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Formation of organopalladium complexes via C–Br and C–C bond activation. Application in C–C and C–N coupling reactions

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ABSTRACT

Reaction of $[Pd_2(dba)_3]$ (dba = dibenzylideneacetone) with two Schiff base ligands (L^1 and L^2), derived from the condensation of 8-aminoquinoline with 2-bromobenzaldehyde or 2-bromoacetophenone, in refluxing *tert*-butanol afforded two organopalladium complexes **1** and **2**. Crystal structure of complex **1** has been determined by X-ray diffraction studies. Structure of complex **2** has been optimized by DFT method. In both the complexes the imine ligands are coordinated, via C–Br bond activation, as tridentate CNN-donor and the fourth coordination position is occupied by an acetylide ion provided by an outgoing dba ligand via C–C bond cleavage. Both the complexes display intense absorptions in the visible and ultraviolet regions. Both the complexes catalyze C–C and C–N coupling reactions efficiently.

1. Introduction

Palladium catalyzed carbon–carbon and carbon–heteroatom bond forming reactions have emerged as some of the most powerful methods in synthetic organic chemistry [1–5], and we have also started exploring this area recently [6–10]. According to the proposed mechanisms of these cross-coupling reactions, all such reactions are initiated by the oxidative insertion of palladium(0) into a carbon–halogen bond of the aryl halide, used as substrate, forming a palladium(II) intermediate. This key step is followed by the coupling of reactants, reductive elimination of the newly formed coupled product and regeneration of the palladium(0) center. For these cross-coupling reactions to occur, ligands with soft donor sites are often required in order to stabilize the palladium(0) state, and also to satisfy the vacant coordination sites of the palladium(II) intermediate. Bulky arylphosphines are particularly popular as soft ligands for these reactions. Encouraged by these very well-known reaction mechanisms, we thought of designing a reaction whereby we could isolate the product, formed by oxidative insertion of palladium(0) into the C–X (X = halogen atom) bond of an aryl halide, as a stable palladium(II) complex. Hence, we thought of a modified bromobenzene ligand with two appropriately located soft donor atoms. In order to achieve our target product, two Schiff base ligands, L^1 and L^2, were prepared by the condensation of 8-aminoquinoline with 2-bromobenzaldehyde or 2-bromoacetophenone. Both the ligands contain an aryl bromide fragment along with two soft nitrogen donor centers, *viz.* the imine–nitrogen and the pyridine–nitrogen. It was anticipated that if a palladium(0) center activates the C–Br bond in these imine ligands to form palladium(II) species (**I**), where the metal center would be coordinated to an aryl-carbon, a bromide and also it would simultaneously get coordinated by the two proximal nitrogen donors, and thus the resulting organopalladium complex should be stable and isolable. Herein, as the source of palladium(0), we chose tris(dibenzylideneacetone)dipalladium(0), $[Pd_2(dba)_3]$, primarily because the π-bonded dba ligands in it seemed to be easily replaceable by the chelating ligands (such as L^1 and L^2). Reactions of the selected Schiff base ligands (L^1 and L^2) with $[Pd_2(dba)_3]$ has indeed been found to afford two interesting organopalladium complexes, but of slightly different nature than **I**. The chemistry of these two complexes is reported here, with special reference to their formation, characterization and, catalytic application in C–C and C–N coupling reactions.

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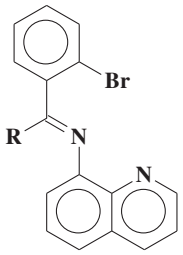
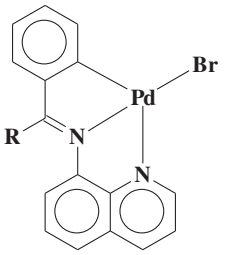


R = H for L^1
R = CH_3 for L^2



I

Table 1
Selected bond lengths (Å) and bond angels (°) for complex **1**.

Bond lengths (Å)			
Pd(1)–C(1)	1.959(12)	C(7)–N(1)	1.279(16)
Pd(1)–N(1)	1.988(9)	C(8)–N(1)	1.390(15)
Pd(1)–N(2)	2.113(9)	C(17)–C(18)	1.099(17)
Pd(1)–C(17)	2.017(13)		
Bond angles (°)			
C(1)–Pd(1)–N(1)	81.9(4)	C(1)–Pd(1)–N(2)	161.6(4)
N(1)–Pd(1)–N(2)	79.8(4)	N(1)–Pd(1)–C(17)	176.5(4)
		Pd(1)–C(17)–C(18)	178.7(11)

2. Results and discussion

2.1. Synthesis and characterization

Reactions of L^1 and L^2 with $[Pd_2(dba)_3]$ have been carried out in refluxing *tert*-butanol, which have afforded complexes **1** and **2**, respectively, in decent yields. ^{1}H NMR spectra of both the complexes indicate that the imine ligands are probably coordinated to the metal center in the expected CNN-mode as in **I**, however, the ligand coordinated to the metal center in the fourth position could not be confirmed. To authenticate composition of the complexes, as well as binding mode of the imine ligand in them, structure of complex **1** has been determined by X-ray crystallography. The structure is shown in Fig. 1 and some relevant bond parameters are listed in Table 1. The structure shows that the imine ligand (L^1) is indeed bound to palladium in the expected CNN-fashion (as in **I**) forming two adjacent five membered rings with C–Pd–N and N–Pd–N bite angles of 81.9(4)° and 79.8(4)° respectively, and the remaining coordination site is interestingly occupied by an acetylide fragment. Thus palladium is nested in a C_2N_2 coordination environment, which is significantly distorted from ideal square planar geometry. The observed Pd–C and Pd–N bond distances are all quite normal [11,12]. Structural characterization of complex **2** by X-ray crystallography has not been possible, as single crystals of this complex could not be grown. However, its structure has been geometrically optimized through DFT calculations [13], and the optimized structure (Fig. S1 and Table S1, Supplementary material) is found to be very similar to the crystal structure of complex **1**. Mass spectral, microanalytical, ^{1}H NMR and IR data of complexes **1** and **2** are also consistent with their compositions.

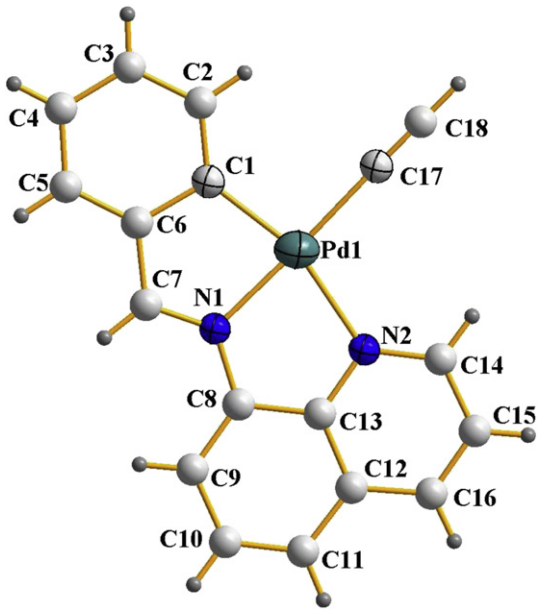
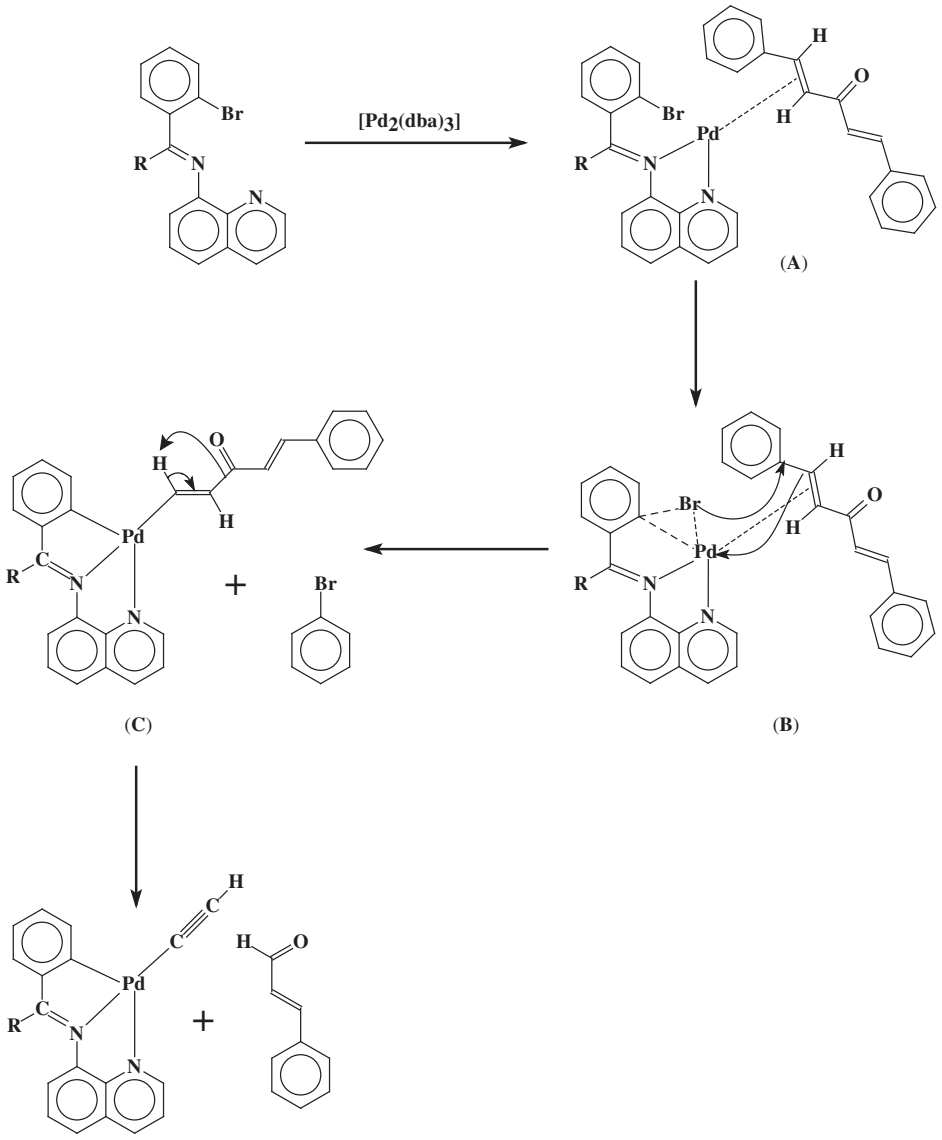


Fig. 1. Molecular structure of complex **1**.

Formation of complexes **1** and **2** containing the acetylide fragment, from rather simple reactions, has been quite intriguing. However, it is apparent that this acetylide fragment has resulted unexpectedly from C–C bond activation of the dibenzylideneacetone attached to the palladium center in the metal precursor. Such C–C bond activation providing an acetylide fragment is, to our knowledge, unprecedented. Though the exact mechanism of formation of complexes **1** and **2** is not clear to us, some speculated sequences, that seem probable, and also adequately supported by mass spectrometry (*vide infra*) [14], are illustrated in Scheme 1. Initially the two nitrogen donor sites of the imine ligand seem to coordinate the palladium center forming an intermediate **A**, whereby a bonding interaction is set between the palladium(0) center and the proximal C–Br bond. This is followed by activation of the C–Br bond and coordination of the anionic carbon center to the oxidized palladium generating another intermediate **B**. Owing to the increased oxidation state of palladium in **B** the π-cloud on the coordinated dibenzylideneacetone gets attracted more strongly toward the metal center and, as a consequence, the terminal benzene ring of dibenzylideneacetone, that is closer to the metal center, becomes more electrophilic and undergoes an intra-molecular attack by the bromide. This leads to elimination of bromobenzene and formation of a σ bond between the palladium center and the sp^2-hybridized terminal carbon of the remaining fragment of dibenzylideneacetone, generating a third intermediate **C**. This intermediate **C** is believed to undergo a rearrangement, as a result of which an acetylide fragment originates, which remains coordinated to the metal center to yield the final product, and cinnamaldehyde is released as a byproduct.

To have an insight into the formation of these interesting organopalladium complexes via C–Br and unique C–C bond cleavage reactions, attempts have been made to identify the possible intermediates by mass spectrometry [14]. The mass spectrum, recorded after the reaction has proceeded for 2 h, shows a weaker peak at $m/z = 675$ corresponding to intermediate **A** (for $[\mathbf{A} + Na^+]$) and a much stronger peak at $m/z = 491$ for **C**. The observed peak for **C** actually depicts the mass of $[(\mathbf{C}\text{-}4H) + H^+]$ species. This is because four protons attached with the two alkene groups in **C** get lost under the mass spectral condition [15,16]. Detection of cinnamaldehyde (*vide infra*) confirms that this loss of protons is not permanent. No peak corresponding to intermediate **B** could be identified, indicating its transient existence. Also formation of complex **1** is observed by this time. But as the reaction proceeds further the peak for **C** vanishes completely and only the



Scheme 1. Probable steps behind formation of complexes **1** and **2**.

peak for complex **1** is observed. So it appears that lifetime of intermediate **C** is the longest among the three proposed intermediates, and the kinetics of formation of complex **1** from **C** is slower than formation of **C** from **A**. However, attempts to isolate intermediate **C** by discontinuing the reaction after 2 h have failed, and complex **1** could be isolated as the only characterizable species in poor yield. Identification and quantification of the organic byproducts, *viz.* bromobenzene and cinnamaldehyde, have been done by GC–MS technique [17]. Hence the mass spectral studies support the proposed reaction sequences behind formation of complexes **1** and **2**.

2.2. Electronic spectra

Complexes **1** and **2** are poorly soluble in dichloromethane, chloroform, acetonitrile, etc., but are readily soluble in dimethyl formamide and dimethyl sulfoxide producing bright yellow solutions. Electronic spectra of these complexes have been recorded in dimethyl sulfoxide solution, and the spectral data are given in Table 2. Each complex shows absorptions in the visible and ultraviolet regions. The absorptions in the ultraviolet region are attributable to transitions within the ligand orbitals. To understand the origin of the absorptions in the visible region, electronic structure of both the complexes has been probed with the help of DFT calculations [13]. Compositions of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are given in Table 3. Contour plots of these molecular orbitals for complex **1** are shown in Fig. 2 and the same for complex **2** are shown in Fig. S2 (Supplementary material) respectively. In both the complexes the HOMO has major (~75%) contribution from the CNN-coordinated imine ligand, much less (~20%) contribution from the metal center, and

Table 2
Electronic spectral data in dimethyl sulfoxide solution.

Complex	λ_{max}, nm (ε, M^{-1} cm^{-1})
1	476 (1500), 452(2300), 367(3300), 328(6900), 250(9700)
2	461(1400), 436(1800), 361(2700), 319(5300), 249(7900)

Table 3
Composition of selected molecular orbitals of the complexes.

Complex	Contributing fragments	% contribution of fragments to	
		HOMO	LUMO
1	Pd	18.9	4.8
	Imine ligand	74.9	95.2
	Acetylide	6.2	0.0
2	Pd	20.0	2.1
	Imine ligand	75.2	97.9
	Acetylide	4.8	0.0

marginal (~5%) contribution from the coordinated acetylide. The LUMO is found to be delocalized mostly (>95%) on the imine ligand. The lowest energy absorption in both the complexes is hence assignable to a transition from a filled orbital of the coordinated imine ligand (HOMO) to a vacant orbital of the same ligand (LUMO).

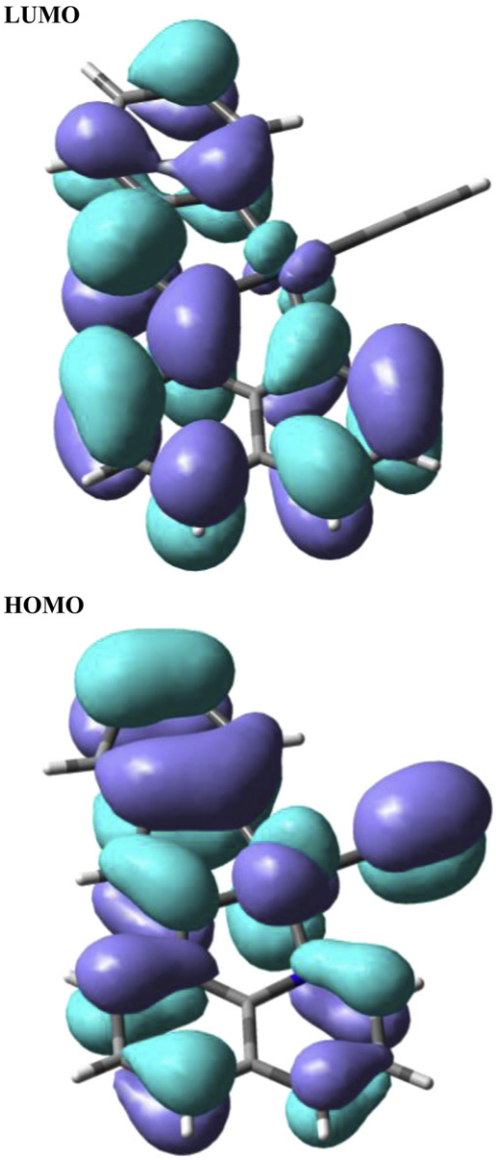


Fig. 2. Contour plots of the HOMO and LUMO of complex **1**.

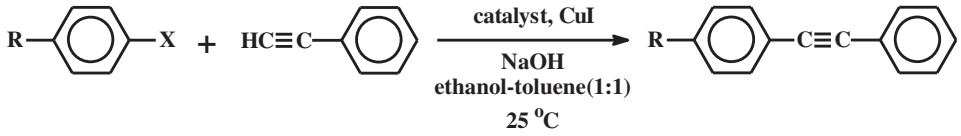
2.3. Catalysis

The reaction mechanisms for the C–C cross coupling reactions propose the formation of palladium(II) intermediates with two adjacent palladium–carbon bonds, just prior to reductive elimination of the coupled product. Presence of two such palladium–carbon bonds, *viz*. the palladium–aryl bond and the palladium–acetylide bond, in complexes **1** and **2** have made them look as promising catalysts for C–C cross-coupling reactions, particularly for Sonogashira cross-coupling reaction. Hence, catalytic activity of these two complexes has been examined first for Sonogashira coupling reaction between aryl iodides and phenylacetylene. Both the palladium complexes are found to catalyze the targeted coupling reactions with comparable efficiency, with only 0.01 mol% catalyst loading at room temperature (25 °C), affording the expected coupled products in good to excellent yields (Table 4, entries 1–6). The *para*-substituent in the aryl iodide is observed to have notable influence on the yield of the product (entries 1–6). For coupling of the corresponding aryl bromides with phenylboronic acid higher (1 mol%) catalyst loading was necessary to achieve similar yield as the corresponding aryl iodides (entries 7–10). Here again complexes **1** and **2** show comparable efficiency (entries 7 and 8). Encouraged by the successful Sonogashira coupling reactions involving aryl iodides and aryl bromides, we attempted similar reactions with aryl chlorides as substrate. The reactions with aryl chlorides are found to be much less facile, and afford the coupled products in poor yield (entries 11–13). Attempts for similar coupling with aryl fluorides were unsuccessful. It is relevant mentioning here that in all these reactions homo-coupling of phenylacetylene has been observed along with the usual Sonogashira cross-coupling. Such homo-coupling reactions of phenylacetylene, where palladium plays a very important role as catalyst, are well known [18].

Encouraged by the facile Sonogashira reactions catalyzed by the palladium imine complexes, Suzuki reactions of phenylboronic acid and *p*-substituted iodobenzenes were tried to yield the biphenyl products (Table 5). Both complexes **1** and **2** showed notable, as well as comparable, catalytic efficiency under relatively mild experimental condition (entries 1–6). Similar coupling between phenylboronic acid and *p*-substituted bromobenzenes also took place smoothly (entries 7–10), but ten times more catalyst and slightly longer reaction time were needed to achieve similar yield. Attempted coupling of phenylboronic acid with *p*-chloroaryls using complex **1** as catalyst was also successful (entries 11–13), but with significantly less catalytic efficiency. Finally we tried Suzuki coupling with *p*-fluoroaryls, and as anticipated, the reactions were found to be very difficult even with 1 mol% catalyst loading and 24 h reaction time, and the coupled products were obtained in poor yields (entries 14–16).

The observed efficiency of the organopalladium complexes **1** and **2** in activating aryl C–X (X = I, Br, Cl) bonds and thereby inducing C–C coupling reactions, has prompted us to try these complexes as catalyst in bringing about C–N coupling reactions between aryl halides and amines. First we attempted the coupling of iodobenzene and *p*-substituted anilines, and as envisaged, the C–N coupling reactions proceeded smoothly affording the desired products in good yields (entries 1–6 in Table 6), and both the complexes showed comparable catalytic efficiency. Smooth C–N coupling was also observed with bromobenzene, but ten times more catalyst loading and twice more time were needed to get similar yield (entries 7–9). C–N coupling reactions using chlorobenzene were found to be rather difficult (entries 10–12), as reflected in much less yield of the products even with much higher catalyst loading. We have also explored the scope for arylation of secondary amines using piperidine and morpholine. With iodobenzene the targeted reactions could be achieved in good and

Table 4
Sonogashira cross-coupling of aryl halides with phenylacetylene.[a]



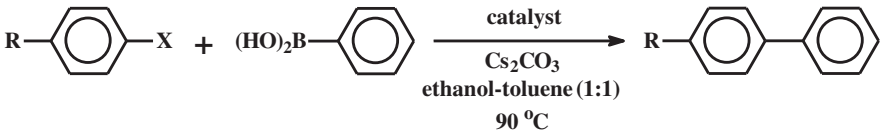
Entry	R	X	Catalyst	Time (h)	mol% of catalyst	Yield[b] (%)
1	$COCH_3$	I	**1**	5	0.01	94
2	$COCH_3$	I	**2**	5	0.01	92
3	CHO	I	**1**	5	0.01	80
4	CHO	I	**2**	5	0.01	77
5	CN	I	**1**	5	0.01	69
6	CN	I	**2**	5	0.01	65
7	$COCH_3$	Br	**1**	5	1	96
8	$COCH_3$	Br	**2**	5	1	80
9	CHO	Br	**1**	5	1	85
10	CN	Br	**1**	5	1	47
11	$COCH_3$	Cl	**1**	24	1	28
12	CHO	Cl	**1**	24	1	15
13	CN	Cl	**1**	24	1	8

[a] Reaction conditions: aryl halide (1.0 mmol), phenylacetylene (1.2 mmol), NaOH (2.0 mmol), Pd catalyst, CuI (10 mol%), solvent (4 mL).
[b] Determined by GC–MS.

comparable yields using both complexes **1** and **2** as catalyst (entries 13–16). However, compared to the primary aromatic amines (entries 1–6), longer reaction time was needed for the secondary amines. Similar C–N coupling reactions with bromobenzene and chlorobenzene proceed with gradually increasing difficulty and decreasing yields (entries 17–20). Attempts for C–N coupling reactions using fluorobenzene were unsuccessful with both primary and secondary amine.

The organopalladium complexes (**1** and **2**), with two Pd–C bonds, are thus found capable of successfully catalyzing Sonogashira and Suzuki type C–C coupling reactions, and also C–N coupling reactions involving both primary and secondary amines. While both the complexes show comparable efficiency, complex **1** has been found to be a slightly better catalyst than complex **2**. These complexes not only activated C–I and C–Br bonds, but also could bring about much difficult C–Cl bond activation successfully, and it is relevant to mention here that cross-coupling reactions involving chloro-substituted arenes have gained prominence in recent years [19–21]. Another noticeable aspect of the observed catalysis is that no additional ligand was necessary for any of the cross-coupling reactions, and such ligand-free catalysis is relatively less common [22–24].

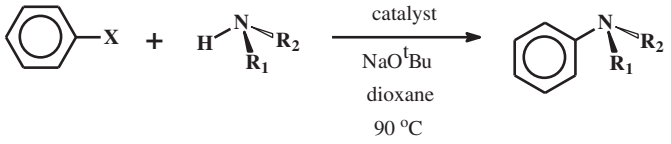
Table 5
Suzuki cross-coupling of aryl halides with phenylboronic acid.[a]

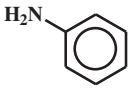
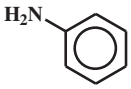
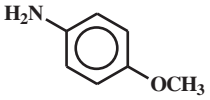
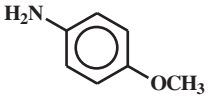
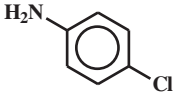
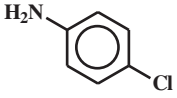
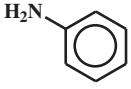
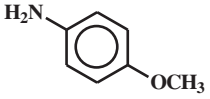
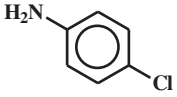
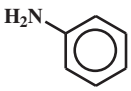
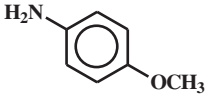
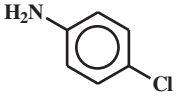
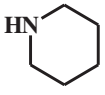
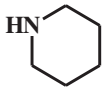
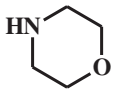
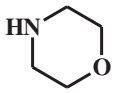
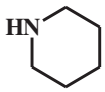
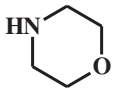
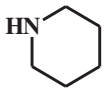
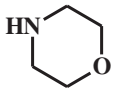


Entry	R	X	Catalyst	Time (h)	mol% of catalyst	Yield[b] (%)	TON[c]
1	$COCH_3$	I	**1**	3	0.001	100	100,000
2	$COCH_3$	I	**2**	3	0.001	97	97,000
3	CHO	I	**1**	3	0.001	100	100,000
4	CHO	I	**2**	3	0.001	95	95,000
5	CN	I	**1**	3	0.001	92	92,000
6	CN	I	**2**	3	0.001	90	90,000
7	$COCH_3$	Br	**1**	5	0.01	100	10,000
8	$COCH_3$	Br	**2**	5	0.01	96	9600
9	CHO	Br	**1**	5	0.01	97	9700
10	CN	Br	**1**	5	0.01	76	7600
11	$COCH_3$	Cl	**1**	8	0.01	51	5100
12	CHO	Cl	**1**	8	0.01	43	4300
13	CN	Cl	**1**	8	0.01	36	3600
14	$COCH_3$	F	**1**	24	1.00	13	13
15	CHO	F	**1**	24	1.00	9	9
16	CN	F	**1**	24	1.00	7	7

[a] Reaction conditions: aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol), Cs_2CO_3 (2.0 mmol), Pd catalyst, solvent (4 mL).
[b] Determined by GC–MS.
[c] TON = turnover number ((mol of product)/(mol of catalyst)).

Table 6
C–N coupling of aryl halide with amines.[a]



Entry	X	Amine	Catalyst	Time (h)	mol% of cat.	Yield[b]	TON[c]
1	I		**1**	12	0.01	100	10,000
2	I		**2**	12	0.01	93	9300
3	I		**1**	12	0.01	100	10,000
4	I		**2**	12	0.01	97	9700
5	I		**1**	12	0.01	98	9800
6	I		**2**	12	0.01	91	9100
7	Br		**1**	24	0.1	93	930
8	Br		**1**	24	0.1	95	950
9	Br		**1**	24	0.1	97	970
10	Cl		**1**	24	1	46	46
11	Cl		**1**	24	1	55	55
12	Cl		**1**	24	1	59	59
13	I		**1**	24	0.01	91	9100
14	I		**2**	24	0.01	87	8700
15	I		**1**	24	0.01	94	9400
16	I		**2**	24	0.01	91	9100
17	Br		**1**	24	0.1	80	800
18	Br		**1**	24	0.1	82	820
19	Cl		**1**	24	1.0	67	67
20	Cl		**1**	24	1.0	62	62

[a] Reaction conditions: aryl halide (1.0 mmol), aniline (1.2 mmol), NaO^{t}Bu (1.3 mmol), Pd catalyst, solvent (4 mL).
[b] Determined by GC–MS on the basis of residual aryl halide.
[c] TON = turnover number ((mol of product)/(mol of catalyst)).

3. Conclusions

The present study demonstrates that the modified phenyl bromides with the two soft N-donor centers, *viz*. L^1 and L^2, undergo facile C–Br bond activation upon reaction with the palladium(0) center in $[Pd_2(dba)_3]$, and bind to the metal center as CNN-donors (as in **I**). In addition, an unexpected C–C bond cleavage of an outgoing dibenzylideneacetone takes place providing an acetylide ligand that takes up the fourth coordination site of the metal. This study also shows that the organopalladium complexes with two Pd–C bonds are good catalysts for bringing about C–C and C–N coupling reactions.

4. Experimental

4.1. Materials

Palladium chloride was obtained from Arora Matthey, Kolkata, India. 8-Aminoquinoline was procured from Sigma–Aldrich. Benzaldehyde, acetone, 2-bromobenzaldehyde and 2-bromoacetophenone were obtained from Merck, India. Dibenzylideneacetone (dba) was prepared by aldol condensation between benzaldehyde and acetone [25]. $[Pd_2(dba)_3]$ were prepared by following a reported methods [26]. The two imine ligands, *viz*. L^1 and L^2, were prepared by condensation of 8-aminoquinoline with 2-bromobenzaldehyde and 2-bromoacetophenone respectively in 1:1 ethanol–water mixture. All other chemicals and solvents were reagent grade commercial materials and were used as received.

4.2. Physical measurements

Microanalyses (C, H, N) were performed using a Heraeus Carlo Erba 1108 elemental analyzer. Mass spectra were recorded with a Micromass LCT electrospray (Qtof Micro YA263) mass spectrometer. ^{1}H NMR spectra were recorded in $CDCl_3$ solution on a Bruker AV-300 spectrometer with TMS as the internal standard. Electronic spectra were recorded on a JASCO V-570 UV–VIS–NIR spectrophotometer. IR spectra were obtained on a Perkin–Elmer (Paragon) FT spectrometer with samples prepared as KBr pellets. Optimization of ground-state structure and energy calculations of the palladium complexes were carried out by density functional theory (DFT) method using the Gaussian 03 (B3LYP/SDD-6-31G) package [13]. For complex **1**, the X-ray crystallographic coordinates were utilized in the calculations. For complex **2** X-ray crystallographic coordinates were not available, and hence the structure was optimized prior to MO calculations. GC–MS study was done with a Clarus 600 (Perkin–Elmer) machine.

4.3. Syntheses of complexes

Both the palladium complexes were prepared by following a general procedure. Specific details are given below for complex **1**.

Complex **1**: To a solution of L^1 (68 mg, 0.22 mmol) in *tert*-butanol (40 mL) was added [$Pd_2(dba)_3$] (100 mg, 0.11 mmol), and the mixture was then refluxed for 4 h to yield a yellow solution. The solvent was evaporated and the solid mass, thus obtained, was subjected to purification by thin-layer chromatography on a silica plate. With 1:3 acetonitrile–benzene solution as the eluant, a yellow band separated, which was extracted with acetonitrile. Evaporation of this extract gave complex **1** as a yellow crystalline solid. Yield: 67%. Anal. Calcd. for $C_{18}H_{12}N_2Pd$: C, 57.39; H, 3.19; N, 7.43. Found: C, 58.15; H, 3.59; N, 7.92%. ^{1}H NMR [27]: 7.19–7.13 (2H)*; 7.56–7.53 (3H)*; 7.87–7.82 (2H)*; 8.13 (d, 1H, $J = 8.1$); 8.41 (d, 1H, $J = 7.2$); 8.73 (d, 1H, $J = 7.7$); 8.87 (d, 1H, $J = 7.8$); 9.3(s, 1H). MS (ESI), positive mode: [complex **1** + Na]$^+$, 386. IR: 435, 486, 675, 710, 785, 824, 1074, 1158, 1307, 1322, 1367, 1384, 1461, 1500, 1525, 1574, 1594, 1643, 2361, 3436.

Complex **2**: Yield: (71%); Anal. Calcd. for $C_{19}H_{14}N_2Pd$: C, 60.57; H, 3.72; N, 7.44. Found: C, 60.77; H, 3.78; N, 7.78%. ^{1}H NMR: 2.91 (s, 3H, CH_3); 7.18–7.08 (2H)*; 7.50–7.47 (2H)*; 7.58(d, 1H, $J = 6.6$); 7.83–7.78 (2H)*; 8.09 (d, 1H, $J = 8.1$); 8.30 (d, 1H, $J = 7.8$), 8.71 (d, 1H, $J = 8.4$), 8.89 (s, 1H). MS (ESI), positive mode: [complex **2** + Na]$^+$, 399. IR: 498, 521, 687, 762, 799, 918, 1020, 1151, 1276, 1310, 1446, 1493, 1626, 2361, 3452.

4.4. X-ray crystallography

Single crystals of complex **1** were obtained by slow evaporation of solvent from a solution of the complex in dimethyl sulfoxide. Selected crystal data and data collection parameters are given in Table 7. Data were collected on a Bruker SMART APEX CCD diffractometer using graphite monochromated and Mo Kα radiation ($\lambda = 0.71073$ Å). X-ray data reduction and, structure solution and refinement were done using SHELXS-97 and SHELXL-97 programs [28]. The structure was solved by the direct methods.

Table 7
Crystallographic data for complex **1**.

Empirical formula	$C_{18}H_{12}N_2Pd,2(O)$
Formula weight	394.72
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	10.0312(11)
b (Å)	7.1014(8)
c (Å)	22.225(2)
β (°)	99.576(8)
V (Å^3)	1561.2(3)
Z	4
F (000)	784
Crystal size (mm^3)	0.32 × 0.17 × 0.11
T (K)	296
μ (mm^{-1})	1.199
$R1$[a]	0.0615
$wR2$[b]	0.1796
Gof[c]	0.98

[a] $R1 = \sum\|F_o| - |F_c\|/\sum|F_o|$.

[b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

[c] Gof $= [\sum[w(F_o^2 - F_c^2)^2]/(M - N)]^{1/2}$, where M is the number of reflections and N is the number of parameters refined.

4.5. General procedure for Sonogashira coupling reactions

To slurry of aryl halide (1 mmol), cuprous iodide (10 mol%) and palladium catalyst (a known mol%) in 1:1 ethanol–toluene (4 mL), phenylacetylene (1.2 mmol) and NaOH (1.7 mmol) were added and heated at 25 °C. After completion of the reaction (monitored by TLC), the flask was removed from the oil bath and water (20 mL) added, followed by extraction with ether (4 × 10 mL). The combined organic layers were washed with water (3 × 10 mL), dried over anhydrous Na_2SO_4, and filtered. Solvent was removed under vacuum. The residue was dissolved in hexane and analyzed by GC–MS.

4.6. General procedure for Suzuki coupling reactions

In a typical run, an oven-dried 10 mL round bottom flask was charged with a known mole percent of catalyst, Cs_2CO_3 (1.7 mmol), phenylboronic acid (1.2 mmol) and aryl halide (1 mmol) with 1:1 ethanol–toluene (4 mL). The flask was placed in a preheated oil bath at 90 °C. After the specified time the flask was removed from the oil bath, water (20 mL) was added, and extraction with ether (4 × 10 mL) was done. The combined organic layers were washed with water (3 × 10 mL), dried over anhydrous Na_2SO_4, and filtered. Solvent was removed under vacuum. The residue was dissolved in hexane and analyzed by GC–MS.

4.7. General procedure for C–N coupling reactions

In a typical run, an oven-dried 10 mL round bottom flask was charged with a known mole percent of catalyst, NaO^tBu (1.3 mmol), amine (1.2 mmol) and aryl halide (1 mmol) with dioxane (4 mL). The flask was placed in a preheated oil bath at 90 °C. After the specified time the flask was removed from the oil bath, water (20 mL) was added, and extraction with ether (4 × 10 mL) was done. The combined organic layers were washed with water (3 × 10 mL), dried over anhydrous Na_2SO_4, and filtered. Solvent was removed under vacuum. The residue was dissolved in hexane and analyzed by GC–MS.

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Appendix A. Supplementary material

CCDC 894631 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary material

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2013.03.006.

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