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1,2,3-Triazolylidene palladium complex with triazole ligand: Synthesis, characterization and application in Suzuki–Miyaura coupling reaction in water

Drishya Sasidharan, Aji C.V. and Paulson Mathew*

*Department of Chemistry, Centre for Sustainability Science, St. Thomas' College, Calicut University, Thrissur-680001, Kerala, India

Abstract: Palladium complex containing 1,2,3-triazolylidene and a labile triazole moiety has been prepared and characterized. Simple azide alkyne click reaction using three fold excess of dibromoethane afforded 1-(2-bromoethyl)-4-phenyl-1H-1,2,3-triazole. The latter on dehydrobromination yields N-vinyl triazole (N_{tzi}) which is subsequently used for preparing its triazolium salt. Further, N_{tzi} -Pd- N_{tzi} complex was prepared from triazole by simple palladation which underwent a ligand substitution reaction when treated with *in situ* generated triazolylidene to form C_{tzi} -Pd- N_{tzi} type complex. This mixed palladium complex was found to be highly effective in catalyzing Suzuki-Miyaura coupling reaction between aryl halides and aryl boronic acids in water at room temperature with very low catalyst loading.

Introduction

Suzuki–Miyaura cross-coupling reaction of organic halides with boronic acids using palladium catalyst is one of the most versatile methods for the synthesis of biaryls [1]. Traditionally, a variety of air and thermal-sensitive phosphine ligands and their metal complexes have been used as catalysts for the coupling reactions [2]. Recently, it has been reported that nucleophilic N-heterocyclic carbenes (NHCs) stabilized by adjacent heteroatom can be employed as auxiliary ligands for coupling reactions [3]. However, these reactions are usually carried out in organic solvents. With growing environmental concern, there is an increasing demand for green chemistry protocols for the development of sustainable technologies [4] such as proper design of catalysts to enable the use of water as a reaction medium. Current developments in this perspective, involve the use of water soluble ligands, micellar catalysis and hydrophilic ligand precursors [5]. Among these, water soluble NHC based complexes are being used as catalysts for C–C bond formation reactions including Suzuki–Miyaura coupling reaction [6]. The discovery of N-heterocyclic carbenes as formally neutral, strongly donating, and covalently binding ligands has triggered the search for newer ligands that can tune the catalytic activity and reactivity of catalyst particularly those having

palladium centre [7]. The current interest in this perspective is to develop new and reliable synthetic routes using N-heterocyclic carbenes with diverse substitution pattern [8].

Recently, few research groups have developed efficient protocols for Suzuki coupling of aryl halides in water at room temperature using water-soluble NHC–Pd catalysts [9]. The catalyst design is based on the concept of “throw away” ligand. This involves a weakly coordinated ligand that can leave the complex immediately before an oxidative addition takes place. A majority of such catalytic systems contain an imidazolylidene palladium core decorated with either PEPPSI (Pyridine Enhanced Precatalyst Preparation, Stabilization and Initiation), amine, (iso)quinoline, DABCO (1,4-diazabicyclo[2.2.2]octane) etc. as N-donor labile ligands. Surprisingly, only limited examples of triazolylidene palladium complexes based on “throw away” ligands are known and used for Suzuki–Miyaura cross-coupling reaction (Fig. 1) [10].

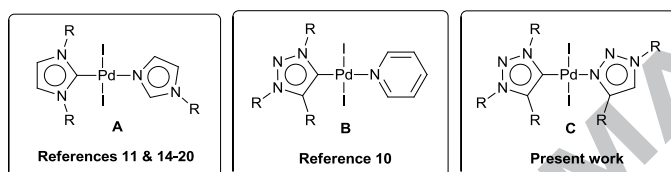


Fig. 1 Development of “through away” ligand concept in NHC–Pd-complexes: C_{1m} –Pd(II)– N_{1m} complex (A), C_{1zl} –Pd(II)– N_{PEPPSI} complex (B) and C_{1zl} –Pd(II)– N_{1zl} complex (C)

Stronger donor capacity of triazolylidene ligands in comparison with the imidazolylidene counterpart is reflected in the improved catalytic activity of such palladium complexes. Based on the above considerations, in the present work an attempt has been made to synthesise triazolylidene palladium complex with a “throw away” ligand and explore it as a catalyst in Suzuki–Miyaura cross coupling in water. The synthetic protocol adopted here resulted in a novel triazolylidene NHC palladium complex containing a vinyl triazole as labile ligand, capable of effectively coupling aryl halides with aryl boronic acid in aqueous media with very low catalyst loading at room temperature. This palladium complex is effective in coupling not only aryl bromides and iodides but also low cost aryl chlorides having strong C–Cl bond. Activation of aryl halides under mild conditions is rather limited with very low catalyst loading.

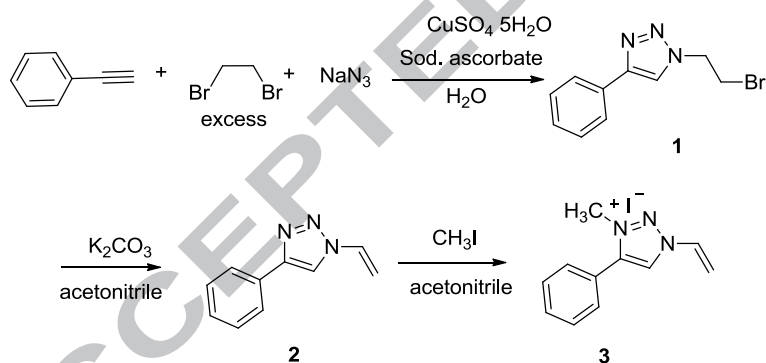
RESULTS AND DISCUSSION

In order to effectively utilize the strong donor capacity of triazolylidene ligand and to incorporate the hydrophilicity of the palladium complex, we have designed a novel C_{1zl} –Pd– N_{1zl} complex **5**. Similar molecules using imidazoles were recently reported by Lu *et al.* and

proved to be effective in catalyzing the Suzuki Miyaura coupling between benzyl chlorides and aryl boronic acids in water [11]. Here we presume that the presence of strong N-heterocyclic carbene C–Pd bonding along with a normal Pd–N bond from the labile triazole moiety can have a twofold effect. Firstly, it can result in ionization of the triazole part and secondly stabilize the complex in protic solvents.

Synthesis of triazole

Click reaction between phenyl acetylene and an *in situ* generated monoazide from 1,2-dibromoethane afforded 1,2,3-triazole **1**. Using threefold excess of 1,2-dibromoethane, monoazide formation takes place and 1-(2-bromoethyl)-4-phenyl triazole **1** was obtained as the sole product in good yields (Scheme 1). In this new protocol, although the dibromide was used in excess, it could be recovered during work up and be reused after distillation. The structure of the triazole **1** was confirmed from spectral data [12]. Similar triazoles were recently reported by Das *et al.* using copper supported polymer [13]. Dehydrobromination of the triazole **1** using K_2CO_3 in DMF afforded the vinyl triazole **2** in 87% yields. Methylation of the vinyl triazole using methyl iodide in acetonitrile as solvent afforded the triazolium salt **3** in quantitative yield.



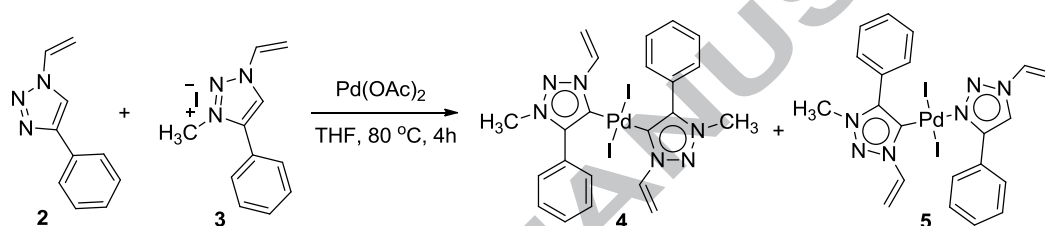
Scheme 1 Synthesis of triazolium salt **3**

Subsequently triazolium salt **3** was used for palladation. However, palladation/metalation can lead to two types of Pd complexes *viz.* $C_{tztl}-Pd-C_{tztl}$ and $C_{tztl}-Pd-N_{tztl}$ depending up on whether two equivalents of salt **3** or one equivalent each of the salt **3** and the vinyl triazole **2** were used. Since our objective was to fabricate a water soluble palladium complex by incorporating a labile triazole moiety, initially we focused our attention on the second method. In literature, similar protocols have been reported for preparing mixed NHC-Pd complexes having labile ligands [10, 11, 14-20].

Synthesis of mixed palladium complex

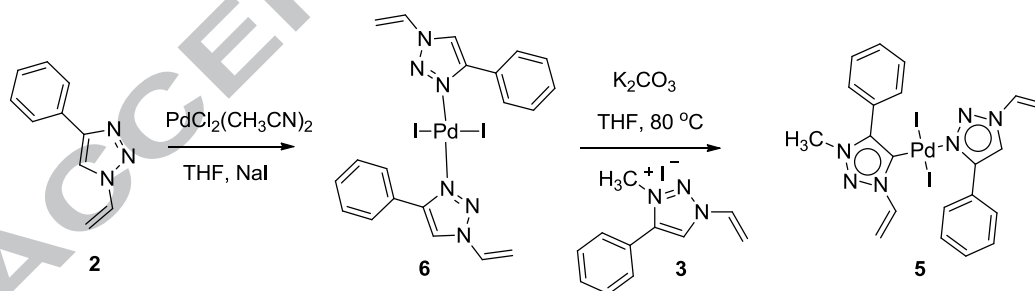
In order to synthesis the palladium triazole complex **5** with a labile triazole moiety, one equivalent each of the triazolium salt **3** was mixed with vinyl triazole **2** and palladium acetate in tetrahydrofuran (THF) solvent followed by heating at 80 °C for 4 hours. The solvent was removed under reduced pressure to afford a red solid. Thin layer chromatography (TLC) showed a mixture of products from which complexes **4** and **5** were isolated in 22% and 15% yield respectively (Scheme 2).

In another experiment, when two equivalents of the triazolium salt **3** were treated with palladium acetate in THF, the C_{tzi} -Pd- C_{tzi} complex **4** was obtained as the sole product with 62% yield.



Scheme 2 Reaction of the triazolium salt **3** with triazole **2**

Alternatively, complex **5** was prepared by a ligand substitution reaction of N_{tzi} -Pd- N_{tzi} complex **6**. Complex **6** was prepared by the reaction of bis(acetonitrile)dichloropalladium(II) with 1,2,3-triazole **2** and allowed to react with the triazolylidene generated from the triazolium salt **3** by heating in K_2CO_3 /THF at 80 °C to afford the air and moisture stable orange coloured palladium complex **5** with 70% yield (Scheme 3).



Scheme 3 Synthesis of triazolylidene palladium triazole complex **5**

In the above synthesis, the reaction takes place by substitution of one of the 1,2,3-triazole ligands by an *in situ* generated triazolylidene. It is noteworthy that such a synthetic strategy has not been reported so far. Pure crystals of **5** were obtained by slow diffusion of pentane into a solution of **5** in dichloromethane at room temperature. The palladium complex was characterized by spectroscopic and single crystal X-ray diffraction (XRD) data (Fig. 2) [12]. 1H NMR spectrum of **5** clearly indicates the presence of both N-bound triazole and C-bound

triazolylidene ligands. Methyl group of the triazolylidene moiety appeared as a singlet at 4.02 ppm, similar to the bistriazolylide complex **4**. Vinylic protons appear as doublet of doublets at 5.1, 5.5, 5.7, and 6.3 ppm, while the NCH protons of both the ligands are shifted downfield to the aromatic region. One proton singlet at 8.0 ppm corresponds to the CH proton of triazole ring which is in consistent with the N-bound bis triazole palladium complex **6**. The ^{13}C NMR resonance peaks also indicates the presence of N and C bound triazole ligands. The CH_3 carbon appeared at 37.1 ppm. Total number of N-vinyl and aromatic carbons also account for the presence of N-bound triazole and C-bound triazolylidene ligands in the palladium complex.

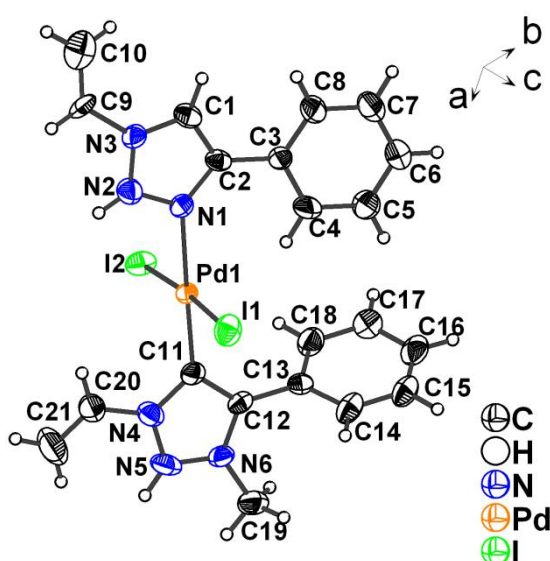
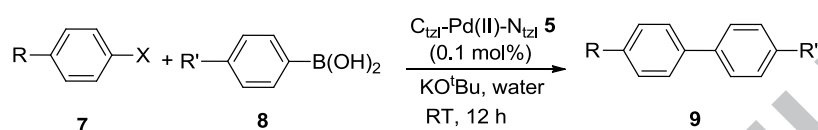


Fig. 2 ORTEP diagram of the palladium complex **5**

Single-crystal XRD shows that the complex **5** adopts a distorted square planar geometry around the palladium centre. In complex **5**, the two C, N ligands and iodide ions, respectively adopt *trans* geometry. The phenyl groups are oriented *cis* to each other with respect to C2-axis passing between the triazolylidene ligands, bisecting the N1–Pd–C11 angle. The Pd–C11 and Pd–N1 distance are 1.962 Å and 2.122 Å respectively. The bond lengths are similar to those of related Pd–C_{carbene} complexes derived from triazolyidene and PEPPSI ligands [10a] or imidazolylidenes stabilized with N-donor ligands such as imidazole [14], piperazine and DABCO [15], benzoxazole [16], dihydrooxazole [17] isoquinoline [18], ethylamine [19] or PEPPSI [20]. Abnormal carbene NHC ligands are considered better σ -donors than their normal analogues and this strong *trans*-influence of 1,2,3-triazolylidene ligand is reflected in the longer Pd–N1 bond length, favouring the “throw away” effect. N1–Pd–C11 bond angle was found to be 178.6(5) °.

Efficiency of other palladium complexes **4** and **6** towards this coupling reaction were also investigated. However, they were found to be less effective than the $C_{tztl}-Pd-N_{tztl}$ complex **5**. Similarly, this catalyst was found to be equally good or even better than other water soluble palladium non-carbene systems.²² The catalyst **5** was very effective in coupling aryl chlorides, bromides or iodides with aryl boronic acids. It was observed that the presence of electron donating or withdrawing groups had very little effect on the overall yield of the product (Table 2).

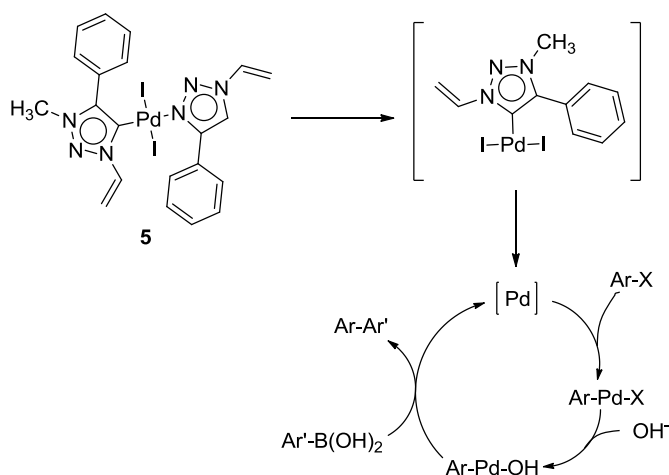
Table2: Suzuki–Miyaura cross coupling reactions of aryl halides at room temperature



Entry ^a	R	R'	X	Yield ^b (%)
1	H	H	I	94
2	H	OMe	I	92
3	CH ₃	OMe	I	88
4	CH ₃	H	I	90
5	H	2-furyl B(OH) ₂	I	92
6	CH ₃	2-furyl B(OH) ₂	I	90
7	H	H	Br	92
8	COCH ₃	H	Br	94
9	H	H	Cl	92
10	COCH ₃	H	Cl	95

^aReaction conditions: Aryl halide (1 mmol), aryl boronic acid (1.1 mmol), catalyst **5** (0.1 mol%), base (KO^tBu, 2 mmol) and 5 mL water. ^bIsolated yield.

The catalytic cycle herein involves heterogenization of the pre-catalyst into palladium nanoparticles which are stabilized by the triazolylidene or triazole present in the system. Imidazolium and ammonium salts are known to stabilize palladium nanoparticles generated from palladium NHC complexes [23]. Mercury poisoning test was used to study the involvement of palladium nanoparticles. Addition of one drop of Hg(0) to the reaction mixture, reduced or decreased the yield of the reaction from 94% to 20% (entry 1, Table 2), clearly indicating the heterogenous nature of the catalyst.



Scheme 4: Proposed mechanism for the Suzuki–Miyaura reaction. Palladium nanoparticle [Pd] is stabilised by triazole or triazolylidene ligands. For clarity coordinated ligands on palladium are omitted.

Reusability of catalyst is of utmost significance with respect to economical and green chemistry perspectives. We have investigated the reusability of the catalyst by performing several catalytic runs in the same reaction vessel. Four catalytic runs were carried out by taking 0.1 mol% of catalyst. After an interval of 12 hours each, the product formed was extracted using diethyl ether and fresh batch of substrate and base was added into the reaction vessel without adding the catalyst. The substrate consumption was monitored by gas chromatography- mass spectrometry (GC-MS) and even after four successive runs it was observed that the overall yield was found to be 90% which indicates that there is no loss of catalytic activity.

Conclusions

In conclusion, a new palladium complex comprising of $C_{tzl}-Pd-N_{tzl}$ bonding pattern was prepared. The structure of the newly synthesized complex was characterized by NMR and single crystal XRD. The palladium complex was found to be an active catalyst for Suzuki-Miyaura cross coupling of aryl iodides, bromides or chlorides with aryl boronic acid. The coupling required very low catalyst loading and the reaction was performed at room temperature using aqueous medium. The catalyst could be reused for four consecutive runs without any significant loss of its activity.

Experimental

Synthesis of 1-(2-bromoethyl)-4-phenyl-1,2,3-triazole (1)

1,2-Dibromoethane (5.65g, 30 mmol), sodium azide (0.65g, 10 mmol), phenyl acetylene (0.1g, 10 mmol), copper acetate monohydrate (0.03g, 0.15 mmol) and sodium ascorbate

(0.03g, 0.15 mmol) were taken in an R B flask containing 20 ml *tert*-butyl alcohol and 10 ml of water. The mixture was then heated at 65 °C for 18 hours. It was then cooled to room temperature. Water (50 ml) was added to it and extracted using ethyl acetate. The solvent and excess dibromoethane were removed using rotavapor. The product was further purified by passing through a silica gel column using a mixture of hexane and ethyl acetate (3:1) as eluent. The product was obtained as pale yellow needles. Yield 2.0 g (80%). m.p. 70 °C. ¹H NMR (CDCl₃ 400 MHz): δ 3.73 (t, *J* = 6 Hz, 2H, CH₂Br), 4.74 (t, *J* = 6 Hz, 2H, NCH₂), 7.28 (m, 1H, H_{Ar}), 7.36 (m, 2H, H_{Ar}), 7.78 (d, 2H, *J* = 7.6 Hz, H_{Ar}), 7.84 (s, 1H, H_{trz}) ppm. ¹³C NMR (CDCl₃ 400 MHz): δ 29.3(CH₂Br), 51.7 (NCH₂), 120.5 (CH_{trz}), 125.8 (C_{Ar}), 128.4 (C_{Ar}), 128.9 (C_{Ar}), 130.1 (C_{Ar}), 147.6 (C_{trz}) ppm. EI-MS [M⁺]: 251 (100%). Anal. found: C, 47.59; H, 4.05; Br, 31.65; N, 16.75. Calc. for C₁₀H₁₀BrN₃: C, 47.64; H, 4.00; Br, 31.69; N, 16.67.

Synthesis of 1-ethenyl-4-phenyl-1,2,3-triazole (2)

To a solution of 1-(2-bromoethyl)-4-phenyl-1,2,3-triazole **1** (1.0g, 4 mmol) in DMF (10 mL), K₂CO₃ (2.8g, 20 mmol) was added and stirred at 110 °C for 3 hours. It was then cooled to room temperature; water was added and extracted with ethyl acetate, dried over anhydrous sodium sulphate and concentrated. The product was purified by silica gel column using hexane and ethyl acetate (3:1) as eluent to afford pale yellow crystals. Yield 0.60g (87%). m.p. 85-86 °C. ¹H NMR: (400 MHz, CDCl₃) δ 5.12 (dd, *J* = 1.2, 10 Hz, 1H, H_{CH2}), 5.64 (dd, *J* = 1.2, 17.2 Hz, 1H, H_{CH2}) 7.2 (m, 2H, H_{Ar}+ H_{NCH}), 7.3 (t, *J* = 7.6 Hz, 2H, H_{Ar}), 7.7 (d, *J* = 7.2 Hz, 2H, H_{Ar}), 7.93 (s 1H, H_{trz}) ¹³C NMR: (100 MHz, CDCl₃) δ 103.6 (CH₂), 115 (NCH), 124.8 (CH_{trz}), 127.4 (CH_{Ar}), 127.8 (CH_{Ar}), 129.0 (CH_{Ar}), 129.3 (C_{Ar}), 147.0 (C_{trz}) ppm. EI-MS [M⁺]: 171 (100%). Anal. found: C, 70.42; H, 5.25; N, 24.84. Calc. for C₁₀H₁₀BrN₃: C, 70.16; H, 5.30; N, 24.54.

Synthesis of 1-ethenyl-3-methyl-4-phenyl-1,2,3-triazolium iodide (3)

1-Ethenyl-4-phenyl-1,2,3-triazole **2** (0.31 g, 1 mmol) was taken in acetonitrile (10 ml) to which iodomethane (2.84 g, 2 mmol) was added and heated at 60 °C over night. After complete consumption of the starting material, the solvent was evaporated under reduced pressure. The solid obtained was washed with dichloromethane: hexane mixture (1:3). The product was obtained as an off-white solid in 96% (0.30 g) yield. m.p. 90 °C. ¹H NMR: (400 MHz, CDCl₃) δ 4.38 (s, 3H, CH₃), 5.19 (dd, *J* = 1.6, 10.4 Hz, 1H, H_{CH2}), 5.70–5.72 (m, 1H, H_{CH2}), 6.56 (dd, *J* = 3.2, 18 Hz, 1H, NCH), 7.44 (t, *J* = 7.2 Hz, 1H, H_{Ar}), 7.64–7.70 (m, 2H, H_{Ar}), 7.79–7.87 (m, 2H, H_{Ar}), 9.74 (s, 1H, H_{trz}). ¹³C NMR: (100 MHz, CDCl₃) δ 39.6 (CH₃),

104.7 (=CH₂), 116.4 (NCH), 125.9 (CH_{Ar}), 127.3 (CH_{Ar}), 128.9 (CH_{Ar}), 129.8 (C_{Ar}), 132.3 (CH_{tzl}), 159.6 (C_{tzl}). Anal. Calc. for C₁₁H₁₁N₃: C, 42.33; H, 3.55; I, 40.66; N, 13.46. Found: C, 42.52; H, 3.42; I, 40.36; N, 13.63.

Synthesis of C_{tzl}-Pd-C_{tzl} complex (4)

To an oven dried Schlenk flask, 10 ml of dried THF was added followed by 1-ethenyl-3-methyl-4-phenyl-1,2,3-triazolium iodide **3** (0.20g, 0.63 mmol). Nitrogen gas was passed through the solution for 10 minutes and palladium acetate (0.07g, 0.32 mmol) was added. The reaction mixture was stirred at 80 °C for 4 h. It was cooled to room temperature and poured into ice water, extracted using ethyl acetate, dried over anhydrous sodium sulphate and concentrated. The product was purified by column chromatography (hexane: ethyl acetate = 4:1) over silica gel to get an orange solid in 62% yield (0.14g). m.p. 120 °C, ¹H NMR: (400 MHz, CDCl₃) δ 3.99 (s, 3H, CH₃), 5.50 (d, *J* = 8.8 Hz, 1H, H_{CH2}), 6.35 (d, *J* = 15.6 Hz, 1H, H_{CH2}), 7.37 (q, *J* = 1.6 Hz, 1H, NCH), 7.48 (t, *J* = 6.4 Hz, 1H, H_{Ar}), 7.52–7.58 (m, 2H, H_{Ar}), 7.81 (s, 2H, H_{Ar}). ¹³C NMR: (100 MHz, CDCl₃) δ 37.9 (CH₃), 101.7 (=CH₂), 110.1 (NCH), 128.8 (CH_{Ar}), 129.1 (CH_{Ar}), 129.2 (HC_{Ar}), 130.1 (C_{Ar}), 130.4 (C_{tzl}-Pd), 144.8 (C_{tzl}-Ph). Anal. Calc. for C₂₂H₂₂I₂N₆Pd: C, 36.16; H, 3.03; I, 34.74; N, 11.50. Found: C, 36.46; H, 3.07; I, 34.92; N, 11.42.

Synthesis of C_{tzl}-Pd-N_{tzl} complex (5)

1-Ethenyl-3-methyl-4-phenyl-1,2,3-triazolium iodide **3** (0.20g, 0.64 mmol) was taken in a Schlenk flask containing 10 ml dry THF. Nitrogen gas was purged through the solution for 10 minutes. Bis triazole palladium complex **6** (0.45g, 0.64 mmol) was added to the solution followed by the addition of K₂CO₃ (0.70g, 5 mmol). The reaction mixture was then heated at 80 °C for 12 hours. It was then cooled to room temperature and solvent was removed in vacuo. The residue obtained was filtered through a silica column using dichloromethane to afford the product as an orange solid in 70% (0.32g) yield. Single crystal was formed by slow diffusion of pentane into dichloromethane. m.p. 160°C (decomposes). ¹H NMR: (400 MHz, CDCl₃) δ 4.02 (s, 3H, CH₃), 5.17 (dd, *J* = 1.6, 10.4 Hz, 1H, H_{CH2}), 5.59 (dd, *J* = 1.6, 10.4 Hz, 1H, H_{CH2}), 5.77 (dd, *J* = 2, 18 Hz, 1H, H_{CH2}), 6.34 (dd, *J* = 1.2, 16.8 Hz, 1H, H_{CH2}), 7.37 (m, 2H, H_{Ar}), 7.43 (d, 2H, *J* = 7.6 Hz, H_{Ar}), 7.47 (m, 1H, NCH), 7.51 (m, 1H, NCH), 7.55 (m, 1H, *J* = 5.2 Hz, H_{Ar}), 7.68 (m, 2H, *J* = 5.6 Hz, H_{Ar}), 7.70 (m, 1H, H_{Ar}), 7.86 (m, 2H, H_{Ar}), 8.00 (s, 1H, H_{tzl}). ¹³C NMR: (100 MHz, CDCl₃) δ 37.1 (CH₃), 104.6 (=CH₂), 109.4 (=CH₂), 116.1 (NCH), 125.9 (NCH), 128.4 (C_{Ar}), 128.6 (C_{Ar}), 128.8 (C_{Ar}), 129.2 (C_{Ar}), 130.0 (C_{Ar}), 130.3, 130.5 (C_{Ar}), 130.6 (C_{Ar}), 130.8 (C_{tzl}), 132.4 (C_{tzl}-Pd), 134.4 (C_{tzl}-Ar), 148.0 (C_{tzl}-Ar).

HRMS: Calc. 588.9829, Found; 588.9819 Anal. found: C, 35.12; H, 2.74; I, 35.57; N, 11.63. Calc. for $C_{21}H_{20}I_2N_6Pd$: C, 35.19; H, 2.81; I, 35.42; N, 11.73; Pd, 14.85.

Synthesis of N_{tzi} -Pd- N_{tzi} complex (**6**)

To a solution of 1-ethenyl-4-phenyl-1,2,3-triazole **2** (0.170g, 1 mmol) in THF, (bisacetoneitrile)dichloro palladium (II) (0.130g, 0.5 mmol) and NaI (0.15g, 1 mmol) were added. The solution was stirred at room temperature overnight. Yellow solid obtained was filtered and washed with pentane. Yield: 0.31g, (90%). m.p. 70 °C, 1H NMR: (400 MHz, $CDCl_3$) δ 5.19 (dd, $J = 2, 10.8$ Hz, 1H, H_{CH_2}), 5.71 (dd, $J = 1.6, 17.6$ Hz, 1H, H_{CH_2}), 7.39 (m, 2H, $H_{NCH+H_{Ar}}$), 7.46 (m, 2H, H_{Ar}), 7.87 (t, 2H, $J = 8.4$ Hz, H_{Ar}), 8.0 (s, 1H, H_{tzi}) ^{13}C NMR: (100 MHz, $CDCl_3$) δ 104.6 (C_{CH_2}), 116.1 (NCH), 125.9 (CH_{tzi}), 128.5 (CH_{Ar}), 128.9 (CH_{Ar}), 130.0 (CH_{Ar}), 130.4 (C_{Ar}), 148.0 (C_{tzi-Ph}). Anal. found: C, 34.32; H, 2.42; I, 34.18; N, 11.75. Calc. for $C_{20}H_{18}I_2N_6Pd$: C, 34.19; H, 2.58; I, 36.12; N, 11.96.

General procedure for the Suzuki–Miyaura coupling reaction between aryl halide and aryl boronic acid

Nitrogen gas was purged through 5.0 mL water taken in a Schlenk reaction tube for 10 minutes. Arylboronic acid (1.0 mmol), aryl halide (1.0 mmol), KO^tBu (1.5 mmol), and the catalyst **5** (0.1 mol%) were successively added to it. The mixture was then stirred at room temperature for 12 h. It was then extracted with diethyl ether and dried over anhydrous Na_2SO_4 . The solvent was evaporated and the product obtained was purified by filtering through a silica gel column using hexane.

Conflicts of interest

“There are no conflicts to declare”.

Appendix A. Supplementary data

CCDC 1474293 contains the supplementary crystallographic data for **5**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or email: deposit@ccdc.cam.ac.uk.

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Technology (CUSAT), Kerala, INDIA for providing NMR and other analytical data respectively.

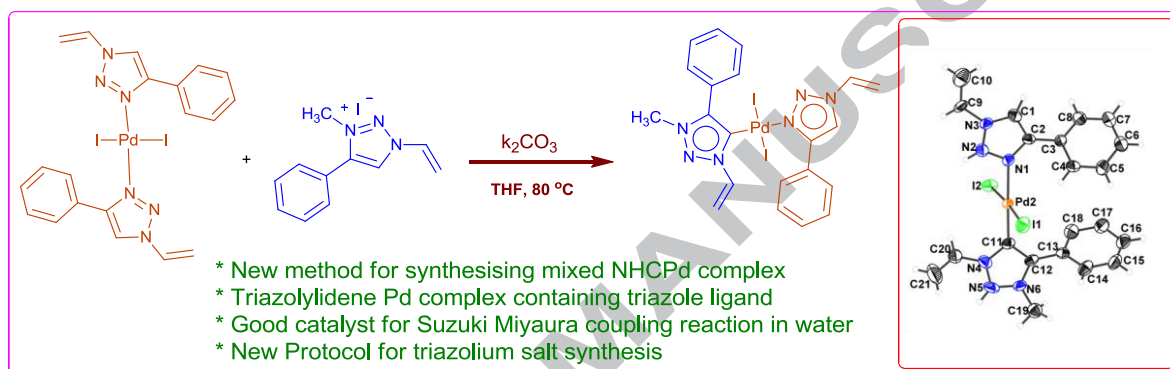
References and notes

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Graphical Abstract



Palladium complex containing 1,2,3-triazolylidene and a labile triazole moiety has been prepared and characterized. This mixed palladium complex was found to be highly effective in catalyzing Suzuki-Miyaura coupling reaction between aryl halides and aryl boronic acids in water at room temperature with very low catalyst loading.