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Pd(II) Coordinated deprotonated diphenyl phosphino amino pyridine: Reactivity towards Solvent, Base, and Acid

Sanjay Pratihar, a, * Rupa Pegu, a Ankur Kanti Guha, b and Bipul Sarma a

The reactivity and stability between P(III)–N and P(III)=N bonds will be different towards various solvents, base, and acid because of their difference in bond strength due to different N-pz-P-dz donor bonding. For this, P=N containing Pd(II) complex, [Pd(DPAP)2] (C1) was synthesized from the reaction between PdCl2(COD) (COD = 1,4-cyclooctadiene) and 2 equiv. DPAP (diphenyl phosphino amino pyridine) ligand, followed by deprotonation of N-H proton of coordinated DPAP. The reactivity and stability of coordinated P=N in complex C1 was determined in various protic, aprotic solvents, base, and acid. The inertness of coordinated P=N towards various solvent and base was observed. Whereas, protonation occurs at nitrogen of P=N in presence of acid to form P-NH, with the generation of dicatonic palladium complexes (C2). The dicatonic complex C2 is found to be stable in presence of bulky mono anionic Sn(IV) reagents. Whereas, in presence of more nucleophilic anion like Br− or I−, dissociation of one DPAP ligand from dicatonic Pd(II) complexes C2 leads to the generation of Pd(DPAP)X2 (x = Br−, I−). Finally, the utility of the complexes towards Suzuki coupling of various aryl bromide and aryl or heteraryl boronic acid have been checked.

Introduction:
During the past few decades, there has been an astounding growth in the application of organometallic compounds in homogenous catalysis for fine-chemicals. Currently, the vast majority of research has focused on the development of new ligands because the use of electron-rich, sterically congested ligands, in conjunction with a transition metal (TM), has become a common recipe in TM catalyzed cross coupling reactions. Therefore, designing a new class of ligand having hybrid and bi-functional properties to support different catalytic intermediates is appealing. In this respect, several new classes of P–N bond-containing phosphorus ligands in combination with transition metal have been demonstrated as a catalyst for number of pivotal synthetic organic reactions. The hemilabile P–N ligand may be constructed in large quantities through the use of relatively simple condensation processes, and from inexpensive starting materials. But in certain cases, compounds containing P–N bonds have proved to be somewhat unstable, notably to protic solvents, which clearly limit their utility. The hydrolysis of P(III)–N bonds toward acid or base-catalyzed cleavage of P(III)–N bonds will lead to P(V) oxide with the liberation of secondary amines. This type of cleavage with aminobis(phosphines) and phosphoryl azides was illustrated by Balakrishna et al. The stability of P(III)–N bonds in various phosphazanes and other ligands depend to a large extent on the substituent on both the phosphorus and nitrogen. Likewise, the presence of one or more P–Cl bonds in the P–N moiety makes them susceptible towards acid/base-catalyzed hydrolysis reactions. But in the absence of P–Cl bonds they are comparatively more stable. In metal complexes of aminobis(phosphines), such P–N bond cleavage in presence of trace amounts of acid was also observed by King and others. Although the coordination chemistry as well as their catalytic properties of pyridylphosphine with both bidentate P-N and tridentate P–N–P framework has extensively been studied, but there are limited studies focused on the stability of P–N bonds in terms of their hydrolytic behavior. As an important contribution, Kirchner et al. showed that on treatment of NiBr2(DME) (DME = 1,2-dimethoxyethane) or anhydrous NiBr2 with 2 equiv. of PNP pincer ligands featuring phosphoramidites in CH2Cl2 yields the novel neutral pentacoordinate complexes [Ni(PNP)(κ1(P)-R3P=O)Br]. Using in-situ 31P NMR, they showed that, over the course of this reaction the P–N bonds of the phosphoramidite units of one PNP ligand are selectively cleaved due to hydrolysis affording an anionic κ3-(P)-coordinated and one intact κ3-(P,N,P)-coordinated PNP ligand (Scheme 1).
On the other hand, P-N and P-N-P bonds are among the most fascinating in main-group chemistry and the nature of P-N and P=N bonds and their coordination behavior has been extensively studied.\(^{11}\) In this regard, Dyson et al. showed the reversible transoformation and rearrangement between P-N and P=N of diphosphinoamines attached to pyridine at the ortho-position and to its corresponding iminobiphosphone isomers in presence of acid and base.\(^{12}\) By taking most simple type aminophosphane ligands PR\(_2\)N\(\approx\)P(III), Krischner et al. showed that coordination takes place exclusively through the phosphorus donor leaving the N-site available for further reactions. They further studied various reactions with available N-site along with various metal complexes.\(^{13}\) Although various rearrangement and reaction have been done with P-N bond, but the protonation behavior of P=N studied rarely. The P(III)–N bonds are nominally single but show partial double bond character due to N-p\(\pi\)-P-d\(\pi\) donor bonding. But, upon removal of one hydrogen from nitrogen centre will increase the N-p\(\pi\)-P\-d\(\pi\) donor bonding and enforce the transformation from P(III)–N to P=N. A major objective of the present work is to generate an insight into the protonation behavior of metal coordinated P(III)=N? With this objective in mind, we have done the protonation behaviour and the reactivity of palladium coordinated P=N in various solvents, acid, and base, based on experimental and theoretical evidences. The complexes have been screened as catalyst in Suzuki coupling involving aryl bromide and aryl or heteraryl boronic acid with appreciable turn over frequency (TOF).

**Results and Discussion:**

**Reactivity of Coordinated P=N:**

The diphenyl phosphino amino pyridine (DPAP) ligand has been synthesized from the reaction between 2-amino pyridine and chloro diphenyl phosphine. The complex C\(_1\) was prepared from the complexation of DPAP and PdCl\(_2\)(COD) followed by deprotonation of N-H proton of coordinated DPAP (Fig. 1) by following the procedure by Woolins et al.\(^{14}\)

![Scheme 1. P-N bond cleavage of PNP ligand observed by Kirchner et al. (ref. 10)](image)

The hydrolytic behavior of coordinated P=N in complex C\(_1\) was checked from the \(^{31}\)P NMR monitoring of complex C\(_1\) in different protic and aprotic solvent. Interestingly no characteristic changes in \(^{31}\)P NMR of C\(_1\) was found in different protic and aprotic solvents like; MeOH, DMSO, H\(_2\)O, and benzene. Further, \(^{31}\)P NMR of complex C\(_1\) in presence of Cs\(_2\)CO\(_3\) in DMSO-d\(_6\) was recorded to check the effect of base. After 1 day, no characteristic changes of complex C\(_1\) was found. Interestingly, even after heating the same solution, we did not observed any change of C\(_1\). All the above mentioned \(^{31}\)P NMR experiment suggest the inertness of coordinated P=N of complex C\(_1\) towards protic, aprotic solvent, and base. However, in presence of acid, C\(_1\) transformed to a new species, which has been characterized by various spectroscopic technique. The in-situ \(^1\)H NMR of complex C\(_1\) showed three peaks at 6.29, 6.68, and 7.26 ppm, assigned to pyridine ring of the coordinated DPAP ligand. Upon addition of HCl to DMSO-d\(_6\) solution of C\(_1\), \(^1\)H NMR signal corresponding to NH (9.98 ppm) appeared. Whereas, pyridine ring protons shifted significantly to downfield (for example, from 6.29 to 7.91 and from 7.26 to 8.34 ppm; refer to Scheme 2). The corresponding \(^{31}\)P NMR spectrum also showed up field shifting of PPh\(_2\) from 88 to 80 ppm (Scheme 2).

![Scheme 2. In-situ NMR monitoring the protonation reaction of Pd\(^\text{II}\) coordinated P=N](image)
chloride and produce bulky mono or di-anionic counterion for di-cationic Pd(II), which will make the crystallization process easier. Three different organo tin(IV) reagents for the study viz. SnCl₄, Me₂SnCl₂, PhSnCl₃ was selected based on their Lewis acidity. Tetra coordinated organo tin(IV) can coordinate up to two chloride anions to form hexachlorostannate dianion via pentachlorostannate anion. The chemical shifts for SnCl₄, SnCl₅⁻, and SnCl₆²⁻ were reported to be -148, -480, and -732 ppm, respectively. In case of SnCl₄, the peak at -496 ppm corresponds to SnCl₅⁻, indicates the formation of two mono anionic SnCl₅⁻ unit in Pd(II) complex, C3. We did not observe any peak corresponding to dianionic SnCl₆²⁻. The ³¹P NMR of complex C3 exhibited one peak at an 80 ppm, which is shifted to up field from its parent complex. The reaction between C1 and PhSnCl₃ leads to complex C4, which showed peak at -201 ppm in ¹¹⁹Sn NMR, corresponds to two mono anionic PhSnCl₃⁻. The ³¹P NMR of complex showed peak at 80.3 ppm. Analytically pure sample of C4 could not be produced, as we failed to remove trapped solvent or unreacted PhSnCl₃ from complex C4. On the other hand, reaction between C1 and Me₂SnCl₂ afforded colorless complex C5, which shows one peak at -172 ppm in ¹¹⁹Sn NMR, corresponds to mono-anionic Me₂SnCl₃⁻ and one ³¹P NMR peak at 79.86 ppm due to the coordinated P-NH in dicaticonic Pd(II) complex (Fig. 2).

To our delight, compound C5 crystallized from dichloroethane solvent in a monoclinic space group P21/c with four dicaticonic Pd(II), eight monoanionic Me₂SnCl₃⁻, along with two dichloroethane solvent molecules in the unit cell. Within an asymmetric unit there are three components, a dicaticonic palladium, two monoanionic Me₂SnCl₃⁻, and dichloroethane (DCE) solvent as shown in Fig. 3.

**Fig. 2.** Characterization of protonated complex after the reaction between C1 and organotin(IV) reagents

The in-situ ³¹P NMR also suggested the transformation of C1 to C7 through protonation followed by ligand dissociation via protonated complex. The in-situ NMR experiments for the reaction between C1 and SnBr₄ in DMSO-d₆ also suggested the
formation of complex C6 via complex C2. The formation of the brominated and iodinated complex (C6 and C7) has been further confirmed from the 31P NMR spectroscopy (Fig. 4). The elemental analyses data of both the complexes deviates from the calculated values as we failed to remove trapped solvent or dissociated ligand from the both the complexes by washing with different solvent to produce analytically pure sample of C6 and C7. To simulate the experimental 31P NMR data, we have optimized all the complexes at PBE1PBE level of theory using the same basis set as detailed in computational details. Subsequently, the 31P NMR chemical shifts were calculated at GIAO/PBE1PBE level of theory. Gratifyingly, we have obtained very close agreement between theoretical and experimental 31P NMR chemical shifts for all the complexes (Fig. 4). The P-N bond distance from the crystal structure of C1 and C5 are found to be 1.64 and 1.69 Å respectively. For better understanding the bonding, the structure optimization of complex C1 and C5 has been done excluding solvent or anion present in the crystal structure of C1 and C5 at PBE1PBE level of theory using 6-31+G* basis set for H, C, N and P atoms and Stuttgart-Dresden effective core polarization (SDD) basis set for Pd. The NBO analysis on the optimized geometry of both the complexes was done. All the bond order along with their structure was shown in Fig. 5. The bond order shows increase in P-N, C-N and N(py)-C bond from complex C2 to C1. So, upon deprotonation of N-H, the negative charge has been delocalized over the entire five member ring surrounded by PdII. In order to understand the reactivity pattern of C1 and C2, we analyzed their frontier molecular orbitals. It is evident from Fig. 5 that the HOMO of C1 preliminary resides on the pyridine ring and the lone pair at the nitrogen atoms where protonation takes place on treatment with HX (X=Cl, Br, I), resulting in the formation of C2. On the other hand, the LUMO of C2 represents the Pd-P or Pd-N σ* orbital. Thus, after protonation of C1, the nucleophile Br- or I attacks the LUMO of C2 which is antibonding with respect to Pd-P or Pd-N bonds (Fig. 6).

![Fig. 5 Bond order of deprotonated and protonated Pd(II) complexes](image)

The attack of nucleophile thus ruptures one of the Pd-P and Pd-N bonds resulting in the formation of the brominated and iodinated products C6 and C7 respectively. The PdII complexes studied so far contained either one or two hemilabile P=N or P-NH ligand. The hemilabile ligand has been very important for its superior activity towards various type of C-C bond formation reaction. We also wanted to check the activity of hemilabile P=N and P-NH containing PdII complexes towards Suzuki coupling reaction.

![Fig. 6 Kohn-Sham molecular orbitals of C1 and C2.](image)

**Catalytic activity of Complexes:**

In 1979, the seminal paper of Miyaura, Yamada, and Suzuki laid the groundwork for what now is the most important and useful transformation for construction of carbon-carbon bonds in modern day organic chemistry. **2223 24 Throughout the past 30 years contributions from myriad research groups have led to vast improvements on what now is known as the Suzuki-Miyaura cross coupling reaction (hereafter Suzuki reaction or Suzuki coupling or SC). In this respect, some of the hemilabile ligand have been successfully utilized towards SC.** **25 We wished to check the catalytic activity of the PdII complexes containing hemilabile P=N and P-NH ligand in biaryl formation from aryl halide and aryloboronic acid. For model studies we had chosen 4-bromo anisole due to the fact that aryl halide having electron releasing group is a challenging substrate in Suzuki reaction (Table 1). **26 From screening of solvent, temperature, and catalyst loading the following condition has been optimized: catalyst solution in acetonitrile, toluene as a solvent; temperature 110 °C. Interestingly, we did not observe any reactivity differences between C1 and C2 towards SC, both showed good turn over frequency (TOF). However, cross coupling proceeded smoothly with all other PdII complexes C5, C6, and C7 bearing hemilabile P-NH ligand. In terms of TOF, we got slightly better activity of C1 over C2. Therefore we have chosen C1 as a candidate for bench-scale studies on SC coupling. Upon decreasing the catalyst loading from 1 to 10^-4 mol% the TOF steadily increases for C1, while product yield drop down drastically below 0.001mol% loading of C1. The Suzuki cross-coupling of different aryl substrates with aryl and heteroaryl substrate was carried out using C1 at low loading to generate a sense for the turnover frequency (h^-1). To check the generality and substrate scope of the C1 catalyzed SC, a library of cross-coupled products was synthesized efficiently (Table 2).
The acid showed a lower TOF. The 4-bromo anisole with phenyl boronic acid completed in 10-11 h in good yield and TOF. On the other hand, coupling between 2-bromo benzaldehyde with aryl boronic acid completed in 4-5 h in good yield and TOF. Biaryl anisole reacted with phenyl boronic acid to give corresponding coupling product in lower yield and TOF. For example electron withdrawing substituent containing aryl bromide reacted with phenyl boronic acid to give corresponding biaryl in 90% yield with TOF 18,000 (Table 2). While, electron donating group containing aryl bromide, 4-bromo anisole reacted with phenyl boronic acid to give corresponding biaryl 1a in 72% yield with TOF 6,000. Note that the reaction of 4-bromo anisole with phenyl boronic acid completed in 10-12 h with moderate TOF, whereas that of thio phenyl-3-boronic acid showed a lower TOF. The C1 promoted reaction between 2-bromo benzaldehyde with aryl boronic acid completed in 4-5 h in good yield and TOF. On the other hand, coupling between 2-bromo benzaldehyde with thienophenyl-3-boronic acid leads to corresponding coupling product 1b in lower yield and TOF.

### Table 1. Effect of Pd complexes in Suzuki Coupling

<table>
<thead>
<tr>
<th>#</th>
<th>Pd-Complex</th>
<th>Mol(%)</th>
<th>Time (h)</th>
<th>TON</th>
<th>TOF (h⁻¹)</th>
<th>Isolated Yield (%)</th>
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<tbody>
<tr>
<td>1</td>
<td>C1</td>
<td>1</td>
<td>3</td>
<td>93</td>
<td>31</td>
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<tr>
<td>2</td>
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<tr>
<td>4</td>
<td>C6</td>
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<td>5</td>
<td>C7</td>
<td>1</td>
<td>3</td>
<td>79</td>
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<td>79</td>
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<tr>
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<td>Pd(dba)$_2$</td>
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<td>4</td>
<td>20</td>
<td>5</td>
<td>20</td>
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<tr>
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<td>PdCl(2PPh$_3$)$_2$</td>
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<td>48</td>
<td>7</td>
<td>48</td>
</tr>
<tr>
<td>8</td>
<td>C1</td>
<td>0.1</td>
<td>4</td>
<td>920</td>
<td>230</td>
<td>92</td>
</tr>
<tr>
<td>9</td>
<td>C2</td>
<td>0.01</td>
<td>6</td>
<td>8,600</td>
<td>1,433</td>
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<tr>
<td>10</td>
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<td>0.001</td>
<td>6</td>
<td>7,700</td>
<td>1,283</td>
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<td>11</td>
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<td>12</td>
<td>72,000</td>
<td>6,000</td>
<td>72</td>
</tr>
<tr>
<td>12</td>
<td>C1</td>
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<td>12</td>
<td>3,800,000</td>
<td>31,667</td>
<td>38</td>
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Experimental Section

**General:** The synthesis of the compounds has been performed under a dry oxygen free argon atmosphere using standard vacuum lines and Schlenk techniques. All solvents used for the ligand and precursor complex synthesis and to perform Suzuki coupling reaction have been dried and distilled by standard methods and previously deoxygenated in the vacuum line. All the protonation reaction was performed in normal moist solvent. $^1$H (200, 400 MHz) and $^{13}$C NMR (54.6, 100 MHz) spectra (chemical shifts referenced to signals for residual solvent) were recorded on 200 and 400 MHz spectrometer at 298 K. $^{119}$Sn NMR (149.2 MHz) spectra (chemical shifts referenced to signals for external tetramethyltin) were recorded in 400 MHz spectrometer at 298 K.

**X-Ray Crystallography:**

X-ray reflections were collected on Bruker SMART APEX II CCD diffractometer. Mo-K$_\alpha$ ($\lambda$=0.71073 A) radiation was used to collect X-ray reflections on the single crystals. Data reduction was performed using Bruker SAINT software. The TD-DFT calculations have been performed in solution phase using polarized continuum model (PCM)$^{31}$ employing acetonitrile as the solvent. All the Sn(IV) compounds were optimized in gas phase at PBE1PBE level of theory using 6-31+G* for H, C, and O atoms and LANL2DZ for Sn atom. The optimized geometries were characterized as stationary points on the potential energy surface at respective levels of theories by evaluating the vibrational frequencies. Electrophilicity (o) of all the Sn(IV) compounds have been performed with $o$ =µ$^2$/2η, which has been defined by Parr et al. as the energy of stabilization of a chemical species when it acquires an additional fraction of electronic charge from the environment and is defined as where $\mu$ is the electronic chemical potential and $\eta$ is the hardness. All the hardness, chemical potential, and electrophilicity of the Sn(IV) compounds were calculated using the Koopmans' theorem.

### Table 2. Substrate scope of C1 catalyzed Suzuki coupling.

<table>
<thead>
<tr>
<th>R</th>
<th>1 eq.</th>
<th>MeCN/Toluene (1:5)</th>
<th>C1</th>
<th>1.2 eq.</th>
<th>yield (%)</th>
<th>TOF (h⁻¹)</th>
</tr>
</thead>
</table>
| Example electron withdrawing substituent containing aryl bromide reacted with phenyl boronic acid to give corresponding biaryl 1C in 90% yield with TOF 18,000 (Table 2). While, electron donating group containing aryl bromide, 4-bromo anisole reacted with phenyl boronic acid to give corresponding biaryl 1a in 72% yield with TOF 6,000. Note that the reaction of 4-bromo anisole with phenyl boronic acid completed in 10-12 h with moderate TOF, whereas that of thio phenyl-3-boronic acid showed a lower TOF. The C1 promoted reaction between 2-bromo benzaldehyde with aryl boronic acid completed in 4-5 h in good yield and TOF. On the other hand, coupling between 2-bromo benzaldehyde with thienophenyl-3-boronic acid leads to corresponding coupling product 1b in lower yield and TOF.

### Computational Details:

Natural bond orbital (NBO)$^{27}$ analysis of C1 and C2 were performed using the optimized geometry of both the complexes at PBE1PBE level of theory. We employed 6-31+G* basis set for H, C, N and P atoms while Stuttgart-Dresden effective core polarization (SDD) basis set has been used for Pd, Br and I atoms. The computed $^{31}$P chemical shifts were obtained at GIAO/PBE1PBE/BS1 (where BS1 stands for 6-31+G* for H, C, N and P atoms while SDD for Pd, Sn, Br and I atoms) level of theory. Isotopic chemical shifts of $^{31}$P are relative to P(CH$_3$)$_3$ (δ -83.9 ppm taken as 0.0 ppm). All the calculations were performed using Gaussian09 suite of program. The TD-DFT calculations have been performed in solution phase using polarized continuum model (PCM)$^{31}$ employing acetonitrile as the solvent. All the Sn(IV) compounds were optimized in gas phase at PBE1PBE level of theory using 6-31+G* for H, C, and O atoms and LANL2DZ for Sn atom. The optimized geometries were characterized as stationary points on the potential energy surface at respective levels of theories by evaluating the vibrational frequencies. Electrophilicity (o) of all the Sn(IV) compounds have been performed with $o$ =µ$^2$/2η, which has been defined by Parr et al. as the energy of stabilization of a chemical species when it acquires an additional fraction of electronic charge from the environment and is defined as where $\mu$ is the electronic chemical potential and $\eta$ is the hardness. All the hardness, chemical potential, and electrophilicity of the Sn(IV) compounds were calculated using the Koopmans' theorem.
Synthesis of 2-(Diphenylphosphinoamino) pyridine (DPPAP) ligand:

2-(Diphenylphosphinoamino) pyridine has been prepared by drop wise addition of neat chlorodiphenylphosphine to a solution of 2-aminopyridine and Et₃N in Toluene over 15 min at 0 °C. The mixture was slowly warmed to room temperature and stirred for 4 h after which it was filtered off to remove precipitated triethylamine hydrochloride. The precipitate was washed with Toluene. The washings and the filtrate were precipitated triethylamine hydrochloride. The precipitate was washed with acetone, and dried in vacuum. Yield 70 %.\(^1\) H NMR (200 MHz, DMSO-d₆) δ (ppm): 6.85 (2H, t, J = 6.8 Hz, Py), 7.0 (2H, Py, d J = 8.2 Hz), 7.20-7.27 (8H, m, Ph), 7.34-7.53 (10H, m, Ph), 7.62 (2H, t, J = 7.4 Hz, Py), 8.31 (2H, s, Py), 9.53 (2H, s, NH). \(^31\)P[H]-NMR (161.9 MHz, DMSO-d₆) δ (ppm): 80.1.

Table 3. Crystal data of C1 and C5.

<table>
<thead>
<tr>
<th>Chemical formula</th>
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<th>C5</th>
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<tr>
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<td>1017560</td>
</tr>
<tr>
<td>Formula weight</td>
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<td>3972.13</td>
</tr>
<tr>
<td>Crystal system</td>
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<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>C2/c</td>
<td>P2₁/c</td>
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<tr>
<td>T/RK</td>
<td>296(2)</td>
<td>100(2)</td>
</tr>
<tr>
<td>a/Å</td>
<td>19.1917(3)</td>
<td>11.1211(2)</td>
</tr>
<tr>
<td>b/Å</td>
<td>14.403(2)</td>
<td>20.2361(4)</td>
</tr>
<tr>
<td>c/Å</td>
<td>39.795(6)</td>
<td>22.0997(4)</td>
</tr>
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<td>90</td>
</tr>
<tr>
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<td>90</td>
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<tr>
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<tr>
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<td>1.772</td>
</tr>
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<td>1.962</td>
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<tr>
<td>Reflns collected</td>
<td>9163</td>
<td>19799</td>
</tr>
<tr>
<td>Unique reflns</td>
<td>6520</td>
<td>15692</td>
</tr>
<tr>
<td>R(1 &gt; 2(I))</td>
<td>0.0687</td>
<td>0.0366</td>
</tr>
<tr>
<td>wR2 (all)</td>
<td>0.1743</td>
<td>0.0803</td>
</tr>
<tr>
<td>Goodness-of-fit</td>
<td>1.064</td>
<td>1.021</td>
</tr>
</tbody>
</table>

\(^{a}\)PLATON Squeeze used to removed highly disordered benzene solvent. Highest peak 1.47 at (0.0026, 0.1054, 0.2239); 1.04 Å from Pd2 and deepest hole -3.41 at (0.0000, 0.3307, 0.2500); 1.48 Å from H47. Total potential solvent area volume 2901.9 Å³ which is ~26.4% crystal cell volume.

Protonation of Pd(DPPAP)₂ using organo Sn(IV) reagents:

A solution of 0.2 mmol of complex C1 was dissolved in 2 ml dichloroethane. To this solution 0.4 mmol of corresponding organo Sn(IV) reagents in 1 ml dichloroethane was added and kept at room temperature. Depending upon the reaction time, a colorless precipitate was isolated and washed with diethyl ether and dried in vacuum. The yield and spectroscopic data of the corresponding compounds are given below:

C2, yield: 60% (The reaction between 0.2 mmol of complex C1 and dilute HCl (400 μL of 35% HCl) was performed in 3ml dichloroethane). \(^1\)H NMR (200 MHz, DMSO-d₆) δ (ppm): 6.85 (2H, t, J = 6.8 Hz, Py), 7.0 (2H, Py, d J = 8.2 Hz), 7.20-7.27 (8H, m, Ph), 7.34-7.53 (10H, m, Ph), 7.62 (2H, t, J = 7.4 Hz, Py), 8.31 (2H, s, Py), 9.53 (2H, s, NH), \(^31\)P[H]-NMR (161.9 MHz, DMSO-d₆) δ (ppm): 80.1.

C3, yield: 78%. Anal. Calc. for C₃₀H₁₆N₅P₄Cl₄PdSn: C, 42.58; H, 3.15; N, 5.84. Found: C, 42.45; H, 3.42; N, 5.55%. \(^1\)H NMR (200 MHz, DMSO-d₆) δ (ppm): 6.87 (2H, t, J = 6.8 Hz, Py), 6.99 (2H, Py, d J = 8.2 Hz), 7.20-7.26 (8H, m, Ph), 7.36-7.52 (10H, m, Ph), 7.63 (2H, t, J = 7.4 Hz, Py), 8.3 (2H, s, Py), 9.51 (2H, s, NH), \(^31\)P[H]-NMR (161.9 MHz, DMSO-d₆) δ (ppm): 80.0.

C4, yield: 73%. Anal. Calc. for C₃₄H₂₈N₄P₄PdSn: C, 41.28; H, 3.01; N, 4.19. Found: C, 42.78; H, 3.92; N, 5.15%. \(^1\)H NMR (200 MHz, DMSO-d₆) δ (ppm): 6.96-7.03 (4H, m, Py), 7.27-7.39 (6H, m, Ph), 7.41-7.52 (20H, m, Ph), 7.64 (2H, t, J = 8.0 Hz, Py), 8.27 (2H, s, Py), 9.63 (2H, s, NH), \(^31\)P[H]-NMR (161.9 MHz, DMSO-d₆) δ (ppm): 80.0.

C5, yield: 91%. Anal. Calc. for C₃₅H₂₆N₆P₄Sn: C, 38.90; H, 3.61; N, 4.78. Found: C, 39.18; H, 3.85; N, 5.05%. \(^1\)H NMR (200 MHz, DMSO-d₆) δ (ppm): 1.02 (s, 6H, -CH₃), \(^¹¹⁹\)Sn satellites at 0.74 and 1.30 ppm with \(^²\)SnSn= 56.2 Hz, 6.96 (2H, t, J = 6.6 Hz, Py), 7.04 (2H, Py, d J = 7.8 Hz), 7.33-7.49 (2H, m, Ph), 7.72 (2H, t, J = 7.8 Hz, Py), 8.3 (2H, s, Py), 9.83 (2H, s, NH), \(^31\)P[H]-NMR (161.9 MHz, DMSO-d₆) δ (ppm): 79.8.

Synthesis of Pd(DPPAP)₂ (C1):

A solution of 2 g (11.3 mmol) of PdCl₂ is dissolved in concentrated HCl (5 mL) under gentle heating (40 °C). The cold solution then diluted with 150 ml 96% ethanol, filtered and 3.0 ml (24 mmol) of 1,5-cyclooctadiene was slowly added to a stirred solution. Immediately, a yellow precipitate forms which was collected by filtration, washed successfully with diethyl ether and dried in a vacuum for 2 hours. Yield: 3.0 g, 93%.

2-(Diphenylphosphinoamino) pyridine (DPPAP) ligand (56 mg, 0.2 mmol) was added to a solution of (COD)PdCl₂ (28 mg, 0.1 mmol) in acetonitrile (3 mL) under an argon atmosphere. The mixture was stirred for 30 min leading to a yellow precipitate. The yellow precipitate was filtered and washed with acetonitrile and followed by diethyl ether and vacuum-dried. The solid \(^1\)BuOK (0.078 g, 0.7 mmol) was poured into a stirred solution of yellow precipitate (0.147 g, 0.2 mmol) in MeOH (10 ml), which causing the immediate precipitation of a yellow solid. After stirring the mixture for 10 min the product was filtered off, washed with MeOH (2 x 3 ml) and cold diethyl ether (2 x 3 ml) and dried in vacuum. Yield: 64%. Anal. Calc. for C₅₀H₃₀N₄P₄Cl₄: C, 61.78; H, 4.24; N, 8.35%. \(^1\)H NMR (400 MHz, DMSO-d₆) δ (ppm): 6.33 (2H, t, J = 6.4 Hz, Py), 6.66 (2H, Py, d J = 8.8 Hz), 7.15-7.21 (14H, m, Ph), 7.26-7.32 (8H, m, Ph), 7.66 (2H, s, Py), \(^31\)P[H]-NMR (161.9 MHz, DMSO-d₆) δ (ppm): 88.0.

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(4H, m), 7.48-7.58 (6H, m), 7.91 (1H, t, J = 7.4 Hz, Py), 8.34 (1H, s, Py), 9.98 (1H, s, NH), 3J{P-H-NMR (161.9 MHz, DMSO-d$_6$) δ (ppm): 93.5.

C7, yield: 85%. Anal. Calc. for C$_{17}$H$_{14}$N$_2$Pd: C, 31.98; H, 2.37; N, 4.39. Found: C, 32.43; H, 2.65; N, 4.85%. H NMR (200 MHz, DMSO-d$_6$) δ (ppm): 7.03 (2H, t, J = 6.4 Hz, Py), 7.16 (2H, d, J = 8.2 Hz, Py), 7.59-7.69 (12H, m, Ph), 7.83-7.88 (8H, m, Ph), 7.93 (2H, t, J = 8.0 Hz, Py), 9.16 (2H, s, Py), 10.1 (2H, s, NH), 3J{P-H-NMR (161.9 MHz, DMSO-d$_6$) δ (ppm): 86.1.

General Procedure for Pd$^{II}$ complex catalyzed Suzuki Coupling between 4-bromo anisole with Ph-B(OH)$_2$:

The reaction was carried out in a 10-mL Schlenk flask using 4-bromo anisole (0.5 mmol), phenyl boronic acid (1.2 mmol) in a mixture of MeCN (0.5 ml)/Toluene (2.5 ml) at 110°C. After completion, the reaction mixture was quenched with aqueous NH$_4$F solution, extracted with ethylacetate (20 mL) and washed with water (10 mL x 3), brine (10 mL) and dried over anhydrous Na$_2$SO$_4$. After removing the solvent the residue was subjected to silica gel column chromatography (60-120 mesh, ethyl acetate-petroleum ether, gradient elution) to afford pure cross coupling product.

Typical procedure for complex C1 catalyzed Suzuki Coupling of Aryl Halide:

A 10-mL Schlenk flask equipped with a magnetic bar, was charged with complex C1 (0.001 mmol), in MeCN/Toluene (0.5/2.5 ml) under an argon atmosphere and stirred vigorously for 5 min. After that the appropriate aryl halide (0.5 mmol) was added to it and placed into a constant temperature bath at 110°C and allowed to stir for 5 min. The appropriate arylboronic acid (0.6 mmol) was added to the latter and the reaction was allowed to continue at 110°C. After completion, the reaction mixture was quenched with aqueous NH$_4$F solution, extracted with ethylacetate (20 mL) and washed with water (10 mL x 3), brine (10 mL) and dried over anhydrous Na$_2$SO$_4$. After removing the solvent the residue was subjected to silica gel column chromatography (60-120 mesh, ethyl acetate-petroleum ether, gradient elution) to afford pure cross coupling product.

4-methoxybiphenyl (1a): δ$_H$(200 MHz; CDCl$_3$) 8.35 (3H, s, OCH$_3$), 6.98 (2H, d, J = 8.6 Hz, CH aromat.), 7.31 (1H, d, J = 7.0 Hz, CH aromat.), 7.42 (2H, t, J = 7.6 Hz, CH aromat.), 7.51-7.57 (4H, m, CH aromat.). δ$_C$(54.6 MHz, CDCl$_3$) 55.3, 114.1, 126.6, 126.7, 128.1, 133.7, 140.7, 159.1. Anal. (C$_{13}$H$_{12}$O) calcd, C: 86.59; H: 5.53 found, C: 86.32, H: 5.74.

Biphienyl-2-carbaldehyde (1d): δ$_H$(200 MHz; CDCl$_3$) 7.76-7.53 (7H, m), 7.61-7.70 (1H, m), 8.04 (1H, d, J = 7.8 Hz) 9.98 (1H, s, CHO), δ$_C$(54.6 MHz, CDCl$_3$) 127.6, 127.8, 128.1, 128.4, 128.5, 130.1, 130.8, 133.6, 137.8, 146.0, 192.5. Anal. (C$_{13}$H$_2$O$_2$) calcd, C: 85.69; H: 5.33 found, C: 85.49, H: 5.74.

4-methoxyphenylthiophene (1e): δ$_H$(200 MHz; CDCl$_3$) 3.84 (3H, s, OCH$_3$), 6.94 (2H, d, J = 8.6 Hz, CH aromat.), δ$_C$(54.6 MHz, CDCl$_3$) 55.3, 114.2, 118.9, 126.0, 126.2, 126.7, 128.8, 142.0, 158.9. Anal. (C$_{13}$H$_2$O) calcd, C: 69.44; H: 5.30 found, C: 69.18, H: 5.60.

Conclusions

In summary, The palladium(II) complex, [Pd(DPAP)$_2$], have been prepared from the reaction between Pd(COD)Cl$_2$ and diphenyl phosphino amino pyridine (DPAP) ligand followed by deprotonation of N-H in coordinated DPAP. The reactivity and stability of the coordinated P-N and P-NH complexes have been checked in various protic and aprotic solvent with or without base and acid. In presence of acid, protonation at nitrogen of coordinated P-N in [Pd(DPAP)$_2$] is found to be stable in presence of bulky mono anionic Sn(IV) reagents. In presence of more nucleophilic anion like Br$^-$ or I$^-$, dissociation of one DPAP ligand from dicaticionic Pd(II) complexes C2 leads to the generation of Pd(DPAP)$_2$X$_2$ (X = Br$^-$, I$^-$). The complexes have been screened as catalyst in Suzuki coupling involving aryl bromide and aryl or hetaryl boronic acid with appreciable turnover frequency.

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Notes and references

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Notes and references
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Electronic Supplementary Information (ESI) available: [Crystallographic .cif files (CCDC Nos. 957985 and 1017560) are available at www.ccdc.cam.ac.uk/data_request/cif or as part of the Supporting Information. Spectral data are available in Supporting Information (SI)]. See DOI: 10.1039/b000000x/


7 (a) M. G. Newton, R. B. King, M. Chang, J. Gimeno, J. Am. Chem. Soc. 1978, 100, 1632.


14 For better understanding the UV-vis transition, TD-DFT calculation on both the C1 and C2 has been carried out, please see ESI.

15 All the experiments with Sn(IV) reagents have been done in normal rack solvents.

16 In order to gain insight into their Lewis acidic behavior, electrophilicity (\( \omega \)) of three reagents have been calculated at PBE1PBE level of theory using 6-31+G* basis set for H, C, N and Cl atoms and LANL2DZ basis set for Sn with \( \omega = \mu^2/\eta \). Please see ESI for details.


The residual water in DMSO-d$_6$ is responsible for the generation of Bronsted acids, as the residual water signal in $^1$H NMR spectra confirms the presence of water in DMSO-d$_6$.


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