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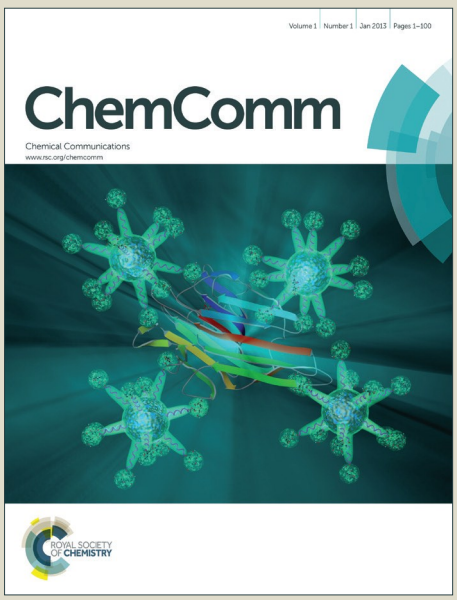

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Mesoionic bis(Py-*tz*NHC) Palladium(II) Complex Catalyses "Green" Sonogashira Reaction Through an Unprecedented Mechanism

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Novel *bis*(pyridyl-functionalized 1,2,3-triazol-5-ylidene)-palladium(II) complex $[Pd(Py\text{-}tzNHC)_2]^{2+}$ catalyses copper-, amine-, phosphine-, and additive-free aerobic Sonogashira alkynylation of (hetero)aryl bromides in water as the only reaction solvent. The catalysis proceeds along two connected Pd-cycles with homogeneous bis-carbene Pd^0 and Pd^{II} species, as demonstrated by electrospray ionization mass spectrometry.

Initiated by the report of Arduengo et al. in 1991 on the first isolation of N-heterocyclic carbene (NHC),[1] this class of compounds has become one of the most important ligands in transition-metal catalysis. NHCs have been introduced as ligands in palladium complexes[2–9] to support and activate palladium in various cross-coupling reactions, in particular the Heck and Suzuki reactions.[10] In this context, pyridine functionalized imidazolin-2-ylidene NHCs as chelating ligands for palladium have been developed (Fig. 1),[11–13] followed by Pd-NHCs from a PEPPSI (pyridine-enhanced precatalyst preparation, stabilization, and initiation) series with further improved stability and activity profile.[14] The success of *normal* NHC ligands is greatly attributed to their superior σ-donating capabilities as compared to phosphines, which is even greater in *abnormal* NHC counterparts.[15,16] Interesting examples are based on mesoionic 1,2,3-triazol-5-ylidene (*tz*NHC) structure[8] including those of the PEPPSI type reported recently.[17,18]

An appropriate balancing of the stability of the palladium species is essential in designing better catalysts. We surmised that bis-bidentate palladium complex of chelating pyridine-functionalized *tz*NHC featuring highly stabilizing mesoionic carbenic structure and donor pyridine substituent should possess unique properties in terms of stability and catalytic activity (Fig. 1). We aimed at developing palladium catalyst for the Sonogashira cross-coupling that would enable copper- and amine-free alkynylation of aryl halogenides that operates in water, in the presence of air, and in the absence of any additive. The Sonogashira reaction[19] has witnessed a tremendous success in both academia and industry, being used as the key step in the synthesis of many natural products, bio-active compounds and pharmaceuticals.[20–22] It should be noted, however, that protocols allowing the presence of air and employ water as the only reaction solvent are scarce[23] and none such example is reported for Pd-NHCs as catalysts.[10,15,16,23,24] Herein, we report a highly efficient novel palladium bis(Py-*tz*NHC) complex (Fig. 1) that catalyses the Sonogashira reaction under green reaction conditions, operating through an unprecedented mechanism.

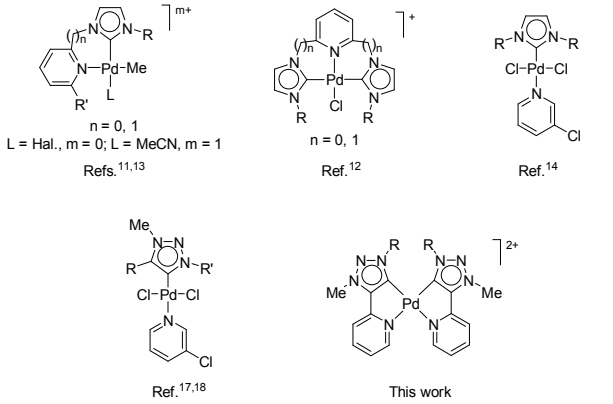
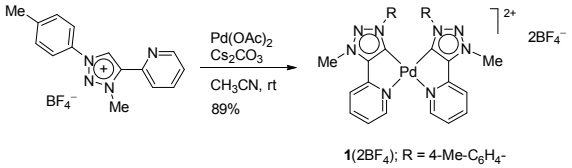


Fig. 1 Selection of pyridine-NHC–Pd complexes.



Scheme 1 The synthesis of the complex **1**($2BF_4$).

Cationic complex **1**($2BF_4$) was easily prepared in air by a one-step route through a direct metalation of the appropriate triazolium cation[25] with $Pd(OAc)_2$ in the presence of a weak base, without requiring preactivation with Ag_2O (Scheme 1). Water soluble air-stable product was isolated in the pure form

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† Electronic Supplementary Information (ESI) available: Experimental procedures, spectra, crystallographic details, CIF file. See DOI: 10.1039/x0xx00000x

in 89% yield by a simple workup. The carbene signal in the ^{13}C NMR spectrum of **1** appears at 143.6 ppm, which is indicative for a *tz*NHC-Pd-complex having pyridine and carbene in *trans* position.[26] In the ^{1}H NMR spectra a small up-field shift of the $Py^{H\text{-}6}$ resonance upon the formation of **1** from the triazolium cation ($\Delta\delta \approx 0.1$ ppm; DMSO-d_6, DMF-d_7, CD_3CN) suggested weak interactions between the two pyridine wingtips and palladium, which is essential to stabilize the complex, yet to provide an open coordination site for a catalysis to occur (ESI†). Interestingly, in solid state, complex **1**($2BF_4$) forms bi-metalic structure **1'** with a short Pd–Pd intermetallic distance of 3.0232(4) Å (Fig. 2). Upon dissolution **1'** instantly transforms into **1** as evident by ^{1}H NMR and ESI-HRMS analyses.

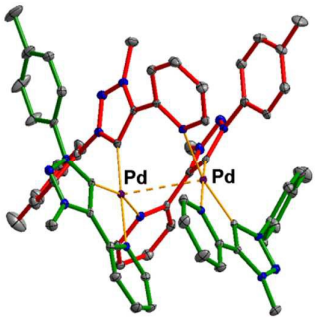


Fig. 2 Ortep drawing (30% probability ellipsoids) of cation **1'** (blue = N, gray = C, violet = Pd) with bidentate (green) and bridging coordination (red). Anions, solvents and hydrogen atoms are omitted for clarity (ESI†).

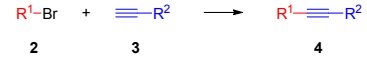
The complex **1**($2BF_4$) was evaluated as precatalyst for the Sonogashira reaction. An initial screening revealed that it effectively cross-coupled acetylenes with aryl iodides and bromides in the presence of air and in water as the only solvent (ESI†).

To identify the optimal reaction conditions for the Sonogashira cross-coupling with **1**($2BF_4$), the effect of the catalyst loading, reaction temperature and base was screened (ESI†). Excellent results were obtained with 1 mol% of **1**($2BF_4$) at 100–140 °C for 1–4 h, with carbonate (K_2CO_3 or Cs_2CO_3) base.

The results of the substrate scope screening are shown in Table 1. In general, 1 mol% of **1**($2BF_4$) effectively catalysed alkynylation of electron-poor and electron-rich aryl bromides. For coupling of those substrates that are sparingly soluble in hot water, i.e. 4-bromonitrobenzene (**2c**), the addition of DMF to the reaction mixture proved to be beneficial. Although a highly deactivated 4-methoxybromobenzene (**2d**) was coupled with **3a** in only 36%, *m*- and *p*-bromotoluene **2e** and **2f** reacted quantitatively. Both electron-rich and electron-poor heterocyclic substrates including 2-bromopyridine (**2g**), 2-bromopyrimidine (**2h**) and 3-bromothiophene (**2i**) reacted with acetylenes in good to excellent yields. The general applicability of **1**($2BF_4$) was also confirmed through the selection of electron-rich and deficient acetylenes as coupling partners including 4-ethynylanisole (**3b**), (triisopropylsilyl)acetylene (**3c**), 4-ethynyl-α,α,α-trifluorotoluene (**3d**) and dimethyl ethynyl carbinol (**3e**), reacting smoothly in excellent yields of **4**(**i–l**). These results clearly demonstrate the robustness and general superior catalytic activity of **1**($2BF_4$) over the monodentate *tz*NHC palladium complexes.[16]

To get a feel of the potency of the catalyst in typical Sonogashira reaction conditions that are normally applied, we selected the alkynylation of **2a** with **3a** at 100 °C in DMF and in the presence of DABCO as a base.[21] By using **1**($2BF_4$) in 0.1 mol% loading the formation of **4a** was quantitative within 1 h. With 0.01 mol%, the transformation was 98% in 8 h (ESI†).

Table 1 Substrate scope screening for the Sonogashira reaction with **1**($2BF_4$).



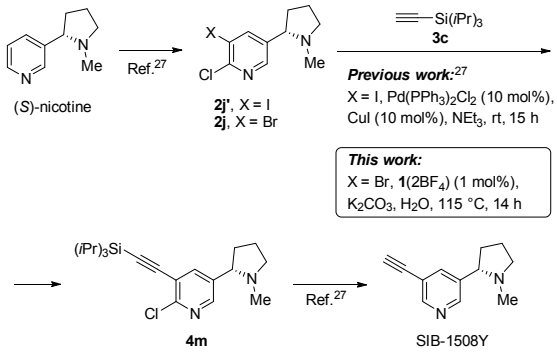
2 3 4

Entry	2	3	Cond.[a]	4	Conv.[b] (Yield)[c]
1	**2a**	**3a**	A[d]		100
2			B		82 (75)
3	**2b**	**3a**	A		100
4			B		100 (92)
5	**2c**	**3a**	B		68 (65)
6			A[d]		100 (91)
7	**2d**	**3a**	B[d]		36
8	**2e**	**3a**	B		100 (95)
9	**2f**	**3a**	A		60 (58)
10			A[d]		100 (86)
11	**2g**	**3a**	B		100 (97)
12	**2h**	**3a**	B		66
13	**2a**	**3b**	B		100 (91)
14	**2f**	**3c**	B		100 (95)
15	**2b**	**3d**	B		100 (89)
16	**2i**	**3e**	A		90 (87)

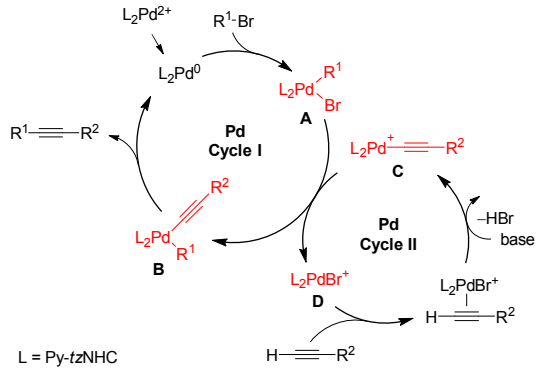
[a] Conditions A: bromide **2** (0.25 mmol), acetylene **3** (0.5 mmol), Cs_2CO_3 (0.5 mmol), complex **1**($2BF_4$) (0.0025 mmol, 1.0 mol%), water (2 mL), 100 °C in ACE tube, 1 h. Conditions B: as for Conditions A but with K_2CO_3 (0.5 mmol) as a base, at 140 °C, for 4 h. [b] Conversion determined from at least two consecutive runs by ^{1}H NMR. [c] Percent yield of the isolated pure product. [d] DMF/H_2O (2/1) as the reaction solvent.

We have been interested in the synthesis of SIB-1508Y (Altinicline), a potential drug for neurodegenerative diseases.[22] An expedient five-step preparation of SIB-1508Y with selective halogenation of natural (*S*)-nicotine into iodide **2j'** and a subsequent "classical" Sonogashira reaction with **3c** into the intermediate product **4m** has been reported (Scheme 2).[27] To demonstrate the robustness of **1**($2BF_4$) and render it practicable, we tested it under green reaction conditions for the synthesis of **4m** from bromide **2j**, instead of the iodide **2j'**. Bromide **2j** was let to react with **3c** in the presence of 1 mol% of **1**($2BF_4$) to afford **4m** in 82% yield in optically pure form, without racemization (Scheme 2).

It is known that some Pd-*tz*NHCs used in the cross-coupling reactions give under very mild conditions palladium nanoparticles as the catalytically active phase.[17] In an



Scheme 2. Synthesis of SIB-1508Y involving the Sonogashira reaction.



Scheme 3 Proposed mechanism and reactive intermediates drawn in red colour as identified by ESI-HRMS.

independent representative experiment by using **1**(2BF$_4$) for the cross-coupling of **2a** with **3a** under the Conditions B from Table 1 (vigorous stirring) a large excess of Hg(0) was added (mercury poisoning experiment)[17,28,29] into the reaction mixture after 30 min (36% conversion). This addition had no effect on the conversion into **4a**, reaching 76% after 4h; a parallel Hg-free reaction reached 75% over the same period (qNMR assay). Similar observation was made when Hg(0) was added to the reaction mixture at the onset (ESI†). Thermal stability of complex **1**(2BF$_4$) was ascertained in solid state at 150 °C and in solution (DMF-d_7, D_2O) at 140 °C (the highest reaction temperatures used herein for the Sonogashira reaction). No decomposition could be detected by qNMR (ESI†) indicating its remarkable stability over some related PEPPSI-type Pd-*tz*NHC complexes.[17] These results suggest that the catalysis with **1**(2BF$_4$) occurs by *in situ* generated homogeneous catalytically active molecular Pd^0 species.

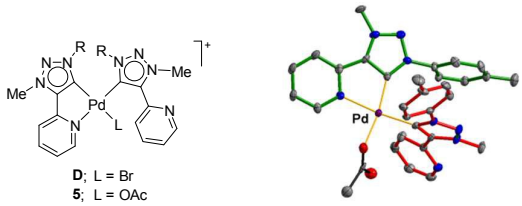
To get the insight into the mechanism of this process, a coupling of **2a** with **3a** in the presence Cs_2CO_3 in DMF was monitored by high-resolution electrospray ionization mass spectrometry (ESI-HRMS).[29,30] All peaks from the mass spectra have been identified. As evident from the characteristic isotopic pattern, only mono-palladium bis-carbene cationic species could be found in the spectra. These include ions at *m/z* 711.1849 (calcd for $C_{37}H_{33}N_8OPd^+$ ([**A** – Br]$^+$): 711.1807), *m/z* 813.2299 (calcd for $C_{45}H_{39}N_8OPd^+$ ([**B** + H]$^+$): 813.2276), *m/z* 707.1856 (calcd for $C_{38}H_{33}N_8Pd^+$ ([**C**]$^+$): 707.1858) and *m/z* 685.0642 (calcd for $C_{30}H_{28}{}^{79}BrN_8Pd^+$ ([**D**]$^+$): 685.0650) (Scheme 3). Peaks for **C** and **D** were the most intensive in the ESI-MS spectra. In contrast to some Pd-NHC complexes,[17,29] neither clusters of the type [Pd$_n$(Py-*tz*NHC)$_{2m}$] (n > m), nor mono-carbene-Pd species, or negatively charged Pd containing ions (ESI–) could be found in the spectra.

The proposed plausible mechanism is shown in Scheme 3 and contains two connected Pd-cycles (**I** and **II**). Much research work has been devoted to address the question whether mono-ligated Pd^0(NHC) or bis-ligated Pd^0(NHC)$_2$ are involved in the catalytic cycle.[31–33] In our case, the fact that no mono-carbene Pd(Py-*tz*NHC) species could be found in the ESI-HRMS spectra suggest Pd^0(Py-*tz*NHC)$_2$ to be the catalytically active species. The latter undergoes the oxidative addition with aryl bromide to form the intermediate **A** via an associative mechanism without dissociation of the Py-*tz*NHC ligand.

The Pd^0(Py-*tz*NHC)$_2$ species may be generated by a reductive elimination (alkyne homocoupling) from [Pd^{II}(Py-*tz*NHC)$_2$(C≡CR^2)$_2$].[34] The species [Pd^{II}(Py-*tz*NHC)$_2$(C≡CR^2)$_2$] was identified by ESI-HRMS as [M + H]$^+$ ion (*m/z* 809.2318, calcd for $C_{46}H_{39}N_8Pd^+$ 809.2327, ESI†).

The acetylene η^2-coordination to the bromido-Pd species **D** and a subsequent base mediated deprotonation produces the alkynylpalladium intermediate **C**, which then undergoes transmetalation with **A** into the intermediate **B**. This was confirmed by an independent ESI-HRMS experiment, where premixing either **1**(2BF$_4$) or **D**, acetylene **3a** and Cs_2CO_3 in DMF at 100 °C resulted in accumulation of **C**. The intermediate **C** completely disappeared from the spectra after the addition of an excess of aryl bromide **2a** with concomitant product **4a** formation (ESI†).

Cation **D** can be formed independently by reacting **1**(2BF$_4$) with KBr. Although we were unable to support the structure of **D** by single crystal X-ray analysis, this was possible for the closely related cation **5**, formed by treating **1**(2BF$_4$) with potassium acetate (Fig. 3) (ESI†).



D; L = Br
5; L = OAc

Fig. 3 Structures of **D** and **5** (R = 4-Me-C$_6$H$_4$-), and Ortep drawing of **5** (ESI†).

In conclusion, a novel type of water soluble and thermally stable Pd-NHC complex **1**(2BF$_4$) based on bidentate pyridyl-1,2,3-triazol-5-ylidene ligand that requires only low synthetic investment has been identified as a highly efficient precatalyst for the Sonogashira cross-coupling. We know of no such efficient aryl bromide–terminal acetylene cross-coupling that proceeds in air and in pure water, and in complete absence of amine, copper, phosphine and other additives, as reported herein for complex **1**(2BF$_4$). To our knowledge, this is the first report on the Sonogashira catalysis with a cationic Pd-complex. Preliminary mechanistic investigation indicates that bis-

carbene palladium reactive species are involved in two connected palladium catalytic cycles.

Financial support from the Ministry of Education, Science and Sport, Republic of Slovenia, the Slovenian Research Agency (Grant P1-0230; Postdoctoral Grant to M.G. (430-168/2013/114), and Grant P1-0175) is acknowledged. This work was partially supported through the infrastructure of the EN-FIST Centre of Excellence, Ljubljana, Slovenia.

Dedicated to Dr. Maja Osmak on the occasion of her 65th birthday.

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