \log k_c)$ kJ/mol, $\Delta\nu$ = 103.2 Hz, $k_c = 229.2\ S^{-1}$, $T_c = 313$ K, $\Delta G^\ddagger = 62.6$ kJ/mol.

nitrogen atom trans to the chlorine atom which include the case of Pd(II) complex in which there is a back bonding from metal to pyrrole ring.[32a]

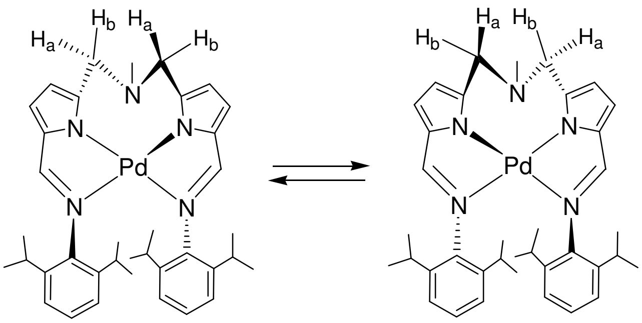


Fig. 5 Up and down movements of the two palladacycles in complex **4** cause the interconversion of the enantiomers with their methylene protons to become the equivalent at 40 °C, which is arrested at 10 °C to give an AB pattern.

The ^{1}H NMR spectrum of **4** in CDCl$_3$ at room temperature shows well separated four 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 ^{1}H 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 room temperature broad resonances begin to resolve into multiplets from 10 °C onwards which remains 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. In high temperatures, there could be a fast up and down movements of the two five-membered palladacycles, owing to the presence of two heavy diisopropylphenyl groups handing on both ends of the plane, by which one enantiomer is converted to another one 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 $\Delta G^\ddagger$ for this process is calculated to be 62.6 kJ/mol.[36] Further, at low temperature, the two imine CH protons appear as a sharp singlet at δ = 7.03 ppm, 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 having a distorted square planar geometry formed by the two five-membered palladacycles which are twisted with the N4–N5–N1–N2 torsion angle value of −20.3°. The two diisopropylphenyl ring planes are perpendicular

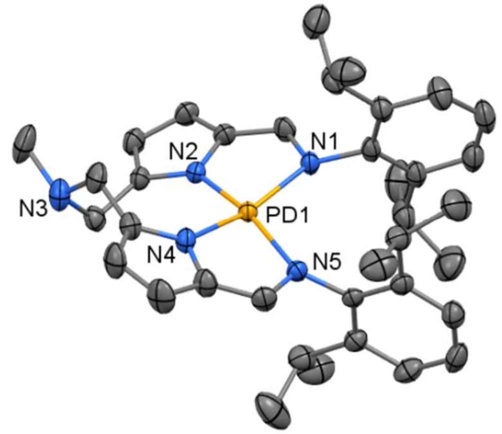
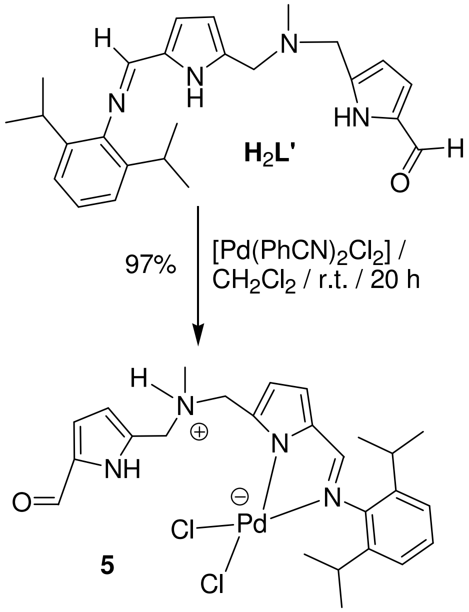


Fig. 6 The X-ray structure of complex **4**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: N1–Pd1 2.076(4), N2–Pd1 1.995(4), N4–Pd1 2.000(4), N5–Pd1 2.078(4), N2–Pd1–N5 166.05(16), N4–Pd1–N1 165.85(17), N4–Pd1–N2 98.28(17), N4–Pd1–N5 80.38(17), N5–Pd1–N1 104.36(16).

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 $C_{(imine\ CH)}$–$C_{(\alpha\text{-pyrrole})}$ bond distances show changes relative to those found in the free ligand **H_2L**, 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°. Further, this $N5_{(imine)}$–Pd1–$N_{(imine)}$ angle is lower than all those found in the reported palladium complexes.[37] This lower angle can 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 to synthesize 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(II) complex **5** was obtained in 97% yield as orange solid (Scheme 3). Complex **5** is soluble in MeOH and DMSO and sparingly soluble in $CHCl_3$ and CH_2Cl_2. The ^{1}H NMR spectrum of **5** in $CDCl_3$ features resonances corresponding to the pyrrolic NH, aldehyde, and ammonium NH groups at δ = 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(II) complex **5** of the monoaldehyde Schiff base **H_2L'**.

The structure of **5** was confirmed by single crystal X–ray diffraction (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 us[38] and others[39]. Further, 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 mode[37] 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 complexes[37] and those found in complex **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 **H_2L** and are attributed to the possible back bonding from the metal atom.[32]

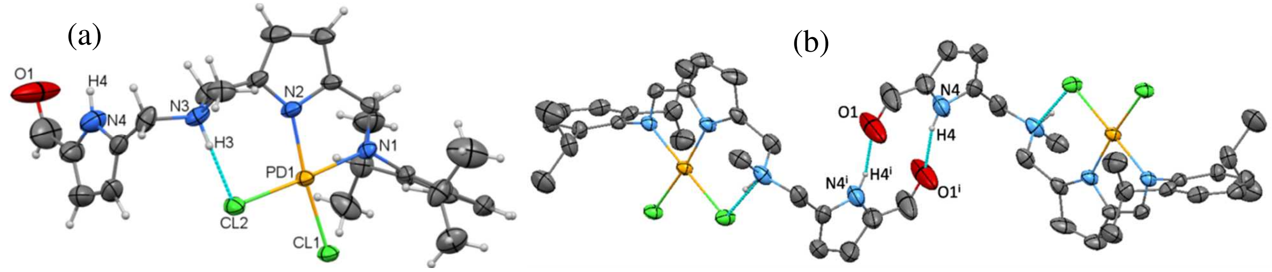
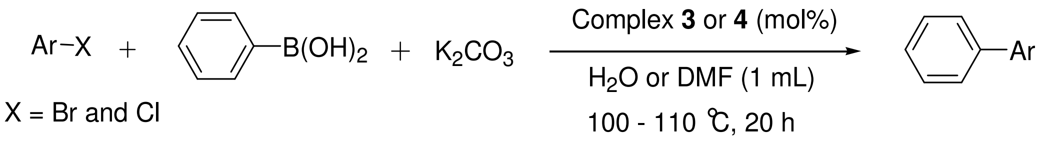
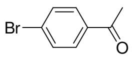
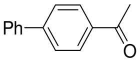
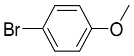
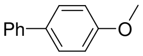
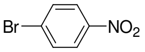
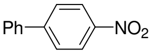
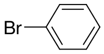
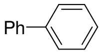
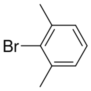
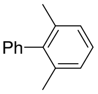
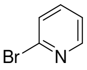
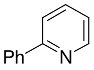
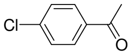
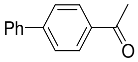
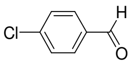
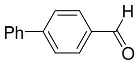
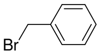
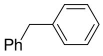
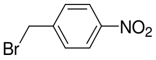
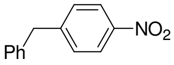
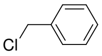
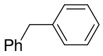


Fig. 7 (a) The X-ray structure of complex **5**·PhCN. The co-crystallized benzonitrile and most hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: N1–Pd1 2.014(5), N2–Pd1 2.015(5), Pd1–Cl1 2.2968(15), Pd1–Cl2 2.3005(17), N1–Pd1–Cl2 176.46(14), N2–Pd1–Cl1 172.95(15), N1–Pd1–N2 81.2(2), Cl1–Pd1–Cl2 91.26(6); (b) shows 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···O1^{i} 2.789(10), H4···O1^{i} 1.97, N4–H4···O1^{i} 159.8. The symmetry operation 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 complex **3** and **4**.



Entry	Ar-X	Product	Catalyst (mol %)	Yield[a] (%)	TON	Catalyst (mol %)	Yield (%)	TON
1			**3** (0.005)	>99	>19800	**4** (0.005)	99	19800
2			**3** (0.005)	79	15800	-	-	
			3 (0.01)	>99	>9900	**4** (0.01)	92	18400
3			**3** (0.005)	99	19800	**4** (0.005)	99	19800
4			**3** (0.005)	75	15000	**4** (0.005)	73	14600
5			**3** (0.005)	68	13600	**4** (0.005)	61	12200
6			**3** (0.005)	57	11400	**4** (0.005)	52	10400
7			**3** (1)	73[b]	73	**4** (1)	63[b]	63
8			**3** (1)	75[b]	75	**4** (1)	65[b]	65
9			**3** (0.005)	33	6600	**4** (0.005)	33	6600
10			**3** (0.005)	79	15800	**4** (0.005)	74	14800
11			**3** (1)	78[b]	78	**4** (1)	72[b]	72

[a] All are isolated yield; [b]1 mL of DMF was used, instead of water at 110 °C.

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 K_2CO_3 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 (entry 5 and 6) were found to give their coupled products in good yields. Remarkably, the *p*-bromoacetophenone reaction goes well even at room temperature ~25 °C and gave the product in 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 were also achieved in DMF at 110 °C for 20 h reaction time in good yields (entry 7 & 8). Moreover, both complexes catalyze coupling of benzyl halides including benzyl chloride with phenylboronic acid in water to give diarylmethanes in good yields (entry 9-11). These $C(sp^3)$–$C(sp^2)$ coupling reactions shows the versatile nature of the catalysts.

As shown in Scheme 2, the formation of the neutral complex **4** from the ionic complex **3** by K_2CO_3 treatment indicates that the catalysis reaction goes 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 K_2CO_3, 0.005 mol% of complex **3** and 500 equiv of mercury[40] 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 goes 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. S22). While, from these observations, it is difficult to claim a mechanism involving palladium(II) species,[41] further studies are required to establish actual catalytic species.

Conclusions

Ligand **H₂L** and **H₂L′** can be regarded as having both proton donor (the pyrrolic NH) and acceptor (the middle amine and the imine N). As a result, in the palladium complexes 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 a competition between the imine and the middle nitrogen atoms for protons. In the absence of metal ion, the imine nitrogen wins the abstraction of proton owing to its stronger basicity to give the amine-azafulvene tautomer. Thus, the ligand **H₂L** and **H₂L′** forms 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. Ligand **H₂L** 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 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 with industrial point of view because an imine ligand was used as compared to toxic and relatively expensive phosphine ligands. In particular, the relatively cheaper aryl chloride coupling with 1 mol % of catalyst loading can have impact as compared to several cases for 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 the standard procedures. Pyrrole-2-carbaldehyde,[43] $[Pd(COD)Cl_2]$[44] and $[Pd(PhCN)_2Cl_2]$[45] were prepared as reported. $[Pd(OAc)_2]$, pyrrole, methylamine hydrochloride, and $CDCl_3$ were purchased from Aldrich and were 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 ^{13}C 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 Perkin Elmer Spectrum Rx. High Resolution Mass Spectra (ESI) were recorded using the 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-Diisopropylanilline (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 HNO_3 (3.21 mL, 51.37 mmol, in MeOH, 10 mL) was added drop wise, 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 the solution was stirred 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 x 25 mL). The combined dichloromethane solution was dried over Na_2SO_4. 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 **H$_2$L** (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 **H$_2$L**. Further elution using ethyl acetate/petroleum ether (1:3 v/v) gave the [1 + 1] Schiff base **H$_2$L′** (2.38 g, 5.88 mmol, 24%) as a colorless solid after removal of the solvents under vacuum.

For **H$_2$L:** ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C, ppm): δ = 7.81 (s, 2H, *H*C=N), 7.09 (s, 6H, aromatic C*H*), 6.59 (d, 2H, ^3J(H,H) = 2.0 Hz, pyrrole β-C*H*), 6.16 (d, 2H, ^3J(H,H) = 4.0 Hz, pyrrole β-C*H*), 3.74 (s, 4H, C*H*$_2$N), 3.00 (q, 4H, ^3J(H,H) = 6.0 Hz, CH$_3$C*H*CH$_3$), 2.35 (s, 3H, NC*H*$_3$), 1.07 (d, 24H, *J*(H,H) = 8.0 Hz, C*H*$_3$CHC*H*$_3$). ^{1}H 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, ^3J(H,H) = 3.6 Hz, pyrrole β-C*H*), 5.98 (d, 2H, ^3J(H,H) = 3.6 Hz, pyrrole β-C*H*), 3.21 (s, 4H, C*H*$_2$N), 3.16 (q, 4H, ^3J(H,H) = 6.8 Hz, CH$_3$C*H*CH$_3$), 1.94 (s, 3H, NC*H*$_3$), 1.07 (d, 24H, *J*(H,H) = 7.0 Hz, C*H*$_3$CHC*H*$_3$). ^{13}C{^{1}H} NMR (50.3 MHz, CDCl$_3$, 25 °C, ppm): δ = 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, CDCl$_3$, 25 °C, ppm): δ = 153.5, 124.5, 123.3, 118.3, 108.7, 55.0, 42.8, 28.0, 23.8. FT-IR (KBr, cm^{-1}): ν = 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$^+$] C$_{37}$H$_{50}$N$_5$ 564.4061, found 564.4063.

For **H$_2$L′**: ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C, ppm): δ = 10.53 (br s, 1H, pyrrole N*H*), 9.47 (s, 1H, C*H*O), 7.88 (s, 1H, *H*C=N), 7.10–7.14 (m, 3H, aromatic C*H*), 6.86 (d, 1H, ^3J(H,H) = 3.6 Hz, pyrrole β-C*H*), 6.55 (d, 1H, ^3J(H,H) = 3.6 Hz, pyrrole β-C*H*), 6.19 (d, 1H, ^3J(H,H) = 3.8 Hz, pyrrole β-C*H*), 6.16 (d, 1H, ^3J(H,H) = 3.6 Hz, pyrrole β-C*H*), 3.64 (s, 2H, C*H*$_2$N), 3.61 (s, 2H, C*H*$_2$N), 3.03 (q, 2H, ^3J(H,H) = 6.8 Hz, CH$_3$C*H*CH$_3$), 2.27 (s, 3H, NC*H*$_3$), 1.15 (d, 24H, ^3J(H,H) = 7.0 Hz, C*H*$_3$CHC*H*$_3$). ^{13}C{^{1}H} NMR (50.3 MHz, CDCl$_3$, 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{^{1}H} NMR (50.3 MHz, CDCl$_3$, 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$_4$O 405.2649, found 405.2654.

Synthesis of the lithium complex [(HL)Li]$_2$, 2

To a solution of **H$_2$L** (0.45 g, 0.78 mmol) in THF (35 mL) under nitrogen atmosphere was added drop wise ^{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 was 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)(H$_2$L)][Cl], 3

To a solution of [Pd(PhCN)$_2$Cl$_2$] (0.10 g, 0.26 mmol) in dichloromethane (10 mL) was added the crystals of **H$_2$L** (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%). ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, ppm): δ = 11.64 (d, 1H, ^3J(H,H) = 17.2 Hz, amine N*H* of the tautomerized arm), 9.00 (d, 1H, ^3J(H,H) = 15.6 Hz, imine C*H* of the tautomerized arm), 8.39 (s, 1H, N$^+$*H*), 6.95–7.48 (m, 6H, aromatic C*H*), 6.73–7.81 (m, 2H, pyrrole *β*-C*H*), 6.20–6.26 (m, 2H, pyrrole *β*-C*H*), 4.45–4.99 (m, 4H, C*H*$_2$N), 3.17–3.91 (m, 4H, CH$_3$C*H*CH$_3$), 2.69 (s, 3H, NC*H*$_3$), 0.60–1.42 (m, 24H, C*H*$_3$CHC*H*$_3$). ^{13}C{^{1}H} NMR (100.6 MHz, CD$_3$OD, 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$_5$Pd 704.2706, found 704.2709; [M − 2Cl$^-$ − H$^+$]$^+$ C$_{37}$H$_{48}$N$_5$Pd 668.2939, found 668.2924. Anal. Calcd. for C$_{37}$H$_{51}$N$_5$OCl$_2$Pd: 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$_2$L** (0.29 g, 0.49 mmol). The color of the solution immediately changed to an orange. The solution was stirred at room temperature for 24 h and washed with water twice. The combined organic layer solution was dried over Na$_2$SO$_4$ and then filtered. The solvent was removed under vacuum to give complex **4** as a brown solid (0.31 g, 0.46 mmol, 95%). ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, ppm): δ = 7.06–7.09 (m, 4H, aromatic C*H*), 7.03 (s, 2H, *H*C=N), 6.79 (d, 2H, ^3J(H,H) = 3.6 Hz, pyrrole *β*-C*H*), 6.72 (br s, 2H, aromatic C*H*), 6.32 (d, 2H, ^3J(H,H) = 3.6 Hz, pyrrole *β*-C*H*), 4.35 (br s, 2H, CH$_3$C*H*CH$_3$), 3.67 (br s, 2H, C*H*$_2$N), 3.44 (br s, 2H, C*H*$_2$N), 2.54 (s, 3H, NC*H*$_3$), 2.30 (br s, 2H, CH$_3$C*H*CH$_3$), 1.43 (br s, 6H, C*H*$_3$CHC*H*$_3$), 1.14 (br s, 6H, C*H*$_3$CHC*H*$_3$), 0.78 (br s, 6H, C*H*$_3$CHC*H*$_3$), 0.50 (br s, 6H, C*H*$_3$CHC*H*$_3$). ^{1}H NMR (400 MHz, CDCl$_3$, 0 °C, ppm): δ = 7.08–7.15 (m, 4H, aromatic C*H*), 7.05 (s, 2H, *H*C=N), 6.79 (d, 2H, ^3J(H,H) = 3.6 Hz, pyrrole *β*-C*H*), 6.69 (d, 2H, ^3J(H,H) = 7.2 Hz, aromatic C*H*), 6.35 (d, 2H, ^3J(H,H) = 4.0 Hz, pyrrole *β*-C*H*), 4.28 (m, 2H, CH$_3$C*H*CH$_3$), 3.46–3.75 (AB quartet, 4H, C*H*$_2$N), 2.58 (s, 3H, NC*H*$_3$), 2.26 (m, 2H, CH$_3$C*H*CH$_3$), 1.41 (d, 6H, ^3J(H,H) = 6.8 Hz, C*H*$_3$CHC*H*$_3$), 1.13 (d, 6H, ^3J(H,H) = 6.8 Hz, C*H*$_3$CHC*H*$_3$), 0.75 (d, 6H, ^3J(H,H) = 6.8 Hz, C*H*$_3$CHC*H*$_3$), 0.48 (d, 6H, ^3J(H,H) = 6.8 Hz, C*H*$_3$CHC*H*$_3$). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$, 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 $C_{37}H_{47}N_5Pd$: C, 66.50; H, 7.09; N, 10.48. Found: C, 66.51; H, 7.20; N, 9.81.

Table 2 Crystallographic data for **2, 3**·0.5(H_2O)**, 4** and **5**·PhCN.

	2	**3**·0.5(H_2O)	**4**	**5**·PhCN
Empirical formula	$C_{74}H_{96}Li_2N_{10}$	$C_{37}H_{50}Cl_2N_5O_{0.5}Pd$	$C_{37}H_{47}N_5Pd$	$C_{32}H_{37}Cl_2N_5OPd$
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	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
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)
α/degree	90	82.68(2)	88.651(16)	77.782(3)
β/degree	94.521(3)	87.07(2)	82.564(17)	78.771(3)
γ/degree	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_{calcd} , g 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 (degree)	1.10 to 25.00	1.01 to 24.99	0.93 to 25.00	1.23 to 25.00
Limiting indices	−11<=h<=11, −21<=k<=21, −43<=l<=43	−11<=h<=11, −12<=k<=11, −24<=l<=24	−12<=h<=12, −17<=k<=17, −26<=l<=26	−11<=h<=11, −12<=k<=12, −20<=l<=20
Total/ unique no. of reflns.	76909 / 11901	20021 / 6877	40581 / 11837	20285 / 5946
R_{int}	0.1442	0.0848	0.0782	0.0883
Data / restr./ params.	11901 / 0 / 781	6877 / 2 / 421	11837 / 0 / 775	5946 / 0 / 373
GOF (F^2)	1.038	1.023	1.012	0.998
R1, *wR2*	0.0708, 0.1679	0.0683, 0.1604	0.0495, 0.0954	0.0534, 0.1086
R indices (all data) *R1*, *wR2*	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

Synthesis of the zwitterionic palladium complex $[PdCl_2(H_2L')]$, 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 is changed to an orange. The solution was stirred at room temperature for 24 h and an orange precipitate is 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, $CDCl_3$, 25 °C, ppm): δ = 11.06 (br s, 1H, N*H* pyrrole), 9.48 (s, 1H, C*H*O), 8.49 (br s, 1H, N^+*H*), 7.26 (s, 1H, *H*C=N), 7.06–7.24 (m, 3H, aromatic C*H*), 6.90 (s, 1H, pyrrole *β*-C*H*), 6.71 (d, 1H, ^3J(H,H) = 3.2 Hz, pyrrole *β*-C*H*), 6.46 (s, 1H, pyrrole *β*-C*H*), 6.22 (d, 1H, ^3J(H,H) = 3.2 Hz, pyrrole *β*-C*H*), 4.08–4.86 (m, 4H, CH_2N), 3.43 (m, 2H,

CH_3CHCH_3), 2.90 (s, 3H, NCH_3), 1.07–1.29 (m, 12H, CH_3CHCH_3). $^{13}C\{^1H\}$ 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}): ν = 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 $[M + H^+]$ $C_{25}H_{33}N_4OCl_2Pd$ 581.1055, found 581.1916. Anal. Calcd. for $C_{25}H_{36}N_4O_3Cl_2Pd$: 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 x 5 mL). The combined dichloromethane solution was dried over Na_2SO_4 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 NMR method.

X-ray crystallography

Single crystal X-ray diffraction data collections for all the compounds were performed using Bruker-APEX-II CCD diffractometer with graphite monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). The structures were solved by SIR-92[46] or SHELXS-97[47] available in WinGX, which successfully located most of the non-hydrogen atoms. Subsequently, least square 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 **H_2L**, **H_2L'** 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 the most of the hydrogen atoms were refined isotropically on calculated positions using a riding model. All the pyrrolic NH hydrogens except that in structure **5** and water hydrogens were located from the difference Fourier map and refined isotropically 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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Notes and references

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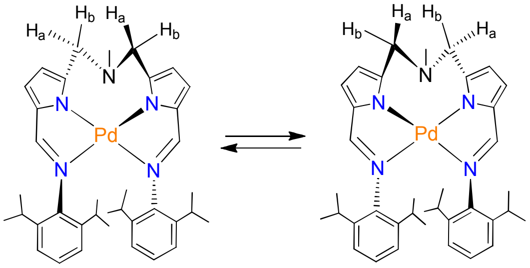
TOC



The Brønsted acid-base character of the versatile multidentate bis(iminopyrrolylmethyl)amine ligand was demonstrated through the X-ray structures of palladium complexes containing an amine-azafulvene tautomeric arm and ammonium cation. The bischelated palladium complex is fluxional studied by VT ^{1}H NMR method and effectively catalyzes Suzuki reactions in water.