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Monomeric triphenylphosphite palladacycles with N-imidazole ligands as catalysts of Suzuki–Miyaura and Sonogashira reactions

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ABSTRACT

Three monomeric triphenylphosphite palladacycles of the formula [PdCl(P–C)(im)], where P–C = $P(OC_6H_4)(OC_6H_5)_2$, im = 1-methylimidazole, **2**, 1,2-dimethylimidazole, **3**, and 1-butylimidazole, **4**, were obtained in reaction of $[PdCl(P–C)]_2$, **1**, with the respective imidazoles. These complexes exhibited high catalytic activity in the Suzuki–Miyaura reaction in ethane-1,2-diol and in the Sonogashira reaction in ionic liquids, [bmim]BF_4 and [bmim]PF_6. While the application of two imidazoles per palladium caused improvement of the reaction yield, an inhibiting effect was found in both reactions when 1-methylimidazole or 1-butylimidazole was used in 20-fold excess relative to palladium.

1. Introduction

Dimeric triarylphosphite-based palladacycles have been obtained in the reaction of $PdCl_2$ with $P(OR)_3$ or, alternatively, with $PdCl_2[P(OR)_3]_2$ [1–3]. These complexes are active catalysts of Suzuki–Miyaura [1,4,5], Hiyama [6], Stille [1], Sonogashira [6], Heck [7] reactions and in the allylation of aldehydes with allyl tributyltin [8]. Most catalytic reactions with triarylphosphite palladacycles have been performed in organic solvents; however, successful application of ionic liquids as reaction media has also been reported [6]. Interestingly, an increase in the catalytic activity of dimeric palladacycles has been observed after their transformation to monomeric complexes in reaction with mono- or bi-dentate phosphorus ligands [4,9]. Particularly high activity in the cross-coupling of deactivated aryl chlorides has been noted for palladium derivatives containing PCy_3 [9].

While the presence of a phosphorus ligand in the coordination sphere of a palladacycle complex mostly improved its catalytic activity, less spectacular results have been found for monomeric palladacycles containing bulky N-heterocyclic carbene ligands, which only gave a modest yield in the Suzuki–Miyaura cross-coupling of aryl bromides [10–12]. The same complexes showed poor activity in reactions with aryl chlorides as substrates [10].

Inspired by the fact that palladium complexes with imidazole ligands exhibited attractive catalytic activity in C–C cross-coupling reactions [13–15], we decided to examine whether N-imidazoles can improve the reactivity of palladacycles. In this paper, we report studies of reactions of triphenylphosphite palladacycles with imidazoles resulting in the formation of monomeric palladacycles. These complexes were next tested in two model reactions, Suzuki–Miyaura and Sonogashira, in organic solvents and in ionic liquids.

2. Results and discussion

2.1. Formation of [PdCl(P–C)(im)] complexes

Monomeric phosphite-based palladacycles with coordinated 1-methylimidazole, **2**, 1,2-dimethylimidazole, **3**, and 1-butylimidazole, **4**, were obtained in the reaction of dimeric palladacycle **1** with a stoichiometric amount of the free imidazole according to Scheme 1.

^{31}P NMR spectra of complexes **2**–**4** exhibited signals in the region of 120–130 ppm, characteristic for the presence of a chelating P–C ligand and slightly shifted downfield compared with **1**. The presence of two signals in the spectra of **2**–**4** is consistent with the formation of two isomers with different localizations of the N-imidazole ligand. On the basis of literature data, it can be proposed that the isomer with imidazole *trans* to phosphorus is dominating [2,10].

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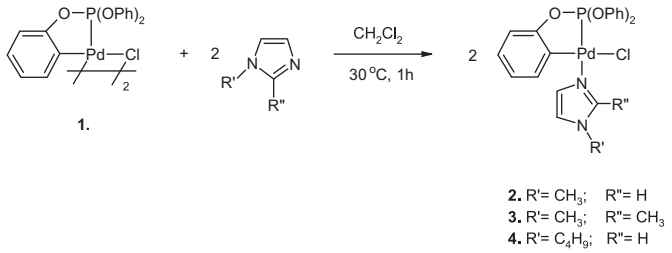


Scheme 1. Synthesis of monomeric palladacycles with coordinated imidazole ligands.

The solid state studies also revealed that the investigated complexes may form two different isomers. The molecular structure of compounds **2** and **4** has been determined by single crystal X-ray diffraction (Figs. 1 and 2). Pd atoms in both the compounds are four-coordinated in a slightly distorted square-planar environment (Table 1). In compound **2** the metallated carbon is in *cis* orientation to Cl. The Pd–Cl bond length in **4** is somewhat longer than in **2**, indicating the *trans* influence of the aryl group. All other bond distances and angles in compounds **2** and **4** are within standard ranges.

Reactions of complex **1** with different N-imidazole ligands were studied *in situ* using ^{1}H and ^{31}P NMR methods in order to get more data about the formation and stability of the new complexes. The completeness of the transformation of **1** to **2**, **3**, or **4** was observed at the [Pd]:[im] ratio equal to 1:2. When the amount of imidazole was smaller and the [Pd]:[im] ratio was 2:1, signals of unreacted **1** (at 122.8 and 125.1 ppm) were present in addition to those of the monomeric products **2**–**4**. In reactions with 20-fold excess of N-imidazole, only peaks originating from the monomeric complexes **2**–**4** were found in the ^{31}P NMR spectrum. It is important to note that signals of free phosphite were not observed, which confirms the stability of Pd–P and Pd–C bonds even in the presence of an excess of N-imidazole.

Studies of the reaction of **1** with 2-phenylimidazole or 4-methyl-2-phenylimidazole at the [Pd]:[im] ratio of 1:20 revealed the presence

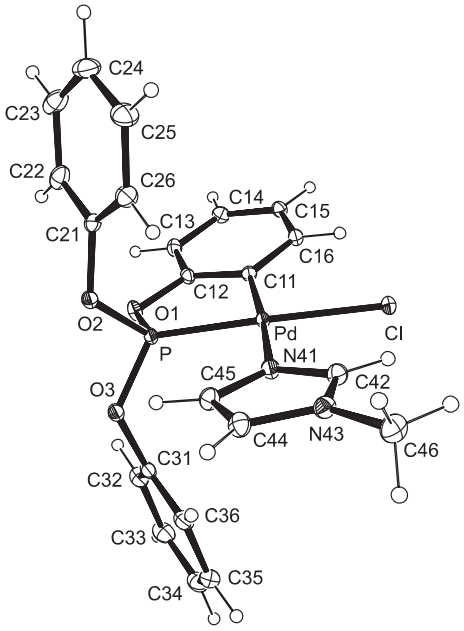


Fig. 1. Molecular structure and atom numbering scheme of **2**. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

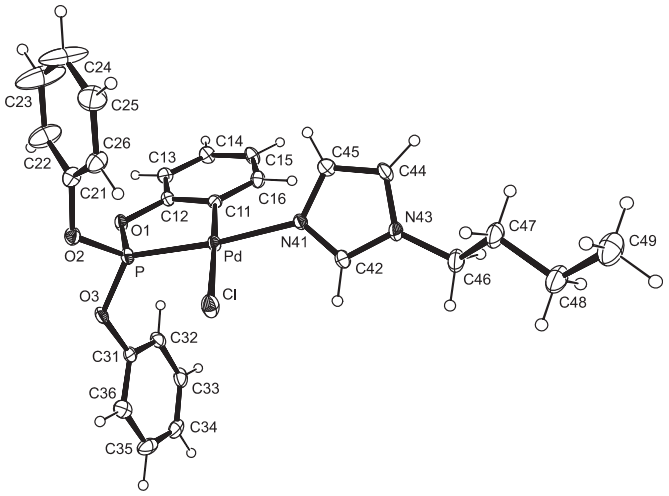


Fig. 2. Molecular structure and atom numbering scheme of **4**. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

of signals of unreacted **1** in ^{31}P NMR, suggesting that the formation of monomeric complexes is slower than in the case of complexes **2**–**4**. Consequently, 28% of **1** was converted to the monomeric complex during reaction with 2-phenylimidazole, and only 19% in reaction with 4-methyl-2-phenylimidazole. The formation of these new complexes was additionally confirmed by ESI-MS(+), where new signals were found at *m*/*z* 559 assigned to $[Pd(P–C)(2\text{-phenylimidazole})]^{+}$ and at *m*/*z* 573 assigned to $[Pd(P–C)(4\text{-methyl-2-phenylimidazole})]^{+}$ (where P–C is the orthometallated ring). Similar cations of the $[Pd(P–C)(im)]^{+}$ composition were also observed in MS spectra measured for complexes **2**, **3**, and **4** in dichloromethane solution or for such complexes formed *in situ* from **1** and the respective N-imidazole. Thus, for **2** a peak at *m*/*z* 497 was found, for **3** at *m*/*z* 511, and for **4** at *m*/*z* 539.

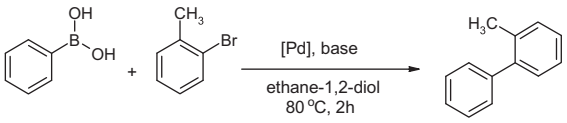
In ^{1}H NMR spectra the most characteristic signal was that of the proton of the orthometallated ring at *ca.* 8.26 ppm. The presence of this signal in the spectra of palladium complexes formed in reaction of **1** with imidazoles is additional evidence of the preservation of the orthometallated rings.

2.2. Suzuki–Miyaura reaction

The obtained monomeric phosphite-based palladacycles with coordinated N-imidazole ligands were tested in a model Suzuki–Miyaura cross-coupling reaction of 2-bromotoluene with phenylboronic acid (Scheme 2).

Table 1
Selected bond lengths (Å) and angles (°) for **2** and **4**.

	2	**4**
Pd–P	2.1583 (10)	2.1658 (12)
Pd–Cl	2.3652 (11)	2.3872 (13)
Pd–N41	2.1259 (17)	2.092 (3)
Pd–C11	2.0186 (19)	2.026 (3)
P–Pd–Cl	172.44 (4)	96.20 (4)
P–Pd–C11	80.70 (5)	81.40 (10)
C11–Pd–N41	174.01 (6)	94.70 (12)
C11–Pd–Cl	93.63 (5)	176.52 (10)
N41–Pd–Cl	90.28 (4)	87.88 (8)
N41–Pd–P	95.79 (4)	174.37 (8)



Scheme 2. Suzuki–Miyaura reaction.

First, the effect of the base was studied and the best results, 100% conversion, were obtained for complexes **3** and **4** with Cs_2CO_3 and for **4** with K_3PO_4 (Table 2). Very good results, 96–97% yield, were also obtained when $NaHCO_3$ was used as a base. Under these conditions, imidazole-substituted palladacycles gave the coupling product with 96% yield, *ca.* 10% higher than the dimeric palladacycle **1**, indicating a positive effect of imidazole ligands. In all experiments with complex **3**, yields of 97–100% were achieved, and consequently 1,2-dimethylimidazole might be considered the most promising modifying ligand. Recycling trials showed that catalyst **3** may be reused although the yield of 2-methylbiphenyl obtained in the second run (69%) was lower than in the first one (100%). Results collected in Table 2 were obtained after 2 h of reaction; however, a kinetic profile shows that the reaction is quite fast and reaches the maximum yield already after 15 min (Fig. 3A). When lower concentration of palladium was used (0.1 mol%), a short induction period was found indicating the transformation of **3** to the active species (Fig. 3B).

2.3. Effect of imidazole excess in Suzuki–Miyaura reaction

The good results obtained in Suzuki–Miyaura reactions with complexes **2**, **3**, and **4** prompted us to study the activity of palladacycle **1** in the presence of imidazole excess. It was expected that catalytically active imidazole-modified complexes would be formed *in situ*. Five different imidazoles were used together with complex **1** and it was discovered that the efficiency of the reaction depended on the [im]:[Pd] ratio (Table 3). When a small amount of imidazole was used, at an [im]:[Pd] ratio equal to 2, conversion in all reactions increased compared with reactions catalyzed by **1** only. Good results were also observed for dimer **5**, which produced 90–97% of the cross-coupling product when a 2-fold excess of imidazole was added. Apparently, increasing the [im]:[Pd] ratio to 20 resulted in the catalytic reaction being totally retarded when 2-methylimidazole and 2-butylimidazole were added. These two imidazoles applied in 20-fold excess with complexes **2** or **3** also stopped the reaction completely. In contrast, imidazoles substituted at C2 with a methyl or phenyl group did not cause any inhibiting effect even when used in excess, as shown for complexes **1** or **5**.

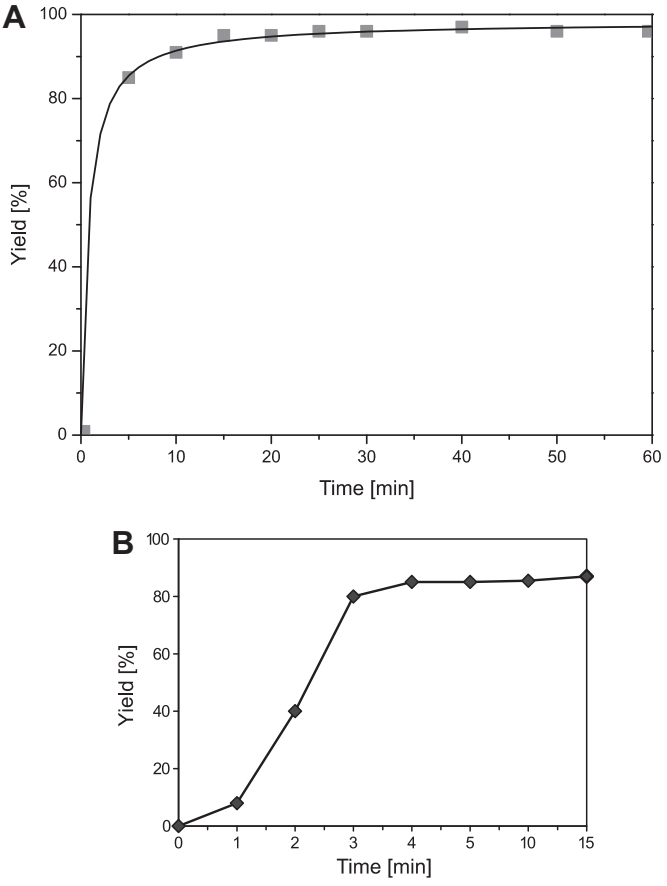
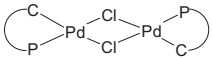
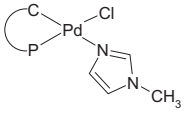
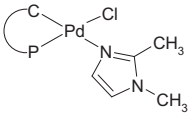
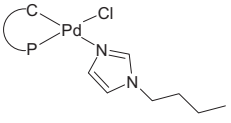


Fig. 3. Kinetic profile of Suzuki–Miyaura reaction catalyzed by **3** at 1 mol% (A) and 0.1 mol% (B).

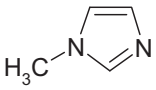
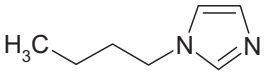
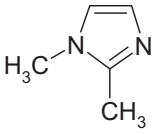
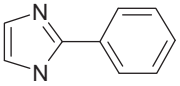
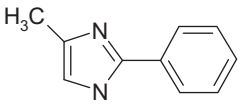
It is also worth noting that the above-presented influence of imidazoles on the Suzuki–Miyaura cross-coupling reaction was independent of the reaction procedure. In the first set of experiments imidazoles were mixed with the catalyst for 10 min to facilitate coordination of imidazole to palladium and then the other reactants were introduced. Subsequently, similar experiments were performed without any pre-treatment. In both cases, practically the same results were obtained, which suggest fast action of imidazoles in the studied systems.

Table 2
Results of Suzuki–Miyaura cross-coupling with catalysts **1**–**4**.

Base	Yield [%][a]			
				
	1	**2**	**3**	**4**
$NaHCO_3$	86	96	97	96
Na_2CO_3		88	99	84
K_3PO_4		85	100	85
Cs_2CO_3	100	98	100/69[b]	100

Reaction conditions: [Pd] 1 mol%, [$PhB(OH)_2$] 1.5 mmol, [2-bromotoluene] 1 mmol, [base] 2 mmol, [ethane-1,2-diol] 2.5 cm^3, 80 °C, 2 h.
[a] Conversion to the coupled product determined by GC.
[b] Recycled catalyst.

Table 3
Effect of imidazoles on the yield of Suzuki–Miyaura cross-coupling.

Catalyst	Imidazole	[Pd]:[Imidazole]	Yield [%][a]
1	None	–	86
1		1:20	1
1		1:40	0
1		1:2	94
2		1:20	0
5		1:2	90
1		1:2	93
1		1:20	0
1		1:40	0
3		1:20	0
5		1:2	96
1		1:20	95
5		1:2	98
5		1:20	92
1		1:20	93
5		1:2	96
5		1:20	95
1		1:20	92
5		1:2	97
5		1:20	97

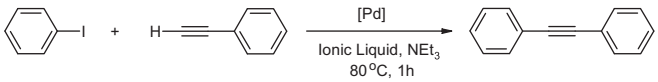
Reaction conditions: [Pd] 1 mol%, [$PhB(OH)_2$] 1.5 mmol, [2-bromotoluene] 1 mmol, [base] 2 mmol, [ethane-1,2-diol] 2.5 cm^3, 80 °C, 2 h.
[a] Conversion to the coupled product determined by GC.

The observed inhibiting effect is not related to the formation or decomposition of palladium complexes, because according to the NMR results, the monomeric palladacycle complexes with imidazole ligands were stable in the range of concentrations used.

2.4. Sonogashira reaction

Imidazole-modified phosphite-based palladacycles **2**, **3**, and **4** were also tested in the Sonogashira cross-coupling of iodobenzene with phenylacetylene (Scheme 3). On the basis of our previous experience, ionic liquids were selected as the reaction media. The presented results (Fig. 4) clearly show a higher yield of the reaction obtained with complexes **2**, **3**, and **4** than with complex **1**. In [bmim]PF_6 conversion increased from 56 to 78–84%, and in [bmim]BF_4, from 44 to 71–81%. When [emim][$EtSO_4$] was used as solvent, the yield of 2-methylbiphenyl was similar for all the complexes **1**–**4** and in this case no improvement relating to the presence of imidazole was observed. Moreover, complex **4** may be indicated as the most efficient of all the investigated catalysts.

To estimate the stability of the catalysts studied, recycling tests were undertaken with the ionic liquid phase containing the palladium catalyst used for the second run. In all cases, the yield of the product was lower than in the first reaction and in the best case *ca.* 50% of 2-methylbiphenyl was obtained with catalyst **4** (Fig. 5). It should be pointed out that the recycling procedure was not



Scheme 3. Sonogashira reaction.

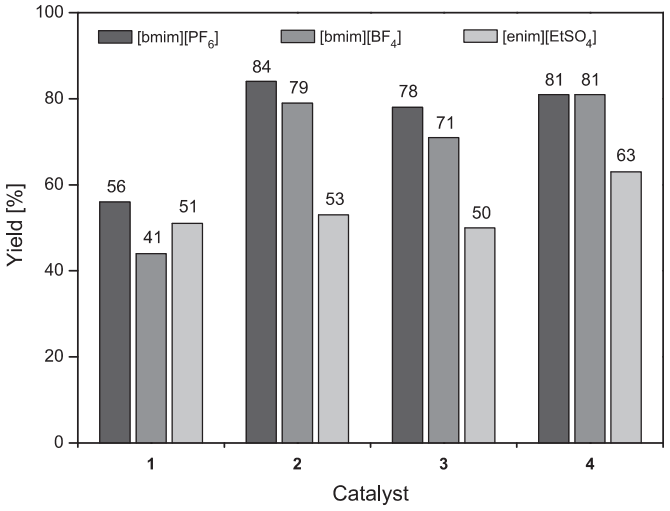


Fig. 4. Sonogashira reaction in ionic liquids with catalysts **1**–**4**.

optimized and besides catalyst deactivation some leaching of palladium to the hexane phase during extraction cannot be excluded.

In order to find a simple and efficient protocol of the Sonogashira cross-coupling, reactions were carried out in [bmim]PF_6 using **1** and free imidazoles as additives. In all five reactions performed at the [im]:[Pd] ratio equal to 2, satisfactory results were obtained with a yield of 80–85%, which is over 20% higher than with **1** alone (Table 4). Also, recycling was relatively good with the best result 75% in the second run when 1-butylimidazole was applied. Generally, the recycling experiments performed with *in situ* formed imidazole palladacycles were more productive than with isolated complexes **2**, **3**, and **4** (Table 4).

Similarly as in the Suzuki–Miyaura reaction, the Sonogashira cross-coupling was inhibited by an excess of free imidazoles. The most dramatic effect was noted for 1,2-dimethylimidazole, which afforded only 6% of the product when used in 20-fold excess. In contrast, 20-fold excess of 1-methylimidazole and 1-butylimidazole, which stopped the Suzuki–Miyaura reaction completely, only caused some decrease in the yield of diphenylacetylene, to 29% and 20% respectively.

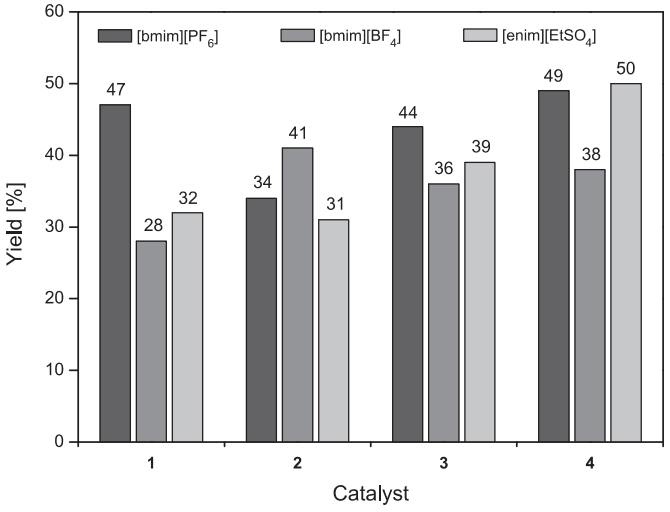
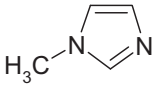
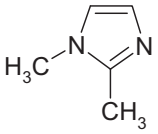
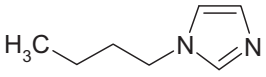
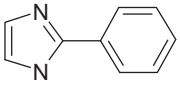
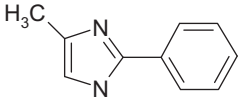


Fig. 5. Sonogashira reaction with recycled catalysts **1**–**4**.

Table 4
Effect of imidazoles on the yield of Sonogashira reaction catalyzed by **1**.

Imidazole	[Pd]:[Imidazole]	Yield [%][a] 1st cycle	Yield [%][a] 2nd cycle
None	–	56	47
	1:2	85	66
	1:20	29	8
	1:2	81	54
	1:20	6	2
	1:2	81	75
	1:20	20	7
	1:2	85	62
	1:20	82	48
	1:2	80	50
	1:20	80	35

Reaction conditions: [Pd] 1 mol%, [PhI] 1 mmol, [phenylacetylene] 1 mmol, [NEt_3] 1.9 mmol, [bmim]PF_6 1.5 cm^3, 80 °C, 1 h.
[a] Conversion to the coupled product determined by GC.

Imidazoles bearing phenyl substituents at C2, 2-phenylimidazole and 4-methyl-2-phenylimidazole, used together with **1** produce 80–85% of diphenylacetylene regardless of their concentration.

3. Mechanistic considerations

According to the present state of knowledge the C–C cross-coupling reactions can be catalyzed by homogeneous, soluble palladium complexes or by Pd(0) nanoparticles [16,17]. In particular, Pd(0) nanoparticles can act as heterogeneous catalysts or, alternatively, they can be a reservoir of soluble palladium species, the real catalytic active form [18]. Although the formation of Pd(0) nanoparticles is not very plausible in the presence of phosphorus ligands, we decided to perform a Hg(0) test to estimate the role of Pd(0) nanoparticles in Suzuki–Miyaura reaction catalyzed by **3**.

The experimental data, obtained at 200-fold excess of Hg(0) with respect to palladium, showed that the catalyst was unaffected by Hg(0) and, consequently, homogeneous mechanism with a Pd(0)/Pd(II) catalytic cycle was highly likely (Table 5). During induction period Pd(0) complex can be formed from the palladacycle precursor by reductive elimination of the orthometallated ring with an aryl group introduced by the boronic acid [1].

Table 5
Effect of Hg(0) on the yield of Suzuki–Miyaura reaction catalyzed by **3**.

Catalyst	Yield [%] 1st cycle		Yield [%] 2nd cycle	
	in air	in N_2	in air	in N_2
3	100	99	88	81
3 + Hg(0)[a]	99	99	14	67
3 + Hg(0)[b]	99	–	11	–

Reaction conditions: [Pd] 1 mol%, [$PhB(OH)_2$] 1.5 mmol, [2-bromotoluene] 1 mmol, [base] 2 mmol, [ethane-1,2-diol] 2.5 cm^3, 80 °C, 1 h; [Hg]:[Pd] = 200.
[a] Hg(0) added together with the catalyst.
[b] Hg(0) added after 4 min of reaction.

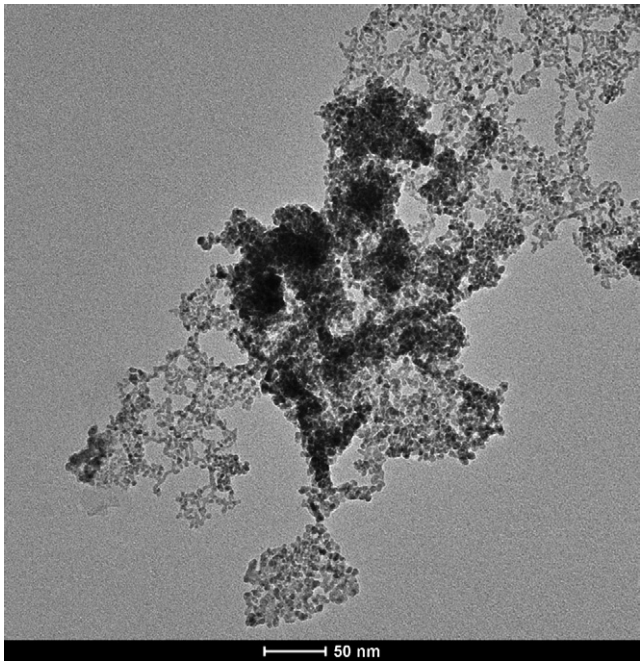


Fig. 6. TEM of **3** after Suzuki–Miyaura reaction.

While homogeneous mechanism operates in the first catalytic run, participation of Pd(0) nanoparticles in the second run cannot be excluded especially, when separation step was performed in the presence of air. When palladium catalyst was recovered together with Hg(0) and used in the next catalytic run, only 24% of product was formed. A better result, 67% of 2-methylbiphenyl, was obtained when extraction of organic products was performed in N_2 atmosphere. Similarly, even 85% of product was formed when the catalyst was recovered after the first reaction under N_2 and Hg(0) was added to the second reaction.

The presence of Pd(0) nanoparticles in post-reaction mixture was evidenced by TEM (Fig. 6). The obtained micrographs showed some small Pd(0) nanoparticles of 7–9 nm diameter and dominating bigger agglomerates of 40–200 nm size.

4. Conclusions

Modification of triphenylphosphite palladacycles with N-imidazole ligands led to the formation of monomeric complexes preserving the orthometallated ligand in the coordination sphere of palladium. These new complexes efficiently catalyzed the Suzuki–Miyaura reaction and 100% yield was obtained with complexes **3** and **4** when Cs_2CO_3 was used as a base. Attempts to use imidazole-modified palladacycles in the Sonogashira reaction resulted in the development of an efficient protocol for ionic liquids, [bmim]BF_4 and [bmim]PF_6. In these two solvents, high yields and good recyclability were obtained for complex **1** used with an N-imidazole additive. However, it should be pointed out that the amount of N-imidazole must be carefully controlled because an excess of imidazole can stop the catalytic process completely. This inhibiting effect is most probably related to interactions between organic components of the reaction mixture rather than to the formation of inactive palladium species.

As far as the influence of N-imidazole is concerned, our results differ from those reported by Welton, who observed an inhibiting effect of imidazoles incorporating N–H bonds in the Suzuki–Miyaura reaction in dioxane as well as in ionic liquids as solvents [13,15]. In

our system, the presence of an N–H bond (in 2-phenylimidazole and 4-methyl-2-phenylimidazole) did not inhibit the catalytic process.

We proposed homogeneous Pd(0)/Pd(II) mechanism as the main pathway in C–C cross-coupling reactions catalyzed by palladium complexes under studies. However, some Pd(0) nanoparticles can be formed in the end of catalytic process or, during separation of products from the catalyst performed in air atmosphere. Small Pd(0) nanoparticles can take part in the catalytic reaction.

5. Experimental

Dimeric palladacycle complex **1** was obtained according to the literature method [3].

[PdCl{k^2–P,C–P(OC_6H_4)(OC_6H_5)$_2$}{1-methylimidazole}], **2**: To the solution of complex **1** (0.20 g; 0.22 mmol) in CH_2Cl_2 (4 cm^3) 1-methylimidazole (0.07 cm^3; 0.88 mmol) was added. Reaction mixture was stirred at room temperature for 1 h, after which the solvent was evaporated *in vacuo* and the white product was precipitated by addition of ethanol and recrystallized from the CH_2Cl_2/EtOH mixture. Yield: 0.2 g, 85%; calcd (%) for $C_{22}H_{20}ClO_3N_2PPd$ (533.26): C 49.55, H 3.78, N 5.25; found: C 49.25, H 3.56, N 5.21. ESI-MS(m/z): 497; ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta = 8.26$ (t, 1H, $J_{H-H} = 6.4$ Hz; orthopalladated ring), 6.69–7.79 (m, Ph), 3.71 (s, 3H, CH_3; *major isomer*), 3.63 (s, 3H, CH_3; *minor isomer*) ppm; ^{31}P NMR (202.5 MHz, $CDCl_3$): 129.91 (*minor isomer*); 126.53 (*major isomer*) ppm.

[PdCl{k^2–P,C–P(OC_6H_4)(OC_6H_5)$_2$}{1,2-dimethylimidazole}], **3**: To the solution of complex **1** (0.30 g; 0.33 mmol) in CH_2Cl_2 (4 cm^3) 1,2-dimethylimidazole (0.127 g; 1.32 mmol) was added. Reaction mixture was stirred at room temperature for 1 h, after which the solvent was evaporated *in vacuo* and the white product was precipitated by addition of ethanol and recrystallized from the CH_2Cl_2/EtOH mixture. Yield: 0.35 g, 97%; calcd (%) for $C_{23}H_{22}ClO_3N_2PPd$ (546.29): C 50.48, H 4.05, N 5.12; found: C 50.30, H 3.98, N 4.93. ESI-MS(m/z): 511; ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta = 8.27$ (t, 1H, $J_{H-H} = 6.1$ Hz; orthopalladated ring), 6.30–7.60 (m, Ph), 3.54 (s, 3H, CH_3; *major isomer*), 3.45 (s, 3H, CH_3; *minor isomer*), 2.29 (s, 3H, CH_3; *major isomer*), 2.07 (s, 3H, CH_3; *minor isomer*) ppm; ^{31}P NMR (202.5 MHz, $CDCl_3$): 132.17 (*major isomer*), 124.70 (*minor isomer*) ppm.

[PdCl{k^2–P,C–P(OC_6H_4)(OC_6H_5)$_2$}{1-butylimidazole}], **4**: To the solution of complex **1** (0.18 g; 0.20 mmol) in CH_2Cl_2 (4 cm^3) 1-butylimidazole (0.105 cm^3; 0.80 mmol) was added. Reaction mixture was stirred in room temperature for 1 h, after which the solvent was evaporated *in vacuo* and the white product was precipitated by addition of ethanol and recrystallized from the CH_2Cl_2/EtOH mixture. Yield: 0.18 g, 78%; calcd (%) for $C_{25}H_{26}ClO_3N_2PPd$ (575.34): C 52.19, H 4.55, N 4.87; found: C 51.42, H 4.88, N 5.87. ESI-MS(m/z): 539; ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta = 8.27$ (t, 1H, $J_{H-H} = 6.2$ Hz; orthopalladated ring), 6.60–8.00 (m, Ph), 3.84–3.96 (m, 4H, CH_2), 1.68–1.82 (m, 4H, CH_2), 1.25–1.37 (m, 4H, CH_2), 0.89–0.96 (m, 6H, CH_3) ppm; ^{31}P NMR (202.5 MHz, $CDCl_3$): 129.60 (*minor isomer*), 126.60 (*major isomer*) ppm.

5.1. Suzuki–Miyaura reaction

The Suzuki–Miyaura reaction was carried out in a Schlenk tube with magnetic stirring. Reagents: phenylboronic acid (0.183 g, 1.5 mmol), 2-bromotoluene (0.118 cm^3, 1 mmol), base (2 mmol), ethane-1,2-diol (2.5 cm^3) and palladium catalyst (1 mol%) were introduced directly to the Schlenk tube. Next, the Schlenk tube was sealed with a rubber stopper and introduced into an oil bath pre-heated to 80 °C. The reaction was carried out at 80 °C for 2 h and after this time cooled down. Organic products were separated by extraction with hexane (4 cm^3, 3 cm^3 and 3 cm^3). The extracts (10 cm^3) were GC–FID analyzed (Hewlett Packard 5890) with 0.076 cm^3 of dodecane as an internal standard. The products were identified by GC–MS (Hewlett Packard 5971A).

Table 6
Crystallographic data for **2** and **4**.

	2	**4**
Chemical formula	$C_{22}H_{20}ClN_2O_3PPd$	$C_{25}H_{26}ClN_2O_3PPd$
Formula mass	533.22	575.30
Crystal system	Monoclinic	Triclinic
a/Å	9.624 (4)	8.378 (3)
b/Å	18.381 (6)	9.488 (4)
c/Å	12.168 (5)	16.360 (6)
α/°	90	97.45 (3)
β/°	99.94 (3)	102.29 (3)
γ/°	90	102.43 (3)
Unit cell volume/Å^3	2120.2 (14)	1219.7 (8)
Temperature/K	100 (2)	100 (2)
Space group	$P2_1/n$	$P-1$
No. of formula units per unit cell, Z	4	2
Absorption coefficient, μ/mm^{-1}	1.104	1.566
No. of reflections measured	14,471	10,391
No. of independent reflections	4813	5447
No. of parameters	272	299
R_{int}	0.0204	0.0423
Final R_1 values ($I > 2\sigma(I)$)	0.0234	0.0420
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0627	0.0726
Final R_1 values (all data)	0.0277	0.0694
Final $wR(F^2)$ values (all data)	0.0641	0.0772
Goodness of fit on F^2	1.076	0.888

5.2. Sonogashira reaction

The Sonogashira reaction was carried out in a Schlenk tube with magnetic stirring. Reagents: iodobenzene (0.11 cm^3, 1 mmol), phenylacetylene (0.11 cm^3, 1 mmol), NEt_3 (1.9 mmol), ionic liquid (1.5 cm^3) and palladium catalyst (1 mol%), were introduced directly to the Schlenk tube. Next, the Schlenk tube was sealed with a rubber stopper and introduced into an oil bath pre-heated to 80 °C. The reaction was carried out at 80 °C for 1 h and after this time cooled down. Organic products were separated by extraction with hexane (4 cm^3, 3 cm^3 and 3 cm^3). The extracts (10 cm^3) were GC–FID analyzed (Hewlett Packard 5890) with 0.05 cm^3 of mesitylene as an internal standard. The products were identified by GC–MS (Hewlett Packard 5971A).

5.3. X-ray studies

Single crystals of **2** and **4** suitable for X-ray measurements were mounted on glass fibers in silicone grease, cooled to 100 K in a nitrogen gas stream, and the diffraction data were collected on a Kuma KM-4 CCD diffractometer with graphite monochromated Mo–Kα radiation (λ = 0.71073 Å). The structures were subsequently solved using direct methods and developed by full least-squares refinement on F^2. Structural solution and refinement was carried out using SHELX suite of programs [19]. Analytical absorption corrections were performed with CrysAlis RED [20]. C, N, O, P, Cl, and Pd atoms were refined anisotropically. The carbon-bonded H atoms were positioned geometrically and refined isotropically using a riding model with a common fixed isotropic thermal parameter. The molecular structure plots were prepared using ORTEP-3 program [21]. Crystal data and selected details of structure determination are summarized in Table 6.

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Appendix A. Supplementary material

CCDC 826119 and 816415 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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