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

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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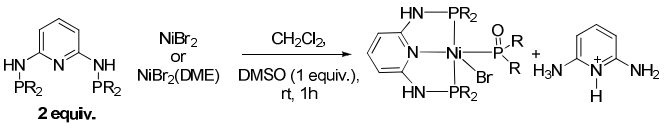
The reactivity and stability between P(III)–N and P(III)≈N bonds will be different towards various solvents, base, and acid because of their difference in bond strength due to different N-$p\pi$-P-$d\pi$ donor bonding. For this, P≈N containing Pd(II) complex, [Pd(DPAP)$_2$] (**C1**) was synthesized from the reaction between $PdCl_2$(COD) (COD = 1,4-cyclooctadiene) and 2 eqv. DPAP (diphenyl phoshino 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 dicationic palladium complexes (**C2**). The dicationic 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 dicationic Pd(II) complexes **C2** leads to the generation of Pd(DPAP)X_2 (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.[1 2] 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.[3] Therefore, designing a new class of ligand having hybrid and bi-functional properties to support different catalytic intermediates is appealing.[4] 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.[5] 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.[6] 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.[7] 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.[8] 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,[9] 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 $NiBr_2$(DME) (DME = 1,2-dimethoxyethane) or anhydrous $NiBr_2$ with 2 equiv. of PNP pincer ligands featuring phosphoramidites in CH_2Cl_2 yields the novel neutral pentacoordinate complexes [Ni(PNP){κ^1(P)-R_2P=O}Br]. Using in-situ ^{31}P 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 κ^1-(P)-coordinated and one intact κ^3-(P,N,P)-coordinated PNP ligand (Scheme 1).[10]



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

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 iminobiphosphine isomers in presence of acid and base.[12] By taking most simple type aminophosphane ligands PR_2NHR, 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-pπ-P-dπ donor bonding. But, upon removal of one hydrogen from nitrogen centre will increase the N-pπ-P-dπ 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 phoshino amino pyridine (DPAP) ligand has been synthesized from the reaction between 2-amino pyridine and chloro diphenyl phosphine. The complex **C1** 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]

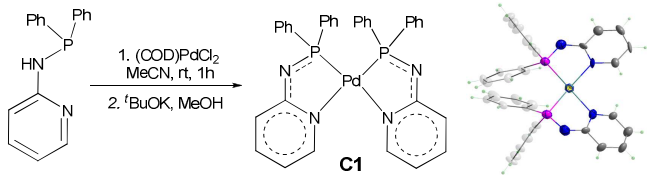
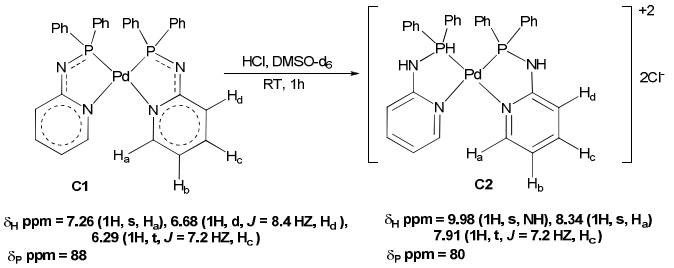


Fig. 1. Synthetic route of complex **C1**.

The hydrolytic behavior of coordinated P≈N in complex **C1** was checked from the ^{31}P NMR monitoring of complex **C1** in different protic and aprotic solvent. Interestingly no characteristic changes in ^{31}P NMR of **C1** was found in different protic and aprotic solvents like; MeOH, DMSO, H_2O, and benzene. Further, ^{31}P NMR of complex **C1** in presence of Cs_2CO_3 in DMSO-d_6 was recorded to check the effect of base. After 1 day, no characteristic changes of complex **C1** was found. Interestingly, even after heating the same solution, we did not observed any change of **C1**. All the above mentioned ^{31}P NMR experiment suggest the inertness of coordinated P≈N of complex **C1** towards protic, aprotic solvent, and base. However, in presence of acid, **C1** transformed to a new species, which has been characterize by various spectroscopic technique. The in-situ ^{1}H NMR of complex **C1** 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 **C1**, ^{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^{II} coordinated P≈N

Corroborating the above, we propose the formation of a Pd(II) dicationic intermediate **C2** in which the P≈N in **C1** has been transformed to P-NH; the downfield shift in ^{1}H NMR being implicative more strong coordination through pyridine ring. Whereas, up field shift in ^{31}P NMR being indicative of relatively weak coordination of phosphorous to Pd(II) in **C2** compared to **C1.** The UV-Vis spectrum of **C1** in acetonitrile displayed three intense absorption bands at 262, 310, 352, and 418 nm with extinction coefficients (ε, $mol^{-1}Lcm^{-1}$) of 2.12×10^5 and 2.56×10^5 respectively (Fig. S1 in ESI). But after the addition of dilute HCl solution to **C1**, the color of the solution changed from yellow to colorless, while two bands for complex **C1** disappeared at 418 nm and 352 nm respectively and two new additional band at 361and 306 nm appeared (Fig. S1 in ESI).[15] We then performed further experiment to gather information about the proposed structure of **C2**. We have used organo tin(IV) reagents as a HCl source and abstracting agent for chloride.[16, 17] In normal moist dichloroethane solvent, organo Sn(IV) compounds will slowly produce HCl, which act as a protonating source for P≈N. After the protonation, the counteranion chloride in complex **C2,** will be trapped by organo Sn(IV) compounds because of its high affinity towards

chloride and produce bulky mono or di-anionic counteranion for di-cationic Pd(II), which will make the crystallization process easier. Three different organo tin(IV) reagents for the study *viz* $SnCl_4$, Me_2SnCl_2, $PhSnCl_3$ was selected based on their Lewis acidity.[18, 19] Tetra coordinated organoin(IV) can coordinate up to two chloride anions to form hexachlorostannate dianion via pentachlorostannate anion. The chemical shifts for $SnCl_4$, $SnCl_5^-$, and $SnCl_6^{2-}$ were reported to be -148, -480, and -732 ppm, respectively.[20] In case of $SnCl_4$, the peak at -496 ppm corresponds to $SnCl_5^-$, indicates the formation of two mono anionic $SnCl_5^-$ unit in Pd(II) complex, **C3**. We did not observe any peak corresponding to dianionic $SnCl_6^{2-}$. The ^{31}P 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 $PhSnCl_3$ leads to complex **C4**, which showed peak at -201 ppm in ^{119}Sn NMR, corresponds to two mono anionic $PhSnCl_4^-$. The ^{31}P 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 $PhSnCl_3$ from complex **C4**. On the other hand, reaction between **C1** and Me_2SnCl_2 afforded colorless complex **C5**, which shows one peak at -172 ppm in ^{119}Sn NMR, corresponds to mono-anionic $Me_2SnCl_3^-$ and one ^{31}P NMR peak at 79.86 ppm due to the coordinated P-NH in dicationic Pd(II) complex (Fig. 2).

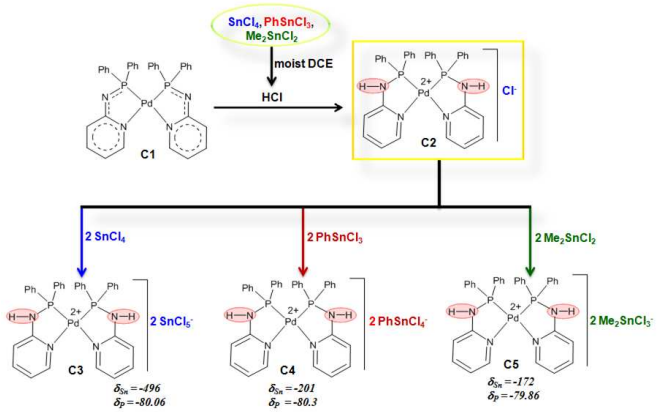


Fig. 2. Characterization of protonated complex after the reaction between **C1** and organotin(IV) reagents

To our delight, compound **C5** crystallized from dichloroethane solvent in a monoclinic space group P21/c with four dicationic Pd(II), eight monoanionic Me_2SnCl_3, along with two dichloroethane solvent molecules in the unit cell. Within an asymmetric unit there are three components, a dicationic palladium, two monoanionic Me_2SnCl_3, and dichloroethane (DCE) solvent as shown in Fig. 3.

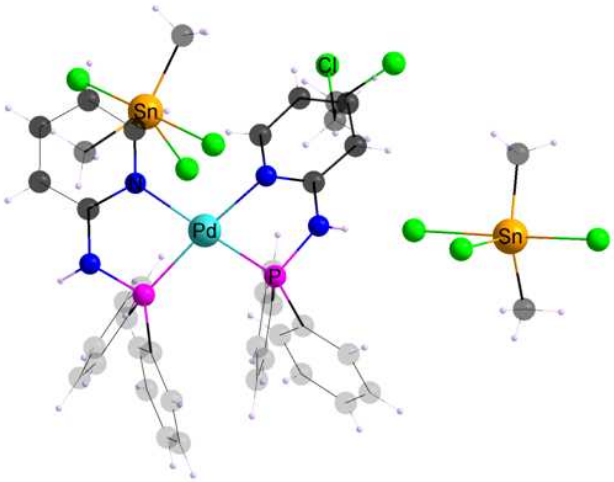


Fig. 3 DIAMOND plot of complex **C5**

Reaction of Coordinated P≈N with Br^- and I^-:

The studies presented so far clearly points out that a coordinated P≈N can easily transformed to P-NH in presence of HCl. Now we were interested to check the effect of other reagents like HBr or HI on P≈N. In this study, instead of using HBr or HI directly, we have used $SnBr_4$ and SnI_4 for their corresponding source. The in-situ NMR experiments of the reaction between **C1** and SnI_4 has been carried out in DMSO-d_6.[21] The ^1H NMR experiments suggested that upon addition of SnI_4 to complex **C1**, a new peak for N-H proton is appeared at 9.5, while all the pyridine ring proton of parent complex shifted towards downfield. Interestingly, after 10 minutes, the protonated complex transformed to a deep red complex **C7**, which shows N-H proton at 10.1 ppm and further downfield shifting of pyridine ring proton (Fig. 4).

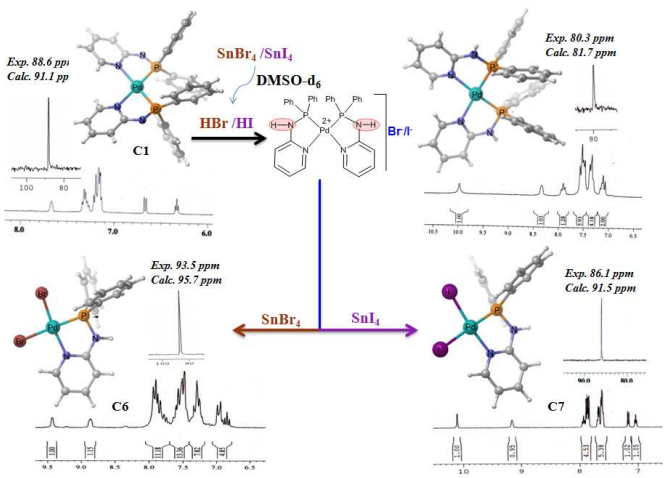


Fig. 4. Mechanism of formation of complex **C6** and **C7** from complex C1.

The in-situ ^{31}P 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 $SnBr_4$ in DMSO-d_6 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 ^{31}P 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 ^{31}P 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 ^{31}P NMR chemical shifts were calculated at GIAO/PBE1PBE level of theory. Gratifyingly, we have obtained very close agreement between theoretical and experimental ^{31}P 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 Stutgard-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 Pd^{II}. In order to understand the reactivity pattern of C**1** and C**2**, we analyzed their frontier molecular orbitals. It is evident from Fig. 5 that the HOMO of C**1** 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 C**2**. On the other hand, the LUMO of C**2** represents the Pd-P or Pd-N σ* orbital. Thus, after protonation of C**1**, the nucleophile Br^- or I^- attacks the LUMO of **C2** which is antibonding with respect to Pd-P or Pd-N bonds (Fig. 6).

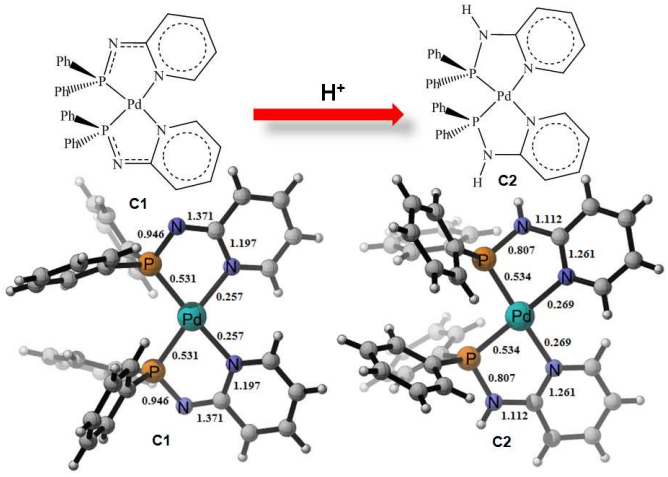


Fig. 5 Bond order of deprotonated and protonated Pd(II)complexes

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 Pd^{II} 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 Pd^{II} complexes towards Suzuki coupling reaction.

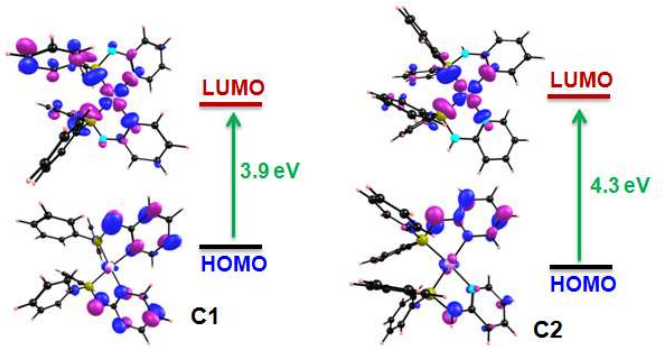
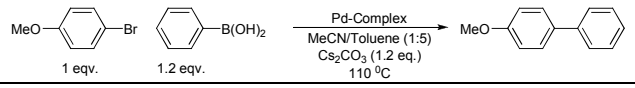


Fig. 6 Kohn-Sham molecular orbitals of **C1** and **C2**.

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. [22][23] [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 Pd^{II} complexes containing hemilabile P≈N and P-NH ligand in biaryl formation from aryl halide and arylboronic 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 Pd^{II} 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).

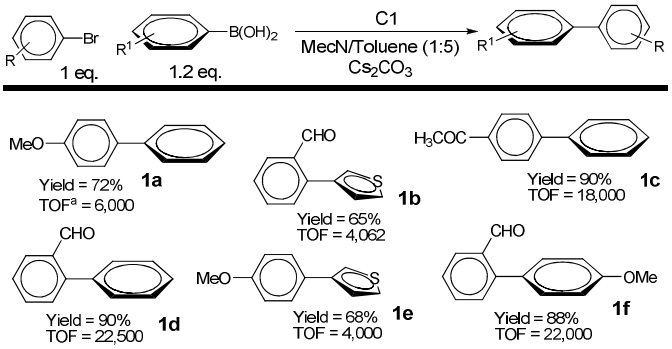
Table 1. Effect of Pd^{II} complexes in Suzuki Coupling



#	Pd-Complex	Mol(%)	Time (h)	TON	TOF (h^{-1})	Isolated Yield (%)
1	**C1**	1	3	93	31	93
2	**C2**	1	3	90	30	90
3	**C5**	1	3	85	28	85
4	**C6**	1	3	81	27	81
5	**C7**	1	3	79	26	79
6	**$Pd(dba)_2$**	1	4	20	5	20
7	**$PdCl_2(PPh_3)_2$**	1	7	48	7	48
8	**C1**	0.1	4	920	230	92
9	**C1**	0.01	6	8,600	1,433	86
10	**C2**	0.01	6	7,700	1,283	77
10	**C1**	0.001	12	72,000	6,000	72
11	**C1**	0.0001	12	3,80,000	31,667	38

For 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 thiophenyl-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 thiophenyl-3-boronic acid leads to corresponding coupling product **1b** in lower yield and TOF.

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



Reaction Condition: C1(0.001 mol%), aryl bromide (0.5 mmol), aryl or heteroaryl boronic acid (0.6 mmol), MeCN/Toluene (0.5/2.5 ml), Cs_2CO_3 (1.2 mmol), Temperature 110 °C. [a] TOF in h^{-1}

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.[28] We employed 6-31+G* basis set for H, C, N and P atoms while Stutgard-Dresden effective core polarization (SDD) basis set has been used for Pd, Br and I atoms.[29] 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. Isotropic 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.[30] The TD-DFT calculations have been performed in solution phase using polarized continuum model (PCM)[5][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 Cl 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 (ω) of all the Sn(IV) compounds have been performed with $\omega = \mu^2/2\eta$, 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 [32] and is defined as where μ is the electronic chemical potential [33] and η is the hardness. All the hardness, chemical potential, and electrophilicity of the Sn(IV) compounds were calculated using the Koopmans' theorem.

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. ^1H (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-Kα (λ=0.71073 A) radiation was used to collect X-ray reflections on the single crystals. Data reduction was performed using Bruker SAINT software.[34] Intensities for absorption were corrected using SADABS. Structures were solved and refined using SHELXL-2008. All non-hydrogen atoms were refined anisotropically and C-H hydrogens were fixed. PLATON was used to check and correct missed symmetry for both structures. Platon SQUEEZE program was used to remove highly disordered solvent molecule (benzene) for structure **C1**.

Table 3. Crystal data of **C1** and **C5**.

	C1[a]	**C5**
Chemical formula	$C_{34}H_{28}N_4P_2Pd$	$C_{40}H_{46}C_{18}N_4P_2PdSn_2$
CCDC No:	957986	1017560
Formula weight	660.94	1272.13
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c*	$P2_1/c$
T/K	296(2)	100 (2)
a/Å	19.197(3)	11.1221(2)
b/ Å	14.403(2)	20.2361(4)
c/ Å	39.795(6)	22.0997(4)
α/°	90	90
β/°	91.688(4)	106.5450(10)
γ/°	90	90
Z	12	4
V/ Å^3	10998 (3)	4769.99 (3)
D_{calc}/g cm^{-3}	1.197	1.772
μ /mm^{-1}	0.618	1.962
Reflns collected	9163	19799
Unique reflns	6520	15692
R1[I > 2(I)]	0.0687	0.0366
wR2 (all)	0.1743	0.0803
Goodness-of-fit	1.064	1.021

[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 Å^3 which is ~26.4% crystal cell volume.

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 Et_3N in Toluene over 15 min at 0 ˚C. The mixture was slowly warmed to room temperature and stirred for 4 h after which time it was filtered off to remove precipitated triethylamine hydrochloride. The precipitate was washed with Toluene. The washings and the filtrate were combined and taken to dryness under reduced pressure leaving pale yellow oil which on cooling spontaneously crystallized. The material was removed from the flask and washed with MeOH then diethyl ether and dried in vacuum. Yield 70 %.^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm): 6.40 (1H, s, br, N-H), 6.76 (1H, t, *J* = 6.4 Hz, Py), 7.2 (1H, d, *J* = 8.4 Hz, Py), 7.37-7.40 (6H, m, Ph), 7.47-7.52 (4H, m, Ph), 7.59 (1H, t, *J* = 7.2 Hz, Py), 8.03 (1H, d, *J* = 5.2 Hz, Py). ^{31}P{H}-NMR (161.9 MHz, CDCl3) δ (ppm): 26.0.

Synthesis of 1,5-Cyclooctadiene Dichloro Palladium(II), $PdCl_2$(COD):

A solution of 2 g (11.3 mmol) of $PdCl_2$ 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 dietheyl ether and dried in a vaccum for 2 hours. Yield: 3.0 g, 93%.

Synthesis of Pd(DPAP)$_2$ (C1):

2-(Diphenylphosphinoamino) pyridine (DPPAP) ligand (56 mg, 0.2 mmol) was added to a solution of (COD)$PdCl_2$ (28 mg, 0.1 mmol) in acetnitrile (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 ^{t}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 × 3 ml) and cold diethyl ether (2 × 2 ml) and dried in vacuum. Yield: 64%. Anal. Calc. for $C_{34}H_{28}N_4P_2Pd$: C, 61.78; H, 4.27; N, 8.48. Found: C, 61.65; H, 4.42; N, 8.35%.^{1}H NMR (400 MHz, DMSO-d_6) 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-d_6) δ (ppm): 88.0

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-d_6) 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-d_6) δ (ppm): 80.1.

C3, yield: 78%. Anal. Calc. for $C_{30}H_{30}N_4P_2Cl_5PdSn$: 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-d_6) 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-d_6) δ (ppm): 80.0.

C4, yield: 73%. Anal. Calc. for $C_{46}H_{40}Cl_8N4P_2PdSn_2$: 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-d_6) 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-d_6) δ (ppm): 80.0.

C5, yield: 91%. Anal. Calc. for $C_{38}H_{42}Cl_6N_4P_2PdSn_2$: 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-d_6) δ (ppm): 1.02 (s, 6H, -CH_3, ^{119}Sn satellites at 0.74 and 1.30 ppm with $^2J_{Sn-H}$= 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 (20H, 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-d_6) δ (ppm): 79.8.

C6, yield: 70%. Anal. Calc. for $C_{17}H_{15}Br_2N_2PPd$: C, 37.5; H, 2.78; N, 5.14. Found: C, 38.0; H, 2.95; N, 5.25%. ^{1}H NMR (200 MHz, DMSO-d_6) δ (ppm): 7.1-7.17 (2H, m), 7.34-7.39

(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), ^{31}P{H}-NMR (161.9 MHz, DMSO-d_6) δ (ppm): 93.5.

C7, yield: 85%. Anal. Calc. for $C_{17}H_{15}I_2N_2PPd$: C, 31.98; H, 2.37; N, 4.39. Found: C, 32.43; H, 2.65; N, 4.85%. ^{1}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), ^{31}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), corresponding Pd^{II} or Pd^0 complex (1to 0.001 mol%), 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_4F solution, extracted with ethylacetate (20 mL) and washed with water (10 mL x 3), brine (10 mL) and dried over anhydrous Na_2SO_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 complexe 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) along with Cs_2CO_3 (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_4F solution, extracted with ethylacetate (20 mL) and washed with water (10 mL×3), brine (10 mL) and dried over anhydrous Na_2SO_4. After removing the solvent the residue was subjected to silica gel column chromatography (60-120 mesh, ethyl acetate-petroleum ether, and gradient elution) to afford pure cross coupling product.

4-methoxybiphenyl (1a): δ_H(200 MHz; $CDCl_3$) 3.85 (3H, s, OCH3), 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, 128.7, 133.7, 140.7, 159.1. Anal. (C13H12O) calcd, C: 84.75; H: 6.57 found, C: 84.69, H: 6.64.

2-(thiophen-3-yl) benzaldehyde (1b): δ_H(200 MHz; $CDCl_3$) 7.18 (1H, d, J = 4.8 Hz), 7.29 (1H, s), 7.42-7.49 (3H, m), 7.59 (1H, d, *J* = 7.2 Hz), 7.99 (1H, d, *J* = 8.0 Hz), 10.12 (1H, s, CHO). δ_C(54.6 MHz, $CDCl_3$) 125.2, 126.4, 127.7, 127.9, 129.5, 130.7, 133.8, 134.2, 138.5, 140.6, 192.5. Anal. ($C_{11}H_8OS$) calcd, C: 70.18, H: 4.28; found, C: 70.37, H: 2.52.

1-(biphenyl-4-yl)ethanone (1c): δ_H (200 MHz; $CDCl_3$) 2.64 (3H, s, CH3), 7.39-7.52 (3H, m, CH aromat.), 7.61-7.71 (4H, m, CH aromat.), 5.91 (1H, s, CH), 6.77-7.00 (8H, m, CH aromat.), 7.23 (2H, d, *J* = 8.8 Hz, CH aromat.), 8.01 (2H, dd, *J* = 1.8 Hz, *J* = 1.6 Hz, CH aromat.). δ_C(54.6 MHz, $CDCl_3$) 26.7, 127.2, 127.3, 128.2, 128.9, 129.0, 135.8, 139.8, 145.8, 197.8. Anal. ($C_{14}H_{12}O$) calcd, C: 85.68, H: 6.16; found, C: 85.49, H: 6.30.

Biphenyl-2-carbaldehyde (1d): δ_H (200 MHz; $CDCl_3$) 7.36-7.53 (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. ($C_{13}H_{10}O$) calcd, C: 86.59; H: 5.53 found, C: 86.32, H: 5.74.

3-(4-methoxyphenyl)thiophene (1e): δ_H (200 MHz; $CDCl_3$) 3.84 (3H, s, OCH3), 6.94 (2H, d, *J* = 8.6 Hz, CH aromat), 7.36 (3H, s, CH thiophenyl) 7.53 (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, 127.6, 128.8, 142.0, 158.9. Anal. ($C_{13}H_{12}O$) calcd, C: 69.44; H: 5.30 found, C: 69.18, H: 5.60.

4'-methoxybiphenyl-2-carbaldehyde (1f): δ_H (200 MHz; $CDCl_3$) 3.87 (3H, s, OCH3), 7.0 (2H, d, *J* = 8.8 Hz), 7.31 (2H, d, J = 8.6 Hz), 7.45 (2H, t, *J* = 8.4 Hz), 7.60 (1H, d, *J* = 7.8 Hz), 8.00 (1H, d, *J* = 7.8 Hz), 9.99 (1H, s, CHO). δ_C(54.6 MHz, $CDCl_3$) 55.4, 113.9, 127.4, 127.6, 130.0, 130.8, 131.3, 133.5, 133.7, 145.6, 159.7, 192.7. Anal. ($C_{14}H_{12}O_2$) calcd, C: 79.22; H: 5.70 found, C: 79.45, H: 5.85.

Conclusions

In summary, The palladium(II) complex, [Pd(DPAP)$_2$ have been prepared from the reaction between Pd(COD)Cl_2 and diphenyl phoshino 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)$_2$ leads to complex $[Pd(DPAP)_2]^{2+}$, in which two coordinated DPAP ligand contain two P-NH. The stability of dicationic $[Pd(DPAP)_2]^{2+}$ complex depends upon the bulkiness and reactivity of anion. The dicationic complex **C2** 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 dicationic Pd(II) complexes **C2** leads to the generation of Pd(DPAP)X_2 (X = Br^-, I^-). The complexes have been screened as catalyst in Suzuki coupling involving aryl bromide and aryl or heteraryl boronic acid with appreciable turnover frequency.

Acknowledgements

Financial support of this work by DST-New Delhi (to SP for INSPIRE fellowship and research grant) is gratefully acknowledged. SP is highly grateful to Professor M. K. Chaudhuri and Professor Sujit Roy for all the help and support. We thank reviewers for their useful suggestions and brought about a new look to the original submission.

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/

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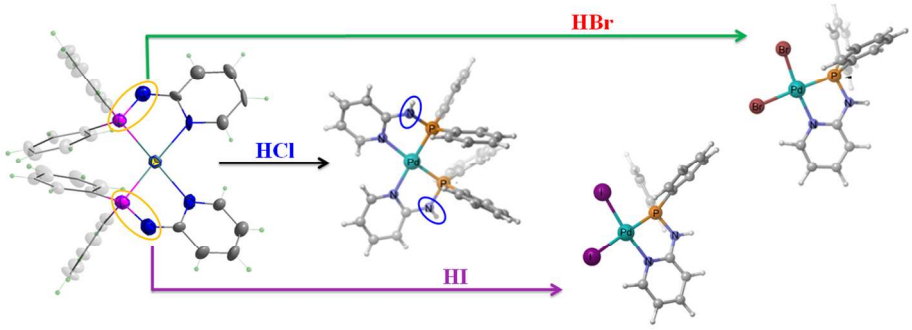

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