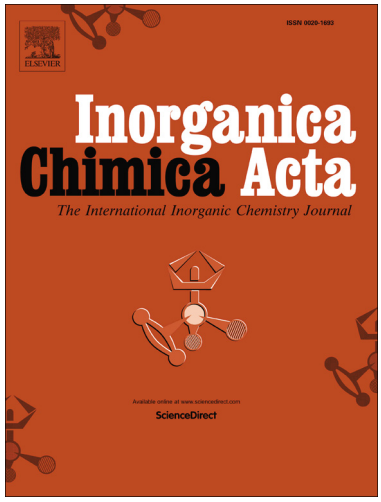

Research paper

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PEPPSI-type palladium 1,2,3-triazolin-5-ylidene complexes – synthesis, structure and catalytic properties in Suzuki–Miyaura coupling

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Abstract: Palladium complexes of the general formula [$PdCl_2$(tzNHC)(pyridine)] bearing a series 1,2,3-triazolin-5-ylidene (tzNHC) ligands were synthesized and characterized by spectroscopic methods and X-ray analysis. Complexes exhibit catalytic activity in the Suzuki–Miyaura coupling of boronic acids with aryl bromides.

Keywords: 1,2,3-triazolin-5-ylidene complexes; palladium; Suzuki–Miyaura coupling

1. Introduction

N-heterocyclic carbenes (NHC) have become valuable ligands for many processes catalyzed by transition metal complexes thanks to a combination of their steric bulkiness, strong σ-donating properties and high stability of metal-carbene bond [1,2]. Rapid development of NHC resulted in the synthesis of new classes of NHC ligands beyond imidazolin-2-ylidenes [3,4]. In 2008 Albrecht reported 1,2,3-triazolin-5-ylidene (tzNHC) metal complexes [5]. These readily accessible [6–9] and easy to modify ligands are characterized by higher values of the Tolman electronic parameter [10] than ligands relative to imidazole derived NHCs. These desirable features make tzNHC potentially useful in homogeneous catalysis. Relatively broad spectrum of palladium 1,2,3-triazolin-5-ylidene complexes have been reported and their catalytic activity has been studied in a number of processes, mainly in Suzuki–Miyaura coupling [12–22] but also in alpha arylation [20], direct arylation [23], hydroarylation of alkynes [24], Heck [25,26], Sonogashira [25] and Hiyama [27] coupling. Recently, a comprehensive review has appeared discussing different aspects of metal complexes of triazole-based ligands [28]. Although the catalytic activity of palladium 1,2,3-triazolin-5-ylidene complexes in the Suzuki–Miyaura reaction has been studied by many research groups, some aspects of the reaction still need to be clarified. Albrecht and Trzeciak shows that less bulky substituents induce higher catalytic activity than bulkier IMes-type analogues. This phenomenon was proposed to originate from a different mode of action of the triazolylidene complexes. Authors emphasized the significance of underligated species generated from palladium nanoparticles in the presence of boronic acids and under conditions of Suzuki–Miyaura coupling [12]. In contrast, Hong [13] and Fukuzawa [14] reported high activity of palladium complexes bearing bulky 1,2,3-triazolin-5-ylidene ligand in the coupling of boronic acids with aryl bromides and chlorides already at room temperature. It may indicate different nature of catalytically active species in the latter systems.

Herein, we report on the synthesis and characterization of palladium complexes of the general formula [$PdCl_2$(tzNHC)(pyridine)] bearing new 1,2,3-triazolin-5-ylidene ligands, describe their catalytic properties in the Suzuki–Miyaura coupling and study the nature of active species.

2. Experimental

2.1. General methods and chemicals

^{1}H- and ^{13}C-NMR spectra were recorded on a Varian 400 or 300 at 25 °C. Chemical shifts (δ in ppm and coupling constants *J* in Hz) were referenced to residual solvent resonances. GC/MS analyses were performed on a Varian Saturn 2100T equipped with (DB-5, 30 m capillary column) and Ion Trap Detector. GC analyses were performed using Varian CP-3800

(column: RTX-5 30 m ID 0,53 mm), equipped with TCD. Mass spectrometric analyses of complexes were performed using Synapt G2-S mass spectrometer (Waters) equipped with the ASAP (Atmospheric Solids Analysis Probe) ion source and quadrupole time-of-flight mass analyzer. Small amounts of samples were applied directly onto the glass probe and the excess of the sample were removed using a paper tissue. The measurements were performed in gradient temperature rate from room temperature to 650 ˚C in 6 minutes with the desolvation gas flow 850 L/h and corona current set to 12 μA. ESI-MS spectra were performed using Waters Micromass ZQ 2000 spectrometer. The chemicals were obtained from the following sources: palladium (II) chloride, potassium carbonate, tetrabutylammonium hydroxide, aryl halides, boronic acids, pyridine, toluene, dichloromethane, chloroform-d, benzene-d_6 were purchased from Aldrich. Potassium hydroxide, ethanol (99.8 %), hexane and ethyl acetate were purchased from POCH S.A. BASIC (Poland).

*2.2. General synthetic procedure and characterization of complexes (**2a-g**)*

Palladium complexes (**2a-g**) were synthesized according to a modified literature procedure [12]. A solution of the appropriate triazole salt (1equiv.) in CH_2Cl_2 (2 mL) and Ag_2O (0.5 equiv.) was added to a Schlenk vessel equipped with a magnetic stirrer. The mixture was stirred in the dark at room temperature for 6 h. Then $PdCl_2$ (1.5 equiv.) and pyridine (1 mL) were added and the mixture was stirred at 100 °C for 12 hours. The reaction mixture was cooled to room temperature, diluted with CH_2Cl_2 (7 mL) and passed through a column of SiO_2 with a layer of celite. After elution of the product with CH_2Cl_2 and subsequently MeOH, all the volatiles were evaporated under reduced pressure. The residue was dissolved in a minimum amount of CH_2Cl_2 and precipitated with Et_2O (50 mL). The precipitate was filtered and the filtrate was evaporated to dryness to give a pure palladium complex. Monocrystals were obtained by crystallization from CH_2Cl_2/hexane.

*Complex **2a***. Yellow solid, isolated yield 87%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.74–8.67 (m, 2H CH_{Ar} py), 8.20–8.10 (m, 2H CH_{Ar} Ph), 7.67–7.51 (m, 3H CH_{Ar} Ph), 7.23–7.13 (m, 3H CH_{Ar} py), 7.06 (s, 2H CH_{Ar} Mes), 4.14 (s, 3H N-CH_3), 2.39 (s, 3H p-CH_3 Mes), 2.31 (s, 6H o-CH_3 Mes). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 151.42, 140.32 (Pd-C), 137.44, 135.92, 130.62, 130.06, 129.27, 128.84, 124.01, 37.66, 21.27, 18.80. HRMS (ESI-TOF, m/z): 497.1245 $C_{23}H_{24}ClN_4Pd$ [M-Cl], calculated: 497.1240.

*Complex **2b*** [24]. Yellow solid, isolated yield = 82%.^{1}H NMR (403 MHz, $CDCl_3$) δ: 8.73–8.69 (m, 2H, CH_{Ar} py), 8.23–8.16 (m, 2H, CH_{Ar} Ph), 7.64–7.52 (m, 5H, CH_{Ar} Ph), 7.38 (d, *J* = 7.8 Hz, 1H, *m*-IPr-H), 7.18–7.14 (m, 2H, CH_{Ar} py), 4.13 (s, 3H, N-CH_3), 2.89–2.73 (m, 2H, CH-*i*-Pr), 1.44 (d, *J* = 6.8 Hz, 6H, CH_3-*i*-Pr), 1.09 (d, *J* = 6.8 Hz, 6H, CH_3-*i*-Pr). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 151.33, 146.57(Pd-C), 143.77, 142.17, 137.39, 134.91, 131.14, 130.66, 130.04, 128.79, 126.96, 124.05, 123.89, 37.67, 28.86, 26.12, 22.86. HRMS (ESI-TOF, m/z): 539.1196 $C_{26}H_{30}ClN_4Pd$ [M-Cl], calculated: 539.1194.

*Complex **2c***. Dark-yellow solid, isolated yield = 58%). ^{1}H NMR (403 MHz, $CDCl_3$) δ: 8.94–8.90 (m, 2H CH_{Ar} py), 8.02–7.96 (m, 2H CH_{Ar} Ph), 7.75–7.68 (m, 1H CH_{Ar} py), 7.60–7.49 (m, 2H CH_{Ar} Ph), 7.32–7.27 (m, 2H CH_{Ar} py), 4.99–4.93 (m, 2H N-CH_2), 3.99 (s, 3H N-CH_3),

2.38 (dt, *J* = 15.2, 7.6 Hz, 2H CH_2), 1.50–1,35 (m, 6H CH_2), 0.97–0.86 (m, 3H CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 151.28, 143.56 (Pd-C), 137.71, 130.37, 129.92, 128.85, 126.85, 124.26, 55.00, 37.34, 31.20, 29.62, 26.33, 22.49, 14.04. HRMS (ESI-TOF, m/z): 463.0860 $C_{20}H_{26}ClN_4Pd$ [M-Cl], calculated: 463.0881.

*Complex **2d**.* Light yellow solid, isolated yield 51%. ^1H NMR (300 MHz, $CDCl_3$) δ: 8.98–8.92 (m, 2H CH_{Ar} py), 8.07 (d, *J* = 8.6 Hz, 4H CH_{Ar} Ph), 7.73–7.63 (m, 2H CH_{Ar} Ph), 7.54–7.39 (m, 2H CH_{Ar} Ph), 7.30–7.26 (m, 1H CH_{Ar} py), 5.00–4.93 (m, 2H N-CH_2), 4.03 (s, 3H N-CH_3), 2.39 (dt, *J* = 15.3, 7.5 Hz, 2H CH_2), 1.70 (s, 2H), 1.58–1.31 (m, 6H CH_2), 0.91 (t, *J* = 7.1 Hz, 3H CH_3).^{13}C NMR (75 MHz, $CDCl_3$) δ: 151.31, 137.70, 130.76, 129.08, 128.88, 127.53, 127.20, 124.26, 55.06, 37.41, 31.24, 29.59, 26.34, 22.47, 14.01. HRMS (ESI-TOF, m/z): 539.0878 $C_{26}H_{30}ClN_4Pd$ [M-Cl], calculated: 539.0880.

*Complex **2e**.* Yellow solid, isolated yield 69%. ^1H NMR (403 MHz, $CDCl_3$) δ: 8.96–8.88 (m, 1H CH_{Ar} py), 7.96–7.91 (m, 2H CH_{Ar} Ph), 7.72–7.63 (m, 3H CH_{Ar} Ph), 7.60–7.50 (m, 3H CH_{Ar} py), 4.85–4.79 (m, 2H N-CH_2), 3.96 (s, 3H N-CH_3), 2.37–2.26 (m, 4H CH_2), 1.08 (t, *J* = 7.4 Hz, 2H CH_3).^{13}C NMR (75 MHz, $CDCl_3$) δ: 151.18, 143,48 (Pd-C), 137.68, 137.59, 130.29, 129.85, 128.76, 124.21, 54.65, 37.30, 31.53, 19.82, 13.57. HRMS (ESI-TOF, m/z): 435.0554 $C_{18}H_{22}ClN_4Pd$ [M-Cl], calculated: 435.0568.

*Complex **2f**.* Yellow solid, isolated yield 82%. ^1H NMR (300 MHz, $CDCl_3$) δ: 8.94–8.89 (m, 2H CH_{Ar} py), 8.01–7.95 (m, 1H CH_{Ar} Ph), 7.82–7.68 (m, 2H CH_{Ar} Ph), 7.59–7.51 (m, 2H CH_{Ar} Ph), 7.43–7.26 (m, 5H CH_{Ar} Ph), 6.20 (s, 2H N-CH_2), 3.95 (s, 3H N-CH_3).^{13}C NMR (75 MHz, $CDCl_3$) δ: 151.30, 143.80 (Pd-C), 138.57, 137.73, 133.90, 130.41, 129.99, 129.76, 128.83, 128.79, 126.72, 124.28, 58.64, 37.50. HRMS (ESI-TOF, m/z): 469.0401 $C_{21}H_{20}ClN_4Pd$ [M-Cl], calculated: 469.0411.

*Complex **2g**.* Light yellow solid, isolated yield 62%. ^1H NMR (403 MHz, $CDCl_3$) δ: 8.95–8.91 (m, 2H CH_{Ar} py), 8.09–8.05 (m, 2H CH_{Ar} Ph), 7.65 (dq, *J* = 2.5, 1.7 Hz, 4H CH_{Ar} Ph), 7.51–7.38 (m, 6H CH_{Ar} Ph), 7.33–7.27 (m, 2H CH_{Ar} py), 6.21 (s, 2H N-CH_2), 4.00 (s, 3H N-CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 151.30, 142.67(Pd-C), 137.75, 133.87, 130.76, 129.77, 128.87, 128.79, 127.82, 127.52, 127.19, 124.22, 58.67, 37.58. HRMS (ESI-TOF, m/z): 545.0720 $C_{27}H_{24}ClN_4Pd$ [M-Cl], calculated: 545.0724.

2.3. General Procedure for Suzuki–Miyaura coupling

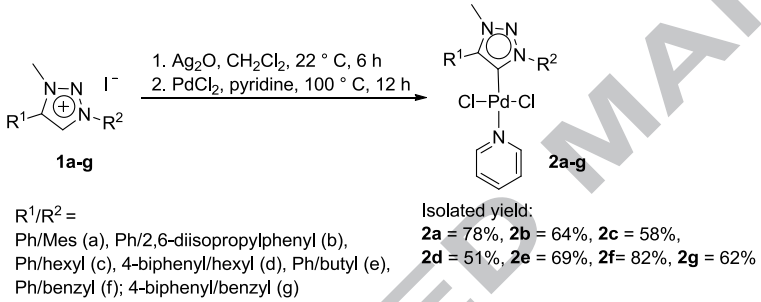
A boronic acid (2.5×10^{-4} moles, 1.05 equiv.) and 1 mL of ethanol (99.8%) were placed in a 2 mL glass reactor equipped with a reflux condenser and magnetic stirrer. The reaction mixture was stirred at 22 °C until complete dissolution of the acid (ca 5 minutes). Then aryl halide (1 equiv.), dodecane (internal standard), a suitable amount of palladium complex and KOH (1.1 equiv.) were added. The reaction mixture was stirred at 22 °C or at 78 °C for 24 hours. The course of the reaction was monitored by gas chromatography and GC / MS. After completion of the reaction, 2 mL of distilled water and 2 mL of hexane were added to the reaction mixture. The organic phase was washed with water (2 × 2 mL). The product was isolated

from the organic phase by column chromatography (SiO_2, hexane). For details see supplementary information.

3. Results and Discussion

3.1. Synthesis of complexes

The synthesis of 1,4-disubstituted 1,2,3-triazoles was performed by Huisgen 1,3-dipolar cycloaddition catalyzed by copper(I) ions according to the literature procedures [32,33]. The obtained triazoles were treated with MeI to form the respective triazolium salts (**1**) [24]. Palladium complexes (**2a-g**) were then obtained via a modified literature method (Scheme 1) [13]. The appropriate triazolium salt was treated in CH_2Cl_2 at 22 °C with silver oxide for 6 h. After that time the ^{1}H NMR spectrum of the reaction mixture does not show the signal assigned to proton at C5. Silver carbene complexes were then treated without prior isolation with $PdCl_2$ and pyridine at 100 °C for 12 h to form palladium complexes **2a-g**. The synthesized complexes were purified by column chromatography and characterized by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry.



Scheme 1. Synthesis of PEPPSI-type 1,2,3-triazolin-5-ylidene complexes **2a-g**

3.2. Crystallographic studies

Structures of complexes **2a**, **2c**, **2e, 2f** and **2g** were confirmed by X-ray diffraction analysis. The perspective views of the complexes are shown in Figures 1 - 5. Some geometrical data are listed in Table S2. The main geometrical features, i.e. bond lengths and angles, of the studied complexes are similar. In all complexes Pd ion is four coordinated, in a very regular square-planar fashion. Both Pd-Cl bonds are equivalent, within an experimental error. In the triazole rings the two N-N and two C-N bonds are quite similar in pairs – suggesting significant delocalization throughout this ring. Interestingly, complex **2c** crystallizes with two symmetry-independent molecules in the asymmetric part of the unit cell, and these molecules exhibit different conformations of the hexane side chain; it is *trans-trans-trans-trans* in the molecule A while *(+)gauche-trans-trans-(-)gauche* in molecule B (Fig. 2). Significant differences are observed in the conformation of molecules, which in this case might be defined by the dihedral angles between the least-square planes of planar fragments: pyridine ring (A), coordination plane (B), triazole ring (C), and additionally – although less important – the phenyl ring at C14. Table S2 lists the appropriate values. The above differences lead to the differences in long-distance contacts within the molecules. The crystal structures are built mainly be weak, unidirectional van der Waals forces; some secondary C-H···Cl contacts (or interactions) are also observed.

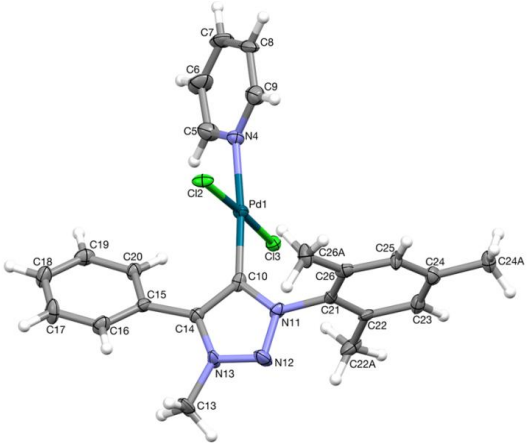


Figure 1. A perspective view of complex **2a**; ellipsoids are drawn at the 50% probability level, hydrogen atoms are shown as spheres of arbitrary radii.

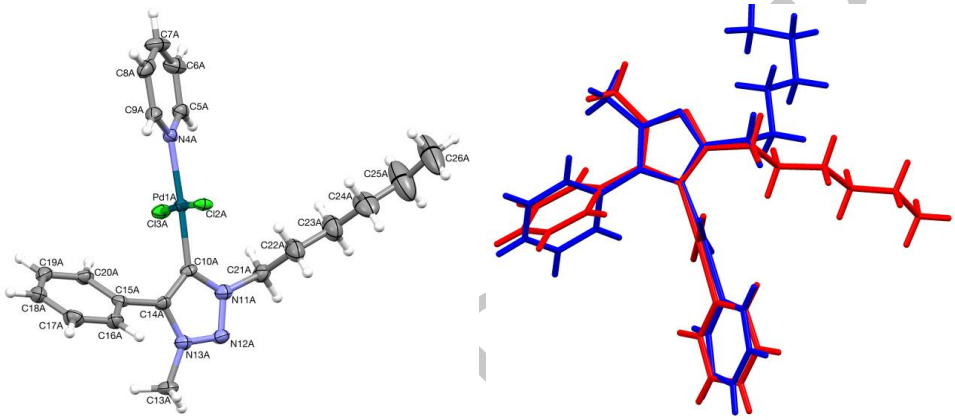


Figure 2. Perspective view of the molecule A of complex **2c** (left); ellipsoids are drawn at the 50 % probability level, hydrogen atoms are shown as spheres of arbitrary radii. A comparison of the two symmetry-independent molecules of **2c** (right).

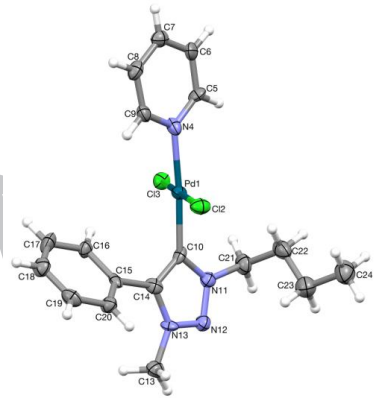


Figure 3. Perspective view of the complex **2e**; ellipsoids are drawn at the 50 % probability level, hydrogen atoms are shown as spheres of arbitrary radii.

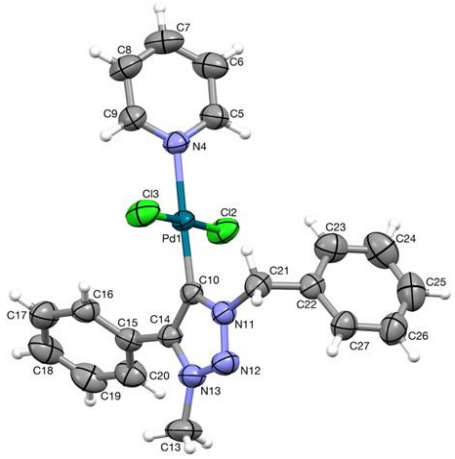


Figure 4. Perspective views of the complex **2f**; ellipsoids are drawn at the 50 % probability level, hydrogen atoms are shown as spheres of arbitrary radii.

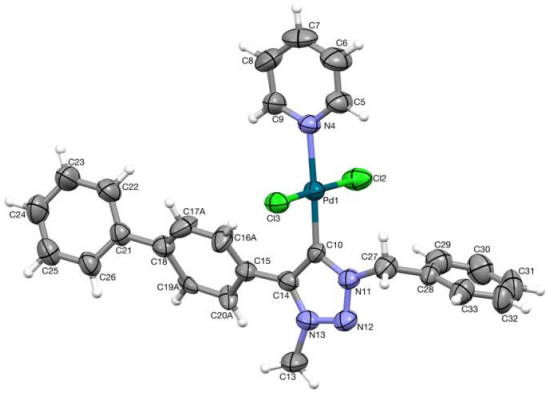
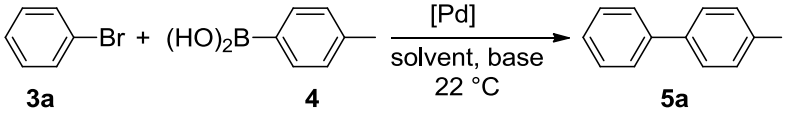


Figure 5. Perspective view of the complex **2g**; ellipsoids are drawn at the 50 % probability level, hydrogen atoms are shown as spheres of arbitrary radii. Only one of the disordered fragments (C15 – C20A) is shown

3.3. Catalytic applications

Synthesized palladium complex **2a** was tested as precatalyst in the Suzuki–Miyaura coupling of 4-tolylboronic acid with bromobenzene (Scheme 2). The results of studies aimed at optimizing the reaction conditions are shown in Table 1.



Scheme 2. Suzuki–Miyaura coupling of 4-tolylboronic acid with bromobenzene.

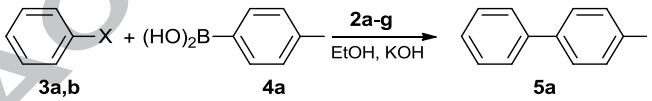
Table 1. Coupling of 4-tolylboronic acid with bromobenzene in the presence of **2a.**

Entry	Base	Solvent	**2a** (mol%)	Yield[a] [%]
1	TBAF	EtOH	1	52
2	KO^{t}Bu	EtOH	1	81
3	H_3COONa	EtOH	1	traces
4	Cs_2CO_3	EtOH	1	79
5	NaOH	EtOH	1	47
6	KOH	EtOH	1	>99
7	KOH	*i*PrOH	1	76
8	KOH	MeOH	1	88
9	KOH	dioxane	1	14
10	KOH	EtOH	0.1	98
11	KOH	EtOH	0.1	70[b]
12	KOH	EtOH	0.05	88
13	KOH	EtOH	0.01	61

Reaction conditions: 22 °C, 24 h, [ArBr]:[$ArB(OH)_2$]:[KOH] = 1:1.05:1.1; air;
[a)] GC yield; [b)] argon

The tests indicated that high yields were obtained using ethanol as a solvent and KOH as a base. The reaction is effective at room temperature. Under such conditions, the quantitative yield of the coupling product was obtained in the presence of 0.1 mol% of catalyst. Further lowering of the catalyst loading resulted in a decrease in reaction yield.

To compare the catalytic activity, the coupling reaction of 4-tolylboronic acid with bromobenzene (Scheme 3) was investigated in the presence of each of the synthesized complexes.



Scheme 3. Suzuki–Miyaura coupling of 4-tolylboronic acid with phenyl halides

Relevant reaction profiles were show in Figure 6. The highest activity was observed for complex **2g**, which allows for quantitative conversion after only 10 minutes of reaction course.

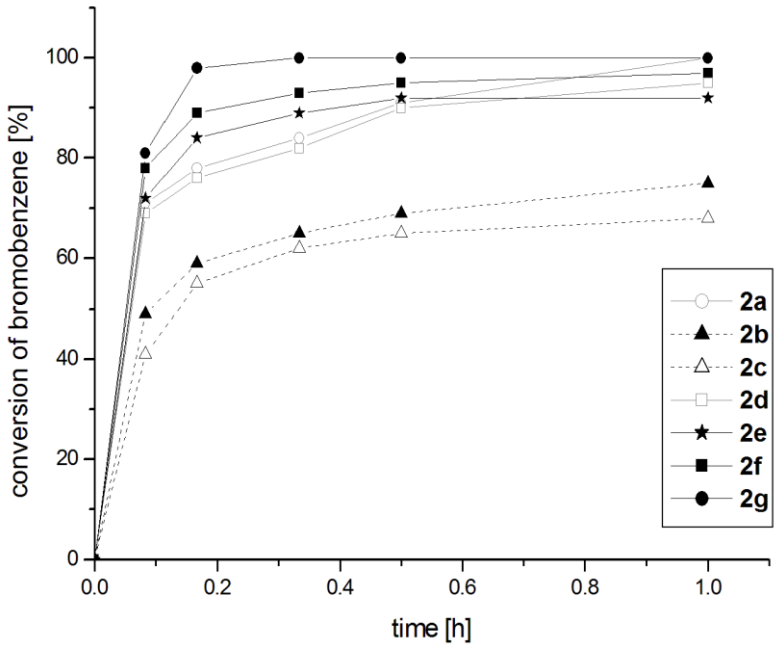


Figure 6. Reaction profiles. Suzuki–Miyaura coupling of bromobenzene with 4-tolylboronic acid. Reaction conditions: cat. = **2a-g** (0.1 mol%), [ArBr]:[ArB(OH)$_2$]:[KOH] = 1:1.05:1.1; EtOH, 22 °C, air.

High activity was observed for complexes **2a**, i **2d-f**, in the presence of which complete conversion was observed after 1 h of the reaction course. The study of the coupling of 4-tolylboronic acid with chlorobenzene (Scheme 3) revealed no reaction at room temperature. Effective coupling was found to require higher reaction temperature (78 °C), increased loading of Pd complex (1 mol%) and prolonged reaction time (Table 2). The highest yields were obtained in the presence of complexes **2a** and **2g**. Increasing the concentration of catalyst to 2 mol% allows moderate yield of the product, i.e. 62% for the catalyst **3a**, and 77% for the complex **3g**.

Table 2. Coupling of 4-tolylboronic acid with ~~bromobenzene and~~ chlorobenzene in the presence of complexes **2a-g**

Entry	X	Cat. (mol %)	Temp [°C]	Yield[a] [%]
1	Cl	**2a** (1)	78	61
2	Cl	**2a** (2)	78	62
3	Cl	**2b** (1)	78	29
4	Cl	**2c** (1)	78	34
5	Cl	**2d** (1)	78	55
6	Cl	**2e** (1)	78	44
7	Cl	**2f** (1)	78	55
8	Cl	**2g** (1)	78	71
9	Cl	**2g** (2)	78	77

Reaction conditions: [ArCl]:[ArB(OH)$_2$]:[KOH] = 1:1.05:1.1; EtOH, 24 h, air; [a)] GC yield;

Optimization tests (Table 1) permitted specification of the conditions for efficient progress of the reaction in the presence of catalyst **2a**. In the optimized reaction conditions a series of aryl bromides were tested in the reaction with 4-tolylboronic acid in the presence of catalyst **2a** to determine the versatility of the method. The results are shown in Figure 7.

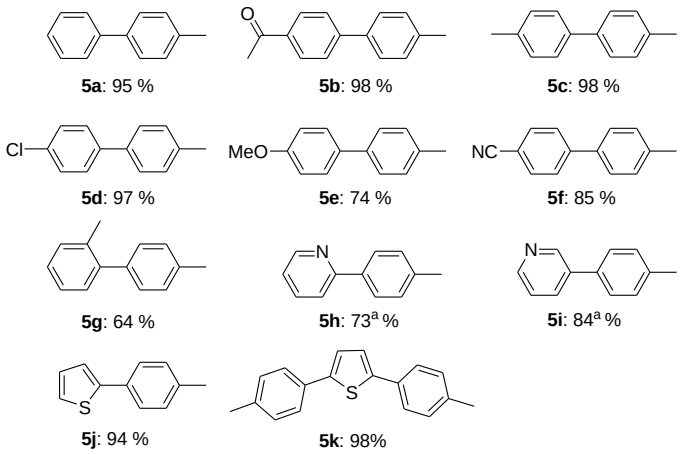
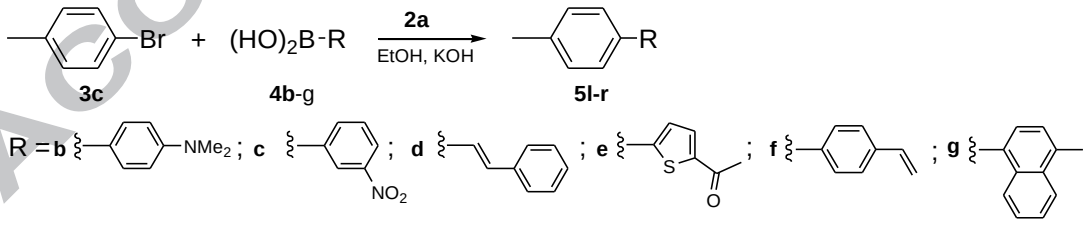


Figure 7. Suzuki–Miyaura coupling of 4-tolylboronic acid with aryl bromides in the presence of complex **2a**. Specified values refer to isolated yields. Reaction conditions: EtOH, 22 °C, 24 h, [ArBr]:[$ArB(OH)_2$]:[KOH] = 1:1.05:1.1; [Pd] = 0.1 mol %, air; [a] 78 °C

High yields were obtained for nearly all tested compounds. Bromobenzene and aryl bromide with a substituent in the *para* position were effectively converted at room temperature at a low catalyst loading (0.1 mol%). It has been shown that complex **2a** tolerates the presence of a variety of functional groups. For high conversion of heteroaryl bromides, the reaction temperature should be raised to 78 °C. The coupling of aryl bromide sterically hindered in the ortho position proceeds with a moderate yield. An attempt to raise the reaction temperature in this case led to the formation of an undesired product of boronic acid homocoupling.

To evaluate the scope of the reaction we performed a number coupling by using 4-bromotoluene as electrophile and selected boronic acids (Scheme 4, Figure 8).



Scheme 4. Suzuki–Miyaura coupling of 4-bromotoluene with selected boronic acids

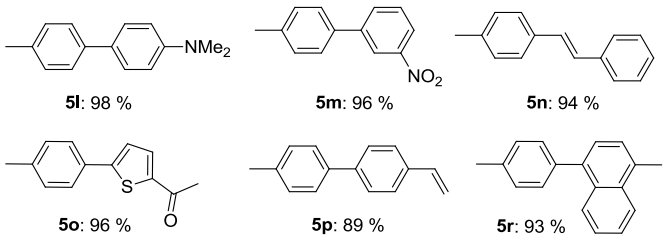


Figure 8. Suzuki–Miyaura coupling of 4-bromotoluene with selected boronic acids in the presence of complex **2a**. Specified values refer to isolated yields. Reaction conditions: EtOH, 22 °C, 24 h, [ArBr]:[ArB(OH)$_2$]:[KOH] = 1:1.05:1.1; [Pd] = 0.1 mol %, air

High isolated yields were obtained for all reagents tested. Nearly quantitative yields were obtained in reaction with phenylboronic acids containing substituents differing in electronic properties. Under the conditions used, an efficient conversion of the thiophenyloboronic acid and selected alkenylboronic acid derivatives was also observed. These results indicate high scope of the proposed procedures.

3.4. Mechanistic insights

The Suzuki–Miyaura coupling initiated by complexes **2a-g** was accompanied by the formation of fine black solid. Therefore, the possibility of the reaction to be catalyzed by palladium nanoparticles was examined by using the mercury poisoning experiment [34]. Accordingly, bromobenzene was treated with 4-tolylboronic acid at 22 °C for one minute followed by the addition of a high excess (1000 equivalents) of mercury to the reaction system. The reaction was carried out upon vigorous stirring for 24 hours. Total inhibition of the reaction was observed by adding mercury excess (Figure 9).

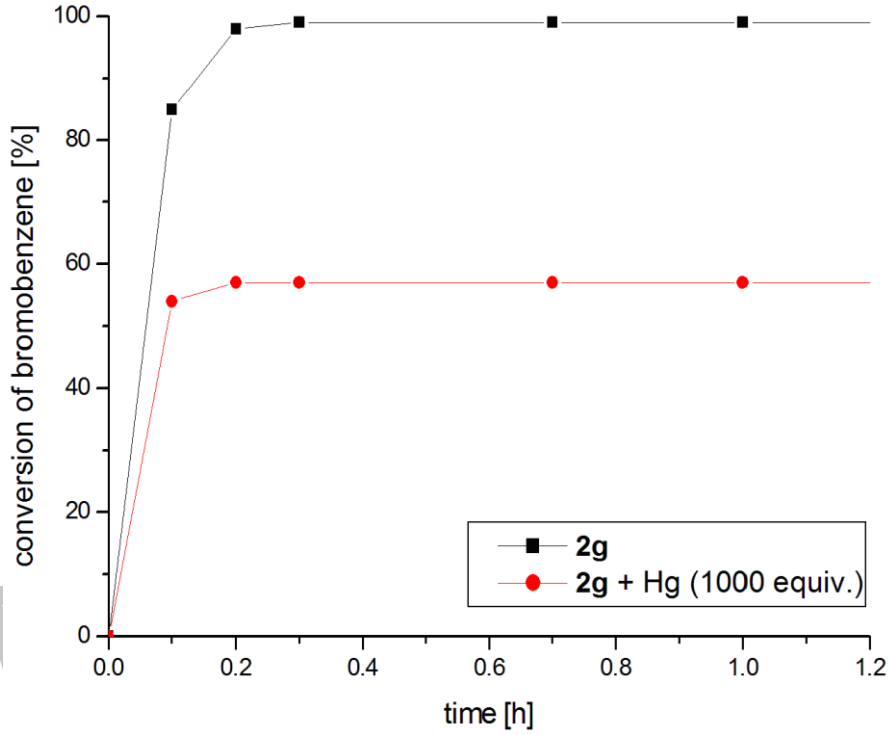


Figure 9. Mercury poisoning experiment. Profiles of the reactions of bromobenzene with 4-tolylboronic acid performed in the presence of **2g** (0.1 mol%) with and without the addition of mercury excess. Reaction conditions: [ArBr]:[ArB(OH)$_2$]:[KOH] = 1:1.05:1.1, air; 22 °C, Hg was added after 1 min. of the reaction course.

Fine solid formed upon the coupling of bromobenzene with 4-tolylboronic acid (EtOH, 22 °C, [PhBr]:[ArB(OH)$_2$]:[KOH]:[Pd] = 1:1.05:1:1.1:1×10^{-2}) was isolated and characterized by scanning and transmission electron microscopy after 5 minutes or 2 hours of the reaction

course (Figures 10 and 11). The experiment revealed formation of palladium nanoparticles and the increase in their average diameter in the course of the reaction from 1.4 nm (after 5 min) to 3.6 nm (after 2 h).

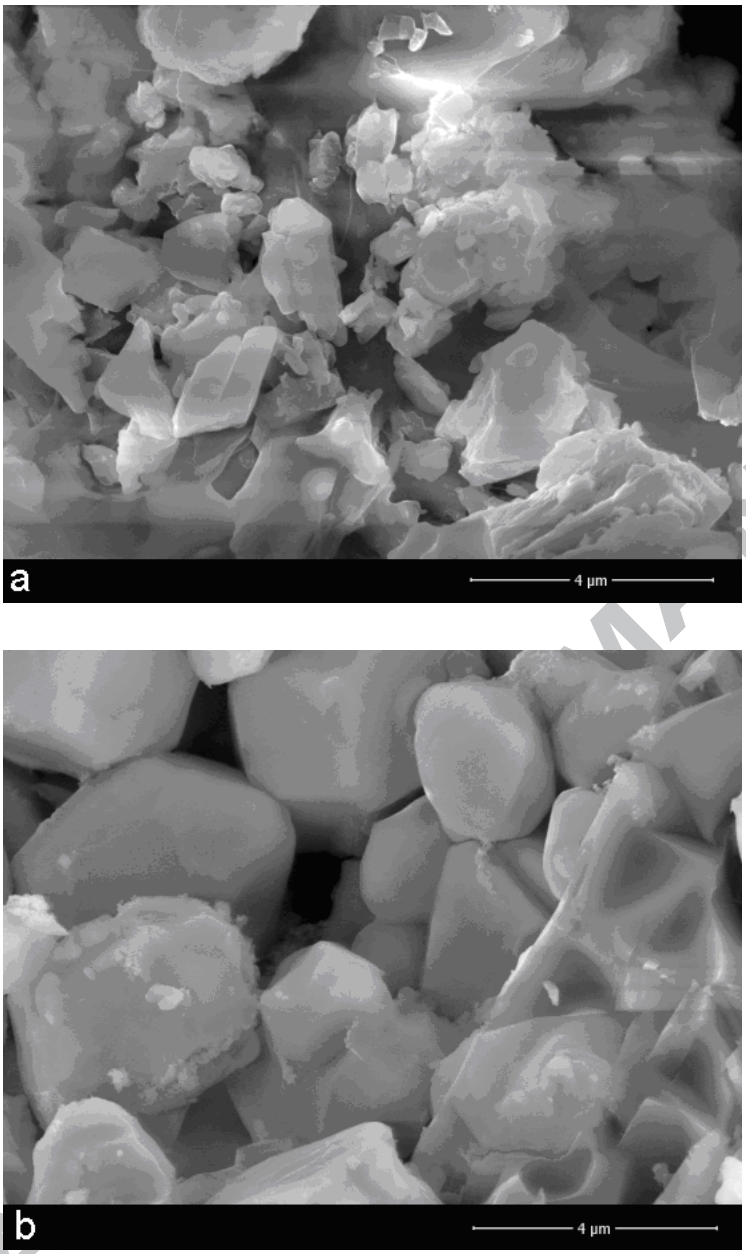


Figure 10. SEM micrographs showing the palladium nanoparticles formed in the reaction mixture after 5 min (a) and 2 h (b) of the reaction course in the presence of complex **2a**.

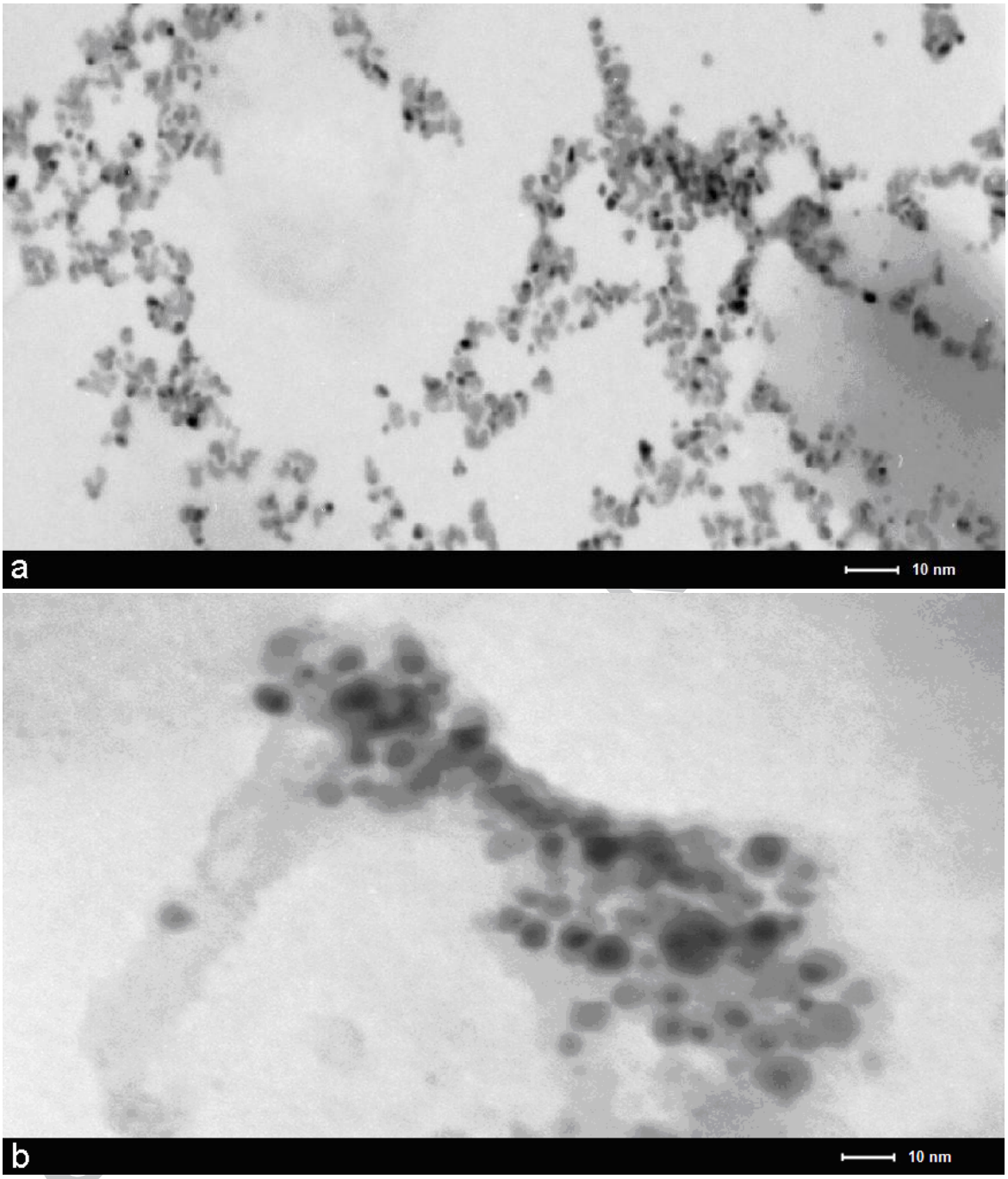


Figure 11. TEM micrographs showing the palladium nanoparticles formed in the reaction mixture after 5 min (a) and 2 h (b) of the reaction course in the presence of complex **2a**.

The nanoparticles isolated from the post-reaction mixture were found inactive in the Suzuki–Miyaura coupling of bromobenzene with 4-tolylboronic acid. Our attempts to isolate catalytically active species have failed. It is very likely that the particles of strictly defined size are catalytically active. During the reaction they grow or dissolve due to Oswald ripening, resulting in the loss of catalytic activity.

ESI-MS analysis of the post reaction mixture from the Suzuki–Miyaura coupling of bromobenzene with 4-tolylboronic acid did not show the formation of dimeric or trimeric complexes, as observed by Albrecht and Trzeciak [12].

4. Conclusions

PEPPSI-type palladium(II) 1,2,3-triazolin-5-ylidene complexes bearing sterically diverse ligands can be easily synthesized via metalation/transmetalation sequence. The complexes are efficient precatalyst in the Suzuki–Miyaura coupling of boronic acids with aryl bromides and exhibit moderate activity in the coupling with of boronic acids with aryl chlorides. Mercury poisoning experiment indicates the participation of nanoparticles or underligated palladium complexes in the catalytic process and 1,2,3-triazolin-5-ylidene palladium complexes act as source of catalytically active species. Despite the catalytic activity observed, synthesized 1,2,3-triazolin-5-ylidene palladium complexes **2a**-**g** does not bring the expected advantages as catalysts of Suzuki–Miyaura coupling.

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1,2,3-triazolin-5-ylidene palladium complexes catalyze effective Suzuki coupling

Triazolin-5-ylidene palladium complexes decompose when treated with boronic acid

Mercury poisoning test indicates contribution of nanoparticles in catalysis