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A mild and efficient method for the synthesis of structurally diverse 1,2,3-triazolylidene palladium(II) diiodo complexes. Comparison of catalytic activities for Suzuki–Miyaura coupling

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ABSTRACT

Synthesis of mononuclear and PEPPSI type palladium diiodo complexes of 1,4-diphenyl-3-methyl-1,2,3-triazol-5-ylidene without the use of strong bases and silver salts and at ambient conditions using $Pd(OAc)_2$ is reported. Using stoichiometric amounts of bidendate ligands such as pyrazine, 4,4′-bipyridine and DABCO bridged binuclear palladium diiodo complexes were obtained in excellent yields. By simple variation of reagents and their stoichiometry, one can control the reactions towards the selective formation of mononuclear $[(Tz)_2Pd(I)_2]$ complexes, iodo bridged binuclear complexes $[(Tz)Pd(I)(\mu\text{-}I)_2Pd(I)(Tz)]$, mononuclear PEPPSI type complexes $[(Tz)Pd(I)_2(Py)]$, bridged binuclear PEPPSI type complexes $[(Tz)Pd(I)_2$-(bridge biPy)-$(I)_2Pd(Tz)]$. The catalytic activities of these three structurally different types of complexes are compared for Suzuki–Miyaura coupling reaction.

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1. Introduction

N-Heterocyclic carbene (NHC) ligands have dominated the scene in transition metal organometallic chemistry during the past two decades due to their ease of synthesis, extraordinary stability and functional group tolerance and excellent catalytic activities [1]. Among the transition metals palladium, iridium and rhodium have led the development in view of their importance in homogeneous catalysis, palladium in cross-coupling reactions [2] and iridium and rhodium in C–H activation [3] and hydrogenation reactions [4]. Among the NHCs imidazol-2-ylidenes (normal NHC) [5] and 1,2,3-triazol-5-ylidenes (mesoionic NHC) [6] are very popular. Palladium complexes of both of these NHC ligands have served as pre-catalysts in a wide range of coupling reactions with unprecedented catalytic activities [7]. One such complex is NHC-PdX_2-Py (X = halogen, Py = pyridine), commonly known as the PEPPSI (Pyridine-Enhanced Precatalyst, Preparation, Stabilization and Initiation) complex, introduced by Organ in 2006 [8]. Since then tremendous progress has been made in the chemistry and catalysis involving Im-PdX_2-Py (Im = imidazol-2-ylidene) type complexes [9]. A few reports have appeared on the synthesis and catalytic activities of Tz-PdX_2-Py (Tz = 1,2,3-triazol-5-ylidene) type complexes [10]. Instead of pyridine whenever bidendate ligands such as 4,4′-bipyridne (bipy), pyrazine (Pz) and 1,4-diazabicyclooctane (DABCO) are used the corresponding bridged binuclear complexes, Im-PdX_2-bidendatePy-PdX_2-Im, were formed [11]. Recently we have reported a new method for the synthesis of normal and mesoionic $(NHC)_2$–PdI_2 complexes [12]. This methodology does not use strong bases [13] or silver salts [14] and more importantly the reactions were carried out at ambient temperature [15]. Herein we describe the utilization of this method for the synthesis of mononuclear PEPPSI type complexes and bridged binuclear complexes using 1,4-diphenyl-3-methyl-1,2,3-triazol-5-ylidene as the mesoionic NHC ligand. We also report an improved version of this method wherein the reaction duration is considerably shortened. In the improved version we used $(n\text{-}Bu)_4NI$ along with triazolium iodide and $Pd(OAc)_2$ in CH_2Cl_2. Under these conditions the reactions were accelerated and went to completion faster than reported earlier and gave the desired palladium diiodo complexes in excellent yields.

2. Results and discussion

2.1. Synthesis of NHC–Pd complexes

We have reported earlier that the reaction of triazolium iodide **1**

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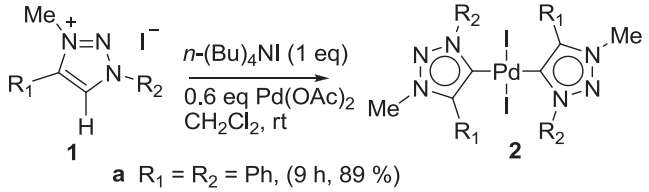
with $Pd(OAc)_2$ in CH_2Cl_2 at room temperature yielded complex **2** in near quantitative yields [12]. The reaction did not depend on the amount of $Pd(OAc)_2$, both 0.6 equivalents and 1.2 equivalents with respect to **1** gave the same result. However, triazolium iodide **(1a–c)** as the iodide source, the reactions were very slow and took several days to go to completion. In order to improve the rates of these reactions we used $(n\text{-Bu})_4NI$ along with the triazolium iodide and $Pd(OAc)_2$. Stoichiometric amounts of $(n\text{-Bu})_4NI$ on reaction with $Pd(OAc)_2$ gave dark black colour solution presumably due to the formation of palladate $[(n\text{-Bu}_4N)_2PdI_2(OAc)_2]$ as an intermediate. Evidence for the formation of the palladate complex is derived from ^1H NMR studies and detailed mechanism of formation of the NHC–Pd complex under base free conditions wherein acetate acts as the base is reported earlier from our group [12]. Further addition of triazolium salts **(1a–c)** yielded the corresponding mono nuclear palladium NHC complexes **(2a–c)** in good yields (Scheme 1). Triazolium iodide as the source of iodide ion the reactions took much longer to attain completion (**1a** and **1b** in 36 h and 1c in 48 h). The reactions were considerably faster with $(n\text{-Bu})_4NI$. Complexes **2a–c** were characterized by comparison of the spectroscopic data with authentic samples prepared in the laboratory (SI) [12] ^1H NMR spectra of **2a–b** (see SI) clearly indicated the presence of *syn* and *anti* rotomers for complex **2** [16]. We then explored the possibility of synthesizing $(Tz)_2PdCl_2$ derivatives using $(n\text{-Bu})_4NCl$ instead of the iodide salt. Triazolium salt **1a** was treated with $(n\text{-Bu})_4NCl$ in CH_2Cl_2 and stirred at room temperature for 2 h then $Pd(OAc)_2$ was added and allowed to stir at rt for 4 d. But, the same mononuclear palladium(II) diiodo compound **2a** was isolated in 66% of yield instead of the corresponding palladium(II) dichloro NHC complex. We also investigated the reaction of **1a** with 1.2 equivalents of $Pd(OAc)_2$ in the presence of excess KI which yielded very cleanly the corresponding bridged binuclear complex **3** in 95% yield as a bright yellow solid (Scheme 2). The ^1H and ^{13}C NMR spectra (in DMSO-d_6) of the product obtained in this reaction were identical to **3** reported earlier by Albrecht [15].

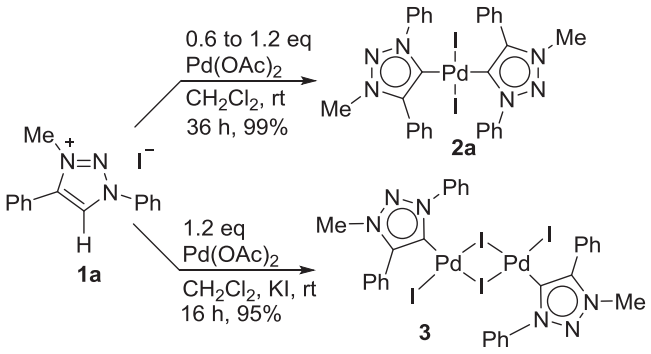
In an attempt to synthesize PEPPSI type complexes initially we investigated the reaction of triazolium iodide **1a** with 1.0 equivalent of $Pd(OAc)_2$ in the presence of excess KI and pyridine in CH_2Cl_2 as solvent at room temperature. The reaction invariably yielded the PEPPSI complex **5** along with $(Py)_2PdI_2$**(4)** as a mixture in 2:1 ratio, respectively (Scheme 3). Despite several attempts, the mixture could neither be separated by fractional crystallization nor by column chromatography. Authentic sample of **4** was prepared as a bright orange solid by the reaction of $PdCl_2(CH_3CN)_2$ in CH_2Cl_2 in the presence of KI and pyridine and it was identified by ^1H and ^{13}C NMR spectroscopic methods.

Hong [10c] has reported the synthesis of 1,2,3-triazol-5-ylidene based PEPPSI type complexes from the corresponding chloro bridged binuclear palladium complex by treatment with pyridine in CH_2Cl_2 at room temperature. Hong's method involved the intermediate silver carbene complex. In the present study treatment of complex **3** with 2.0 equivalents of pyridine gave complex **5** in

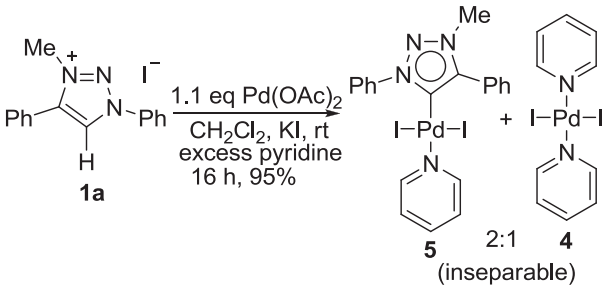


a $R_1 = R_2$ = Ph, (9 h, 89 %)
b R_1 = Ph, $R_2 = CH_2OH$, (12 h, 82 %)
c $R_1 = CH_2OH$, $R_2 = CH_2Ph$ (8h, 86 %)

Scheme 1. Synthesis of mononuclear palladium NHC complexes.



Scheme 2. Synthesis of mononuclear and iodo bridged binuclear complexes.

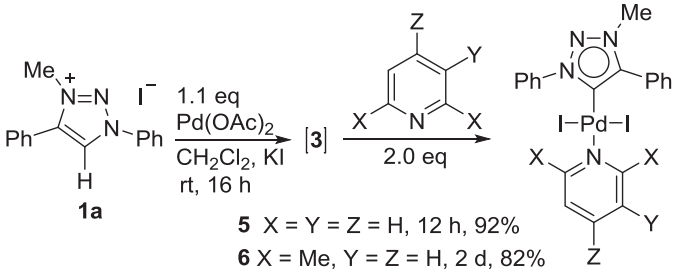


Scheme 3. Initial attempt towards the synthesis of PEPPSI type complexes.

near quantitative yield. A simple one pot procedure has been developed in which complex **3** was prepared *in situ* as shown in Scheme 2 and further treated with 2.0 equivalents of pyridine to obtain **5** without any contamination of complex **4** (Scheme 4).

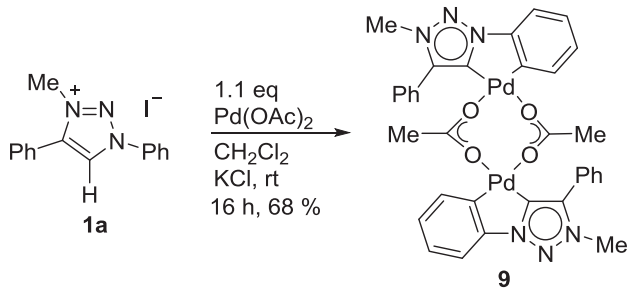
There are several advantages of this method compared to the existing ones. First of all the present method, unlike the earlier reports, [9,10] does not involve the use of any strong base or silver salts. The reactions required only stoichiometric amounts of pyridine derivatives. The reactions were carried out at ambient conditions. No side products were observed in these reactions and hence the PEPPSI type complexes **(5–8)** were easily obtained in pure form (Scheme 4).

Under similar conditions used for the synthesis of **3** as in Scheme 2, we attempted the synthesis of the corresponding chloro bridged complex from the reaction of triazolium salt **1a**, $Pd(OAc)_2$ (1.2 equiv) in the presence of excess KCl. To our surprise it gave the corresponding acetate bridged palladocycle complex **9** in 68% yield as greenish yellow solid (Scheme 5) [16] The ^1H and ^{13}C NMR spectra of the product **9** obtained in this reaction were identical to that of the literature [16a]. Although the role of KCl in the formation



5 X = Y = Z = H, 12 h, 92%
6 X = Me, Y = Z = H, 2 d, 82%
7 X = Y = H, Z = Me, 12 h, 89%
8 X = Z = H, Y = Cl, 12 h, 91%

Scheme 4. Synthesis of 1,2,3-triazol-5-ylidene based PEPPSI type complexes.



Scheme 5. Synthesis of acetate bridged palladocycle complex **9**.

of complex **9** is not clear, its presence was necessary because in the absence of KCl only complex **2a** was obtained (Scheme 2).

Huynh [11a] has reported the conversion of a bromo bridged binuclear palladium complex to the corresponding bipyridine bridged binuclear complex [Im-Pd(Br)$_2$-bipy-Pd(Br)$_2$-Im] by treatment with 4,4'-bipyridine in CH_2Cl_2 at room temperature. The corresponding linearly bridged binuclear complexes of the type [Tz-Pd(X$_2$)-bipy-Pd(X$_2$)-Tz] are not known till now. In the present study when 0.6 equivalents of bidendate ligands such as 4,4′-bipyridine (bipy), pyrazine (Pz) and 1,4-diazabicyclooctane (DABCO) were used instead of pyridine derivatives the corresponding linearly bridged binuclear complexes **10**–**12**, respectively, were obtained in high yields (Scheme 4). Unlike in the case of synthesis of PEPPSI type complexes **5**–**8** it was not necessary to add $Pd(OAc)_2$ and bidendate ligands sequentially. All the reagents can be mixed simultaneously and bridged complexes **10**–**12** were the sole products formed in these reactions (Scheme 6). It must be emphasized that in all of these reactions presented in Schemes 1–6 presence of acetate is crucial as an in-built base. Hence the source of palladium has to be $Pd(OAc)_2$ base free synthetic method reported herein. When $PdCl_2(CH_3CN)_2$ was used as a source of palladium the reactions did not occur. For instance there was no reaction when **1a** was treated with $PdCl_2(CH_3CN)_2$ up to 20 h under otherwise identical conditions as in Scheme 2. Similarly there was no reaction when **1a** was treated with $PdCl_2(CH_3CN)_2$ in the presence of 1 equivalent of *n*-Bu_4NI under otherwise identical conditions as in Scheme 1.

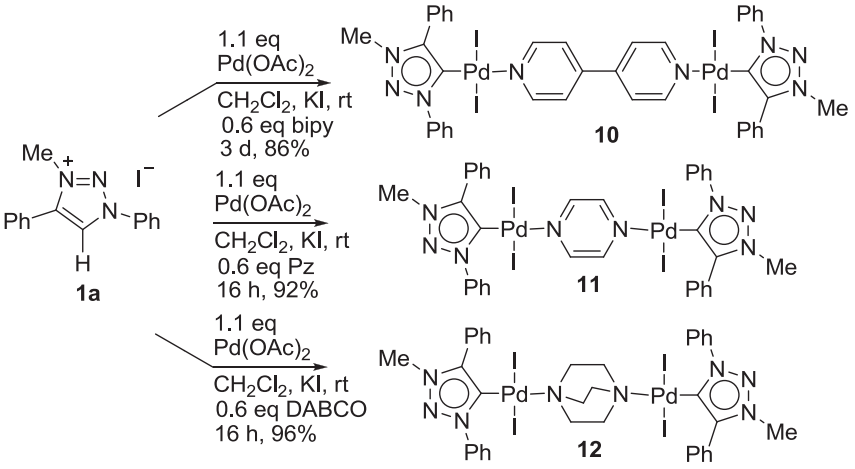
2.2. Structural characterization

The structures of complexes **5**, **8** and **11** were established by single crystal XRD data (Fig. 1, Table 1). In all the complexes the geometry around palladium is square planar and the ligands occupy trans positions as expected. The Pd–Ccarbene bond length in all the complexes is around 1.96(1) Å and the Pd–N bond length is around 2.10(1) Å, comparable to other triazolylidene-Pd PEPPSI type complexes [10]. In complex **11** both the I–Pd–I units are coplanar and this plane is perpendicular to the plane containing both the triazolylidene rings.

2.3. Comparison of catalytic activities

Crudden [10a] has reported Heck coupling of aryl bromides and aryl iodides with methyl acrylate using 1,2,3-triazolylidene based mesoionic PEPPSI type complexes as catalysts. Hong [10c] has reported Suzuki–Miyaura coupling of 1-chloro-2,6-dimethylbenzene with phenylboronic acid to give high yield of 2,6-dimethylbiphenyl at room temperature using PEPPSI type complex of sterically hindered 1,4-bis(2,6-diisopropylphenyl)-1,2,3-triazol-5-ylidene palladium complex in ethanol using potassium *t*-butoxide as base at room temperature. Albrecht [10b] has reported the coupling between *m*-bromo anisole and phenylboronic acid using a variety of bases and solvents and best yield was reported when the reaction was carried out in 2-propanol using tetra-*n*-butyl ammonium fluoride at 50 °C using 1,2,3-triazolylidene based mesoionic carbene complex. Organ [10f] has used sterically hindered PEPPSI complexes to carry out Suzuki coupling of sterically demanding substrates for the synthesis of biaryls and binaphthyls. Herein, compounds **2a, 3, 5** and **11** were screened and used as pre-catalysts for Suzuki–Miyaura coupling reactions of aryl bromides with phenylboronic acid. A mixture of $Pd(OAc)_2$ and PPh_3 was examined for comparison of catalytic activity with that of the NHC complexes. The coupling reaction of 4-bromoanisole with phenylboronic acid was taken as model reaction and the reactions were carried out in ethanol as solvent. The results are summarized in Table 2.

These results clearly show that the PEPPSI type complex **5** is catalytically more reactive than complexes **2** and **3** (compare entires 1, 3 and 6, Table 2). With complex **2a** after 2.5 h only 40% yield of 4-phenylanisole was obtained and the reminder was unreacted 4-bromoanisole and it took more than 12 h for the completion of the reaction. In the presence of complex **3** (2 mol%) and **11** (2 mol%) the reactions were complete only after 5 h and 6 h, respectively (Table 2, entries 4 and 9). When PPh_3 (2 mol%) was added along with **3** the reaction was faster and had gone to completion within 2.5 h to give 94% yield of the product. Under these conditions the bridged binuclear complex **3** most likely coordinates with PPh_3 to



Scheme 6. Synthesis of bridged binuclear complexes **10**–**12**.

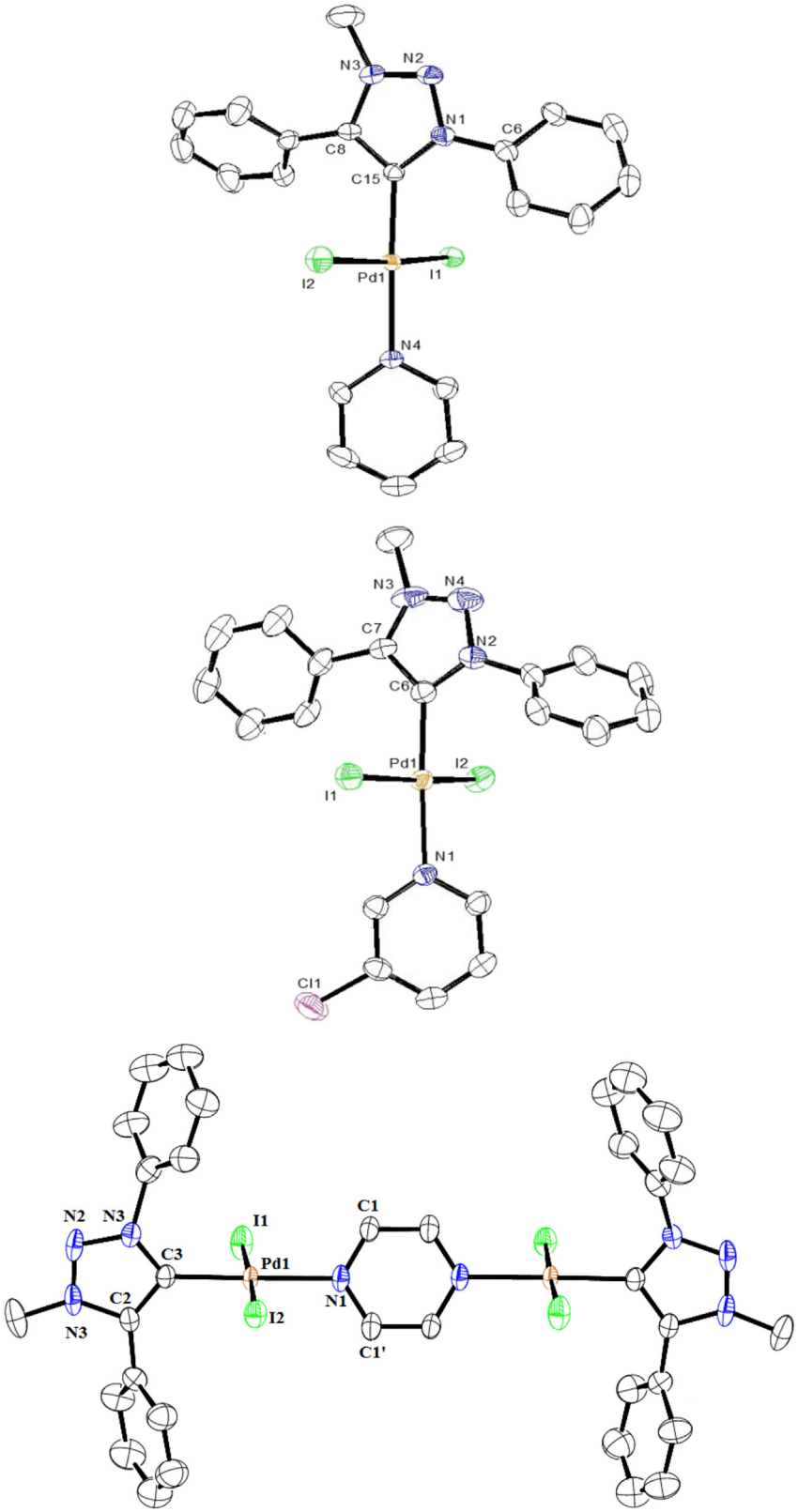


Fig. 1. ORTEP diagram (50% probability) of the structure of complexes **5** (top), **8** (middle) and **11** (bottom). Hydrogen atoms are omitted for clarity.

give the corresponding mononuclear [(Tz)Pd(Cl)$_2$(PPh$_3$)] which in turn forms the active catalyst. Using catalyst 5the reaction was complete within 2.5 h and addition of PPh$_3$ did not affect the duration of the reaction significantly (Table 2, entries 6 and 7). When Pd(OAc)$_2$and PPh$_3$ were used, reaction took much longer (14 h) for the completion (Table 2, entry 13). The palladium NHC

Table 1
Crystallographic data of compounds **5, 8** and **11**.

Parameters	5	8	11
Formula	$C_{20}H_{18}I_2N_4Pd$	$C_{20}H_{17}ClI_2N_4Pd$	$C_{34}H_{30}I_4N_8Pd_2$
Formula weight	674.58	709.03	1271.06
Radiation λ (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1/c$	*Pbcn*	*Pnnm*
a (Å)	12.6404 (5)	17.398 (4)	10.2717 (5)
b (Å)	9.8042 (4)	16.028 (4)	12.9221 (6)
c (Å)	17.7388 (7)	16.715 (4)	15.6387 (8)
α°	90	90	90
β°	99.932 (2)	90	90
γ°	90	90	90
V (Å^3)	2165.41 (15)	4661.1 (2)	2075.75 (18)
T (K)	296 (2)	293 (2)	293 (2)
Z	4	8	2
Reflections/unique/	3805/	4718/	1903/
R_{int}	0.039	0.039	0.082
μ mm^{-1}	3.72	3.57	3.87
F(000)	1272	2672	1188
θ range	2.38 to 28.33	2.1 to 26.05	2.4 to 26.7
Goodness-of-fit on F^2	1.052	1.048	1.170
Final *R* indices	$R_1 = 0.0397$	$R_1 = 0.0272$	$R_1 = 0.0392$
	$wR_2 = 0.0894$	$wR_2 = 0.0549$	$wR_2 = 0.0980$
R indices	$R_1 = 0.0464$	$R_1 = 0.0485$	$R_1 = 0.0489$
(all data)	$wR_2 = 0.0950$	$wR_2 = 0.0654$	$wR_2 = 0.1046$

complexes **2a, 3, 5** and **11**showed higher catalytic activity compared to $Pd(OAc)_2$ and PPh_3. The results in Table 2 show that compound **5** is the most efficient catalyst among the ones tested for the Suzuki–Miyaura coupling of aryl bromides with phenyl boronic acid. When 1 mol% of **5** was employed in the Suzuki–Miyaura reactions, both electron-rich and electron-deficient aryl bromides gave moderate to good yields of the corresponding biphenyl derivatives (Table 3). Complex **5** was inactive towards the coupling of aryl chlorides unless activated such as 2-chloropyridine (Table 3, entries 7–10).

3. Conclusions

We have prepared mononuclear $[(Tz)_2PdI_2]$ complexes **(2a–c)** in good yields in short duration using $(n\text{-}Bu)_4NI$ with triazolium iodide **(1a–c)**, $Pd(OAc)_2$ in CH_2Cl_2. Surprisingly, acetate bridged pallado cycle complex **9** was formed in the presence of KCl. Synthesis and structural characterization of mononuclear PEPPSI type palladium complexes $[(Tz)Pd(I)_2(Py)]$ **(5–8)** and bridged binuclear palladium complexes $[(Tz)Pd(I)_2$(Bridging bidendatePy)$Pd(I)_2(Tz)]$ **(10–12)** of 1,4-diphenyl-3-methyl-1,2,3-triazol-5-ylideneare reported. The method of synthesis involves mild conditions using only stoichiometric amounts of pyridine ligands. The methodology presented herein avoids the use of strong bases to generate the NHC and devoid of silver carbene complexes which normally results in stoichiometric amount of silver waste. Finally, in comparison with other NHC complexes **(2, 3** and **11)** the PEPPSI type complex **5** was found to be catalytically more reactive for Suzuki–Miyaura coupling of aryl bromides at ambient conditions. Aryl chlorides failed undergo Suzuki–Miyaura coupling under identical conditions.

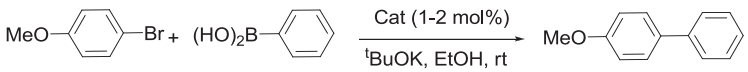
4. Experimental section

All the reactions were performed under nitrogen atmosphere and in distilled dichloromethane. $Pd(OAc)_2$(Aldrich) was used as received. 1,2,3-triazolium salts **1a** [16], **1b** [17], **1c** [18] were prepared according to literature procedure.

4.1. Instrumentation

Infrared (IR) spectra were recorded on a JASCO 4100 FT-IR spectrometer. ^{1}H NMR spectra were measured on Bruker AVANCE 400 MHz and 500 MHz spectrometers. Chemical shifts were reported in ppm from tetramethylsilane as internal standard.^{13}C NMR spectra were recorded on Bruker 100 MHz and 125 MHz spectrometers with complete proton decoupling. Chemical shifts were reported in ppm using residual solvent peaks as internal standard. High-resolution mass spectra (HRMS) were performed on Micromass ESI Q-TOF micro mass spectrometer equipped with a Harvard apparatus syringe pump. X-ray crystallographic data were collected on a Bruker-AXS Kappa CCD-Diffractometer with graphite-monochromator Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least squares techniques against F2 (SHELXL-97). Hydrogen atoms were inserted from geometry consideration using the HFIX option of the program. For thin layer chromatography

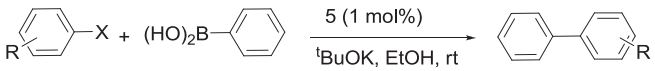
Table 2
Suzuki–Miyaura reactions of 4-bromoanisole with phenylboronic acid in the presence of NHC-Palladium catalysts.[a]



Entry	Pre-catalyst	Time (h)	Yield (%)[b]
1	**2a**	2.5	40
2	**2a**	12	90
3	**3**	2.5	54
4	**3**	5	94
5	**3** + PPh_3	2.5	94
6	**5**	2.5	95
7	**5** + PPh_3	2.5	95
8	**11**	2.5	45
9	**11**	6	93
10	**11** + PPh_3	2.5	95
11	**11** + PPh_3	6	94
12	$Pd(OAc)_2$ + PPh_3	2.5	Trace
13	$Pd(OAc)_2$ + PPh_3	14	84

[a] Reaction conditions: 4-bromoanisole (1 equiv), phenylboronic acid (1.2 equiv), palladium complex **2a** (1 mol%), **5** (1 mol%), **3, 11** (0.5 mol%), $Pd(OAc)_2$ (1 mol%), t-BuOK (1.5 equiv) in EtOH at rt.
[b] Isolated yields.

Table 3
Suzuki–Miyaura reactions of aryl halides with phenylboronic acid using **5** as catalyst.[a]



Entry	Aryl halide (R)	Time (h)	Yield (%)[b]
1	4-bromoanisole	2.5	95
2	2-bromoanisole	2.5	92
3	4-bromobenzoic acid	3.5	92
4	2-bromobenzoic acid	8	89
5	1,4-dibromobenzene	3	99[c]
6	1,3,5-tribromobenzene	6	93
7	2-chloropyridine	8	38
8	4-chlorotoluene	24	0
9	4-chlorobenzaldehyde	24	0
10	4-trifluoromethyl-chlorobenzene	24	0

[a] Reaction conditions: Aryl halide (1 equiv), phenylboronic acid (1.2 equiv), palladium complex **5** (1 mol%), *t*-BuOK (1.5 equiv) in EtOH at rt.
[b] Isolated yields.
[c] *p*-terphenyl is the product.

(TLC) analysis, E-Merck pre-coated TLC plates (silica gel 60 F254 grade, 0.25 mm) were used.

4.2. Synthesis and characterization

4.2.1. General procedure for the preparation of mononuclear palladium(II) diiodo NHC complexes (**2a–c**)

A mixture of $Pd(OAc)_2$ (0.6 equiv) and $(n\text{-}Bu)_4NI$ (1 equiv) in dichloromethane (20 mL) was stirred at room temperature under N_2 atmosphere for 2 h to give a dark brown to black colour solution. 1,2,3-Triazolium salt iodide **(1a–c)** (100 mg, 1 equiv) was added to the mixture and stirring was continued for 8–12 h depending upon the substrate to give orange or light yellow solution. Evaporation of solvent gave a gummy product. The product was purified by column chromatography on silica gel using CH_2Cl_2: MeOH (9:1) as eluent. Complexes **2a–c** were reported from our laboratory [12] and their characterization data are given in the SI.

4.2.2. General procedure for the synthesis of PEPPSI type complexes

A mixture of triazolium iodide **1a** (100 mg, 0.27 mmol), $Pd(OAc)_2$ (67 mg, 0.3 mmol), KI (180 mg, 1.1 mmol) in dichloromethane gave a dark brown solution which was allowed to stir at room temperature for 16 h. The reaction mixture was filtered and solvent was evaporated to give binuclear complex **3** in 95% of yield. In a one pot synthesis pyridine derivative (0.26 mmol, 2 equiv.) in CH_2Cl_2 was directly added dropwise to the above reaction mixture. Upon addition of pyridine derivatives the colour of the reaction mixture changed from dark brown to dark yellow instantaneously. The reaction mixture was stirred at room temperature for 12 h (**5**, **7**, and **8**) and 2 d (**6**), respectively. Evaporation of the solvent gave the crude product which was purified by washing with hexane and ether to give PEPPSI type complexes as dark orange or yellow crystalline solids.

Complex **5**: 170 mg, 92%, mp.225 °C.^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 8.76–8.78 (m, 2H), 8.44–8.46 (m, 2H), 8.0–8.02 (m, 2H), 7.56–7.65 (m, 7H), 7.17–7.20 (t, 2H), 4.06 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 37.8, 124.3, 125.7, 127.4, 128.8, 129.0, 130.2, 130.8, 135.5, 137.3, 139.8, 144.4, 153.9; IR (KBr, cm^{-1}): 3072, 2976, 2840, 1615, 1550, 1490, 790, 692; HRMS: [M^+–I] *m/z* calcd for $C_{20}H_{18}N_4$ PdI 546.9611, found 546.9630.

Complex **6**: 159 mg, 82%; mp.255 °C.^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.31–8.34 (m, 2H), 7.97–8.0 (m, 2H), 7.56–7.64 (m, 6H), 7.36 (t, 1H, $J = 8$ Hz), 6.89–6.92 (t, 2H, $J = 8$ Hz), 4.06 (s, 3H), 2.80 (s, 3H), 2.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 27.3, 27.4, 37.6, 122.4, 122.5, 126.3, 127.3, 128.7, 128.9, 130.2, 130.2, 131.1, 137.8, 139.6, 144.5, 159.4, 159.8; IR (KBr, cm^{-1}): 3050, 2977, 2917, 2356, 1624, 1472, 1318, 1164,793, 698; HRMS: [M^+–I] *m/z* calcd for $C_{22}H_{22}N_4$PdI 574.9924, found 574.9933.

Complex **7**: 168 mg, 89%; mp.230 °C.^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.58–8.60 (m, 2H), 8.44–8.47 (m, 2H), 8.0–8.02 (m, 2H), 7.56–7.65 (m, 6H), 6.99–7.01 (d, 2H, $J = 8.0$ Hz), 4.06 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 21.1, 37.8, 125.3, 125.7, 127.5, 128.8, 129.0, 130.2, 130.8, 139.9, 144.4, 149.2, 153.2; IR (KBr, cm^{-1}): 3050, 2927, 2850, 1620, 1494, 1333, 1066, 810, 761. HRMS: [M^+–I] *m/z*calcd for $C_{21}H_{20}N_4$PdI 560.9767, found 560.9791.

Complex **8**: 178 mg, 91%; mp.240–245 °C.^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.79 (d, 1H, $J = 4$ Hz), 8.71 (d, 1H, $J = 4$ Hz), 8.41 (d, 2H, $J = 8$ Hz), 7.98 (d, 2H, $J = 8$ Hz), 7.57–7.66 (m, 7H), 7.13–7.17 (m, 1H), 4.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 37.8, 124.6, 125.7, 127.3, 128.9, 129.0, 130.3, 130.7, 132.1, 134.1, 137.5, 138.5, 139.7, 144.3, 151.9, 152.8; IR (KBr, cm^{-1}): 3078, 2921, 2850, 2366, 1596, 1462, 1066, 761, 691; HRMS: [M^+–I] *m/z*calcd for $C_{20}H_{17}ClN_4$PdI 580.9221, found 580.9226.

4.2.3. Synthesis of complex **9**

A mixture of 1,2,3-triazolim salt iodide 1a (100 mg, 0.28 mmol) and KCl (81 mg, 1.1 mmol) in CH_2Cl_2 stirred at room temperature for 1 h. Then $Pd(OAc)_2$ (67 mg, 0.30 mmol) was added. The reaction mixture stirred at room temperature for 15 h. The mixture was filtered and evaporates the solvent to give crude product. The crude product dissolved in acetone and evaporates the solvent to give greenish yellow product. Complex **9** has been reported from our laboratory [16] and its characterization data are given in the SI.

4.2.4. General procedure for the synthesis of bridged binuclear complexes

A mixture of triazolium iodide **1a** (100 mg, 0.27 mmol), $Pd(OAc)_2$ (67 mg, 0.3 mmol), KI (91 mg, 0.55 mmol), bridging ligand (0.16 mmol, 0.6 equiv.) in dichloromethane gave a dark brown solution which was stirred at room temperature for16 h (**11** and **12**) and 3 d (**10**). During this period the dark brown colour changed to dark orange. The reaction mixture was filtered and solid was washed with CH_2Cl_2. The filtrate was evaporated to give the crude product which was purified by washing with hexane and ether to give the desired complexes as yellow solids.

Complex **10**: 165 mg, 86%; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.91 (d, 4H, $J = 8$ Hz), 8.42 (d, 4H, $J = 8$ Hz), 7.98–8.0 (m, 4H), 7.57–7.65 (m, 12H), 7.32 (d, 4H), 4.07 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 37.8, 122.0, 125.7, 127.3, 128.9, 129.0, 130.3, 130.8, 134.8, 139.8, 144.4, 145.7, 154.7; IR (KBr, cm^{-1}): 3057, 2927, 2846, 2356, 1603, 1494, 1329, 1269, 1178, 1073, 1020,765, 694; HRMS: [M+1] *m/z*calcd for $C_{40}H_{35}N_8Pd_2I_4$ 1346.7233, found 1346.7232.

Complex **11**: 160 mg, 92%; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.84 (s, 4H), 8.31 (d, 4H, $J = 8$ Hz), 7.90 (d, 4H, $J = 8$ Hz), 7.56–7.62 (m, 12H), 4.04 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 37.9, 125.7, 127.0, 128.9, 129.1, 130.4, 130.7, 139.5, 144.2, 149.2; IR (KBr, cm^{-1}): 3050, 2921, 2846, 1596, 1476, 1455, 1420, 1333, 1185, 1069, 1020,771, 694; HRMS: [M+Na] *m/z*calcd for $C_{34}H_{30}N_8Pd_2I_4Na$ 1292.6740, found 1292.6735.

Complex **12**: 162 mg, 92%; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.32 (d, 4H, $J = 4$ Hz), 7.89 (d, 4H, $J = 8$ Hz), 7.54–7.57 (m, 12H), 3.99 (s, 6H), 3.30 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 29.8, 37.8, 54.1, 125.5, 127.2, 127.7, 128.7, 128.8, 130.2, 130.2, 130.6, 139.6, 143.7; IR (KBr, cm^{-1}): 3057, 2927, 2850, 1592, 1490, 1464, 1329, 1269, 1182, 793, 758; HRMS: [M+1] *m/z*calcd for $C_{36}H_{39}N_8Pd_2I_4$ 1302.7546, found 1302.7543.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2015.10.002.

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