Journal of Organometallic Chemistry 710 (2012) 44-52

Contents lists available at SciVerse ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Orthometallated palladium trimers in C-C coupling reactions

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ARTICLE INFO

Article history: Received 13 January 2012 Received in revised form 6 March 2012 Accepted 7 March 2012

Keywords: Palladium Palladacycles Aryl phosphite C–C coupling reactions Ionic liquids Pd(0) nanoparticles

ABSTRACT

A series of trimeric palladium complexes of the $[Pd_3(\mu-Cl)_4(P-C)_2]$ (P-C = orthometallated aryl phosphite) formula have been prepared and structurally characterized using ³¹P NMR and ESI-MS methods. The structure of $[Pd_3(\mu_2-Cl)_4\{k^2-P,C-P(O-o-CH_3C_6H_3)(O-o-CH_3C_6H_4)_2\}_2]$, **1c**, was determined by X-ray diffraction. It is compared with the structure of the dimeric complex $[Pd_2(\mu-Cl)_2\{k^2-P,C-P(O-m-CH_3C_6H_4)_2\}_2]$, **3b**. The trimeric palladium complexes very efficiently catalyzed the Suzuki–Miyaura and Hiyama reactions in ethane-1,2-diol and the Sonogashira cross-coupling in ionic liquids. The mercury test confirmed the homogeneous pathway of the Suzuki–Miyaura reaction, although Pd(0) nanoparticles were observed by TEM in the post-reaction mixture.

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1. Introduction

The strong ability of palladium compounds to catalyze C–C bond forming reactions is well documented in the literature [1-9]. Palladium catalysts have found many applications in the production of pharmaceuticals, new materials, agrochemicals, or biologically active compounds. In particular, palladium complexes incorporating phosphorus ligands are the most intensively investigated due to the fact that their catalytic activity can be effectively modulated by the electronic and steric properties of the ligands [1-9].

Typically, reactions of $PdCl_2$ with tertiary phosphines lead to monomeric, square-planar complexes of the $PdCl_2P_2$ formula, which form *cis* or *trans* isomers depending on the steric hindrance of the P-ligand [10]. Besides the formation of *trans* monomeric compounds, more bulky phosphines form dimeric species with halide bridges of the $[PdX_2P]_2$ type, containing one phosphine per palladium atom [11,12]. Trimeric complexes, containing two phosphine ligands per three palladium atoms have been formed in reaction of PdCl₂ with very bulky phosphines, TRIP (tris(2,2",6,6"-tetraisopropyl[1,1':3',1"-terphenyl]-5'- yl)phosphine) or TRMP (tris(2,2",6,6"-tetramethyl[1,1':3',1"-ter-phenyl]-5'-yl)phosphine) [11,13].

With triaryl phosphites used instead of phosphine, monomeric and dimeric palladium complexes have also been formed; however, in this case orthometallation may proceed, leading to the formation of palladacycles with Pd–C and Pd–P bondings [14]. Orthometallated palladium complexes were obtained in the reaction of PdCl₂ with PdCl₂P₂, and the yield of the reaction increased when HCl, formed as a byproduct, was removed with a stream of N₂ [14]. For bulkier phosphites, such as $P(OC_6H_3-2,4^{-t}Bu_2)_3$ or $P(OC_6H_4-2^{-t}Bu)_3$, a more efficient procedure leading to palladacycles consisted in direct reaction of PdCl₂ with phosphite in 2-methoxyethanol or toluene under reflux [15,16]. The formation of trimers in such reactions has not been reported till now.

Monomeric and dimeric palladium complexes with phosphito ligands show excellent catalytic activity in cross-coupling reactions [15,17–21]; therefore, it was interesting to check whether trimeric complexes can also be successfully applied in these reactions. Phosphine-free trimers with a $(PdX_2)_3$ fragment [22–26] have not been tested in catalytic reactions and nothing is known about the catalytic activity of trimeric [$(PdX_2)_3P_2$]-type complexes.

In this paper we present the first example of successful synthesis of palladium trimers containing orthometallated triarylphosphito ligands and their catalytic activity in Suzuki–Miyaura, Hiyama, and Sonogashira reactions.





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2. Results and discussion

2.1. Synthesis of trimeric complexes $[Pd_3(\mu-Cl)_4(P-C)_2]$ (P-C = orthometallated aryl phosphite)

During our studies of synthetic methods leading to orthometallated palladium complexes with triphenylphosphito ligands. a new family of palladium trimers of the $[Pd_3(u-Cl)_4(P-C)_2]$ (P-C = orthometallated aryl phosphite) formula, containing a [Pd₃(µ-Cl)₄] core and chelating orthometallated phosphito ligands, was discovered. Trimeric palladium complexes were obtained under slightly modified conditions in respect to those used in the preparation of dimeric complexes with orthometallated phosphites, $[Pd_2(\mu-Cl)_2(P-C)_2]$ [14–16] (Scheme 1). Further studies showed that two different pathways leading to palladium trimers could be considered, starting from PdCl₂ or PdCl₂P₂ ($P = P(OAr)_3$), respectively. Two parameters are the most important for the successful synthesis of trimeric complexes: an excess of PdCl₂ relative to P(OAr)₃ and a reaction temperature of *ca.* 130 °C. In our experience, the method with the application of PdCl₂P₂ as the substrate generates a higher yield of the product in shorter time.

The synthesis of trimeric palladium complexes was carried out with four different triaryl phosphites, and as a result complexes **1a–1d** were obtained with a 40–50% yield. In the ³¹P NMR spectra of complexes **1a–1d**, two signals of different intensity were observed in the region of 118–126 ppm, indicating the presence of two isomers. The position of the signals is very close to that of the signals observed for the dimeric complexes **3** (Scheme 1), and it is characteristic for the presence of an orthometallated ligand coordinated to palladium [15,16]. However, on the basis of ³¹P NMR it is impossible to distinguish trimers (**1**) from dimers (**3**).

To characterize complexes **1a–1d** in solution, the ESI-MS method was used (Table 1). In the spectra of the trimeric complexes (**1a–1d**), the most intensive signals were assigned to $[Pd_2Cl(P-C)_2]^+$ and $[Pd_3Cl_2(P-C)_3]^+$ fragments. The spectrum of the dimeric complex **3a** shows a similar bimetallic fragment, $[Pd_2Cl(P-C)]^+$. Interestingly, only in the ESI-MS spectra of trimeric complexes there were fragments containing three or four palladium atoms, $[Pd_3Cl_2(P-C)_2]^+$ and $[Pd_4Cl_4(P-C)_3]^+$, observed. Although these species can be formed under the ESI-MS conditions, such a process does not occur for monomeric and dimeric palladium complexes (Table 1). Thus, trimeric complexes show the strongest tendency to form clusters.

2.2. Structural studies of 1c and related palladium complexes with phosphito ligands

Single crystals of **1c**, **2b**, **3b**, and **3d** were obtained by recrystallization from CH₂Cl₂/pentane and characterized structurally by X-ray diffraction. Selected bond distances and angles are given in Table 2.

The structure of the trimeric complex **1c** (Fig. 1) consists of two independent molecules. Each of the molecules is formed by three Pd atoms linked by bridging chloride ligands with the Pd2 and Pd4 atoms residing at crystallographic inversion centers. The Pd1–Cl1 and Pd3–Cl3 bond lengths are slightly longer than Pd1–Cl2 and Pd3–Cl4, indicating a *trans* influence of the orthometallated ligand. There is practically no difference between the Pd2–Cl1, Pd2–Cl2 and Pd4–Cl3, Pd4–Cl4 bond lengths, which are close to the Pd–(µ–Cl) bond distances in the central PdCl₄ unit of the chloride-bridged trinuclear palladium(II) complexes (2.29–2.31 Å) [11,13,25] as well as the Pd–Cl bond of [PdCl₂]_n (2.31 Å) [27]. The coordination geometry of Pd1 and Pd3 is square-planar, substantially distorted



Table 1

ESI-MS(+) data for trimeric (1a, 1b, 1c), dimeric (3a) and monomeric (2a, 2b, 2c) palladium complexes.

Complex	<i>m</i> / <i>z</i> (% rel. int.)
1a	455 (48) [Pd(P _a)Cl] ⁺ , 672 (40), 809 (45) [Pd ₃ (P _a)Cl ₅] ⁺ , 866 (100)
	$[Pd_2(P_a-C)_2Cl]^+$, 1042 (28) $[Pd_3(P_a-C)_2Cl_3]^+$, 1221 (16)
	$[Pd_4(P_a-C)_2Cl_5]^+$, 1316 (62) $[Pd_3(P_a-C)_3Cl_2]^+$, 1493 (12)
	$[Pd_4(P_a-C)_3Cl_4]^+$
1b	498 (23) [Pd(P _b)Cl] ⁺ , 853 (13) [Pd(P _b) ₂ Cl] ⁺ , 951 (81)
	$[Pd_2(P_b-C)_2Cl]^+$, 1126 (14) $[Pd_3(P_b-C)_2Cl_3]^+$, 1305 (9)
	$[Pd_4(P_b-C)_2Cl_5]^+$, 1444 (100) $[Pd_3(P_b-C)_3Cl_2]^+$, 1620 (8)
	$[Pd_4(P_b-C)_3Cl_4]^+$, 1936 (8)
1c	498 (4) $[Pd(P_c)Cl]^+$, 951(100) $[Pd_2(P_c-C)_2Cl]^+$, 1050 (41); 1128 (7)
	$[Pd_3(P_c-C)_2Cl_3]^+$, 1443 (96) $[Pd_3(P_c-C)_3Cl_2]^+$
2a	762 (100) $[Pd(P_a)_2Cl]^+$
2b	847 (100) $[Pd(P_b)_2Cl]^+$,984 (62) $[Pd(P_b-C)(P_b)Cl_2]^+$
2c	846 (100) $[Pd(P_c)_2Cl]^+$
3a	415 $[Pd(P_a-C)]^+$ (60) 866 $[Pd_2(P_a-C)_2Cl]^+$ (100)

 $P_a = P(OC_6H_5)_3$; $P_b = P(O-m-MeC_6H_4)_3$; $P_c = P(O-o-MeC_6H_4)_3$.

with P1–Pd1–C16 and P2–Pd3–C46 angles of about 80° and P1–Pd1–Cl1, P2–Pd3–Cl3 approximately 100° . The coordination plane of Pd1 is inclined at 19.8° to the Pd2 plane. Similarly, the angle between the Pd3 and Pd4 coordination planes is 10.0° .

The molecular structure of the dimeric complex **3b** (Fig. 2) consists of two Pd atoms linked by bridging chlorides. The bond lengths and angles in this compound are similar to those found in other orthopalladated binuclear phosphite complexes [15,16,19]. The square-planar coordination geometry of the palladium atoms is distorted; however, the distortion of the bond angles is slightly smaller than in the case of the trimeric complex **1c**. Bond distances are practically the same as in **1c**. The coordination plane of Pd1 is inclined at 57.8° to the Pd2 plane.

A molecule of **3d** (Fig. 3) contains a dimetallacyclic Pd_2Cl_2 core with a crystallographic center of inversion at the mid-point of the $Pd1\cdots Pd1^i$ line [symmetry code: (i) 1-x, 1-y, 1-z]. As a result of the presence of the inversion center, the $Pd1/Cl1/Pd1^i/Cl1^i$ ring is strictly planar. Surprisingly, the Pd1-Cl1 and $Pd1-Cl1^i$ bond lengths are almost identical: 2.4064(7) and 2.4052(9) Å, respectively, indicating that in this complex the *trans* effect of the phosphorus ligand is not observed. However, the structure of this complex already reported in the literature also showed a very weak *trans* effect: the difference between the Pd-Cl bond lengths was merely about 0.01 Å [28]. All other bond distances and angles in **3d** are similar to those in **3b**.

Table 2

Selected bond lengths (Å) and angles (°) for 1c , 2b , 3b and 3	d.
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The Pd atom of the mononuclear complex **2b** (Fig. 4) is fourcoordinated in a square-planar geometry. The molecule adopts the *cis* configuration in the solid state. The angles between adjacent ligands deviate only slightly from the expected value of 90° (Table 2). The Pd1–Cl1 and Pd1–Cl2 bond distances are within a range typical for palladium complexes: 2.298–2.354 Å [29]. The measured Pd–P bond lengths, 2.22–2.23 Å, are also commonly observed in complexes of this kind [30].

2.3. Catalytic activity of complexes **1a–1d** in C–C coupling reactions

Three cross-coupling reactions, Suzuki–Miyaura, Hiyama, and Sonogashira, were selected for tests of the catalytic activity of the new trimeric palladium complexes (Scheme 2). We had studied these model reactions before with the monomeric and dimeric palladium complexes with triphenylphosphito ligands including orthometallated derivatives [17,18]. Consequently, the reaction conditions optimized during the previous studies were applied, and ethane-1,2-diol was used as a solvent for Suzuki–Miyaura and Hiyama reactions, whereas Sonogashira reactions were carried out in ionic liquid media.

The first screening experiments (Table 3), performed with 1c as the catalyst precursor, resulted in the selection of the most suitable bases: Cs_2CO_3 for the Suzuki–Miyaura reaction (wich had also been found to be an optimal base for this process during our previous studies [18,31]) and NaOH for the Hiyama reaction [18].

As can be concluded from the data presented in Table 3, complexes 1a-1c exhibit high catalytic activity (94–98% yield) in the Suzuki–Miyaura cross-coupling. Only 1d provided a slightly lower yield of 2-methylbiphenyl (82%). Even better results were obtained in the Hiyama reaction, with yields reaching 93–98%, which is higher than with other palladium triphenylphosphito complexes.

Further experiments showed that complexes 1a-1d also efficiently catalyze the Sonogashira reaction in ionic liquid media. Typically, a yield of ca. 80% was obtained in the first run in all reactions (Fig. 5). Interestingly, comparable results were obtained in three different ionic liquids containing imidazolium cations, [bmim]PF₆, [bmim]BF₄, and [emim][EtSO₄], whereas in previous studies a remarkably lower productivity of palladium phosphito complexes was observed in [bmim]BF₄.

1c (first molecule)		1c (second molecule)		2b		3b		3d	
Pd1-P1	2.1504(17)	Pd3-P2	2.1619(16)	Pd1-P1	2.2268(12)	Pd1–P1	2.1535(13)	Pd1-P1	2.1603(8)
				Pd1-P2	2.2297(7)	Pd2–P2	2.1589(12)		
Pd1-C16	2.011(4)	Pd3-C46	2.007(5)			Pd1-C16	2.003(4)	Pd1-C16	2.0076(16)
						Pd2-C46	2.006(4)		
Pd1-Cl1	2.4203(14)	Pd3–Cl3	2.4314(14)	Pd1-Cl1	2.3372(8)	Pd1–Cl1	2.4267(12)	Pd1-Cl1	2.4064(7)
Pd1-Cl2	2.4089(16)	Pd3–Cl4	2.3928(16)	Pd1–Cl2	2.3288(12)	Pd2–Cl1	2.3943(12)	Pd1–Cl1 ⁱ	2.4052(9)
Pd2–Cl1	2.3009(16)	Pd4–Cl3	2.3082(15)			Pd1–Cl2	2.3991(14)		
Pd2–Cl2	2.2999(13)	Pd4–Cl4	2.2808(14)			Pd2–Cl2	2.4372(13)		
P1-Pd1-C16	79.44(14)	P2-Pd3-C46	78.69(14)	P1-Pd1-P2	92.45(3)	P1-Pd1-C16	80.68(11)	P1-Pd1-C16	80.70(5)
						P2-Pd2-C46	81.42(11)		
P1–Pd1–Cl1	99.72(5)	P2-Pd3-Cl3	103.69(5)	P1-Pd1-Cl1	87.60(3)	P1–Pd1–Cl1	96.39(5)	P1-Pd1-Cl1	98.48(2)
						P2–Pd2–Cl2	95.80(4)		
C16-Pd1-Cl2	97.78(13)	C46–Pd3–Cl4	94.42(14)	P2–Pd1–Cl2	88.31(3)	C16–Pd1–Cl2	96.81(11)	C16–Pd1–Cl1 ⁱ	95.71(5)
						C46–Pd2–Cl1	96.75(11)		
Cl1-Pd1-Cl2	82.88(5)	Cl3–Pd3–Cl4	83.01(5)	Cl1-Pd1-Cl2	91.64(3)	Cl1–Pd1–Cl2	86.17(4)	Cl1-Pd1-Cl1 ⁱ	85.15(2)
						Cl1–Pd2–Cl2	86.04(4)		
Cl1-Pd2-Cl2	88.01(5)	Cl3–Pd4–Cl4	88.32(5)						
Cl1–Pd2–Cl2 ⁱ	91.99(5)	Cl3–Pd4–Cl4 ⁱⁱ	91.68(5)						

Symmetry codes: (i) 1–*x*, 1–*y*, 1–*z*; (ii) 1–*x*, 1–*y*, –*z*.



Fig. 1. Molecular structure and atom numbering scheme of **1c**. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Unlabeled atoms are symmetrically dependent via inversion centers [symmetry codes: (i) 1–x, 1–y, 1–z; (ii) 1–x, 1–y, –z].

When considering the activity of complexes 1a-1d, complex 1b could be pointed out as the most productive one in all three ionic liquids. It also provided the best results in the second run, especially in an [emim][EtSO₄] medium, where 80% and 81% of the product was formed in the first and the second run, respectively. These good results correspond well with the high activity of the dimer **3b** with the same P(O–m-MeC₆H₄)₃ ligand.

2.4. Comparative analysis of catalytic activity

Having in hand monomeric, dimeric, and trimeric palladium complexes with triphenylphosphito ligands, it was interesting to compare their catalytic activity. A kinetic experiment performed under the Suzuki–Miyaura reaction conditions for complexes **1a**, **2a**, and **3a** showed a similar profile in all three cases (Fig. 6). Only the initial step of the reaction with the trimer **1a** was slightly slower, but already after 5 min ca. 90% of the product had been formed. This may indicate that the trimeric complex is more difficult to reduce to Pd(0).

Further reactions were performed at different concentrations of palladium complexes in the range [bromotoluene]: [Pd] = 100–10000. It is worth noting that after 15 min a high yield of cross-coupling product was obtained in all reactions (Table 4). As can be concluded from the data presented in Table 4, high TOF values, 25,000–30,000 h⁻¹, were obtained in all the systems studied, regardless of the structure of the catalyst



Fig. 2. Molecular structure and atom numbering scheme of 3b. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.



Fig. 3. Molecular structure and atom numbering scheme of 3d. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Solvent molecules (toluene) have been omitted for clarity. Unlabeled atoms are symmetrically dependent via an inversion center [symmetry code: (i) 1–x, 1–y, 1–z].

precursor. The high catalytic activity of the studied complexes is in agreement with reports of Bedford who also found an extremely active catalyst formed in reaction of orthometallated palladium dimer with PCy₃ [15].



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

On the other hand the stability and, in particular, recyclability of palladacycles formed from phosphito ligands have so far not been tested. Therefore, attempts were undertaken to recover the catalyst and to use it in a second run. Two series of experiments were conducted, in air atmosphere and under N₂, with complexes **1a**, **2a**, **3a** and **4a** (Table 5). The experiment was quite successful, although the cross-coupling product was formed with a lower yield than in the first run, 62–82%, with one exception (40%) for **1a** in air. Interestingly, better results in the second run were obtained under an N₂ atmosphere than in air.

According to the literature, palladacycles undergo ring-opening process in Suzuki-Miyaura conditions to generate catalytically active "underligated" Pd(0) complexes [6]. However in the absence of stabilizing agents, as it is in our conditions, transformation of Pd(0) complexes to Pd(0) nanoparticles seems to be possible. In order to estimate a role of Pd(0) nanoparticles in the Suzuki-Miyaura reaction with phosphito palladium catalysts, the Hg(0) test was performed, using a 200-fold excess of Hg(0) relative to palladium. According to the literature, an inhibiting effect of Hg(0) is expected when Pd(0) nanoparticles or "naked" Pd(0)species catalyze the reaction [3]. It is clear from the data collected in Table 5 that in the first run Hg(0) had no effect and in all reactions the product was formed in high yield (90-100%). Thus, homogeneous reaction pathway was confirmed. For the analysis of the second run the results obtained under N₂ can be considered more representative because decomposition of phosphorus ligands is less plausible under these conditions. In particular, the activity of complex 2a in the second reaction was practically not affected by Hg(0) (69% vs. 68%), indicating the presence of a soluble palladium catalyst. A similar feature we observed earlier for palladium



Scheme 2.

complexes with imidazole ligands [31]. An inhibiting effect of Hg(0) was, however, clearly seen in reactions catalyzed by the orthometallated monomer **4a**. Similarly, a decrease of 2-methylbiphenyl yields was noted when Hg(0) was added to the recovered palladium catalysts **3a** (dimer) and **1a** (trimer).

Thus, it can be concluded that at the end of the catalytic reaction catalyzed by soluble palladium complexes originated from palladacycles, some Pd(0) nanoparticles were formed. However, based on the results of catalytic reactions performed without Hg(0), these nanoparticles can participate in the Suzuki–Miyaura reaction as catalysts or as a source of soluble catalytically active forms [32].

To confirm the presence of Pd(0) nanoparticles, TEM measurements were performed for post-reaction mixtures with 1a as catalyst. Agglomerates of Pd(0) nanoparticles, from 40 to several hundred nanometers in diameter, were observed together with a few nanoparticles of 6-7 nm (Fig. 7).

3. Conclusions

Trimeric palladium complexes with orthometallated triarylphosphito ligands were synthesized for the first time in reaction of PdCl₂ with a phosphite or with PdCl₂P₂ (P = aryl phosphite) compounds. These synthetic procedures enabled us to obtain trimeric palladium complexes regardless of the steric hindrance of the aryl phosphite.

The trimeric compound $[Pd_3(\mu-Cl)_4\{k^2-P,C-P(O-o-CH_3C_6H_3)(O-o-CH_3C_6H_4)_2\}_2]$ and the analogous dimeric complex $[Pd_2(\mu-Cl)_2\{k^2-P,C-P(O-m-CH_3C_6H_3)(O-m-CH_3C_6H_4)_2\}_2]$ were obtained as single crystals suitable for X-ray diffraction analysis. Both structures are characterized by similar geometric parameters. On the other hand, the structure of another dimeric complex, $[Pd_2(\mu-Cl)_2\{k^2-P,C-P(2,4^{-t}Bu_2C_6H_2)(2,4^{-t}Bu_2C_6H_3)_2\}_2]$, revealed that a slight modification of the phosphorus ligand may influence the Pd–Cl bond lengths in the metallacyclic core.

Trimeric palladium complexes exhibited high catalytic activity in C–C bond forming reactions, and the results obtained in the

Table 3 Results of the Suzuki–Miyaura and Hiyama reactions catalyzed by complexes 1a - 1d.

Catalyst	Suzuki–Miyaura		Hiyama	
	Base	Yield (%)	Base	Yield (%)
1a	Cs ₂ CO ₃	94	NaOH	95
1b	Cs ₂ CO ₃	96	NaOH	98
1c	Cs ₂ CO ₃	98	Cs ₂ CO ₃	81
	K ₃ PO ₄	96	K ₃ PO ₄	80
	NaHCO ₃	95	NaHCO ₃	35
	NaOH	97	NaOH	93
1d	Cs ₂ CO ₃	82	NaOH	96

Suzuki—Miyaura reaction were similar to those with the application of dimeric and monomeric palladium complexes with triarylphosphito ligands. This may be explained by the presence of the same catalytically active palladium forms in all systems. Based on the results of the Hg(0) test, the homogeneous mechanism dominated. Palladium exhibited a strong tendency to form polymetallic species, as was also seen in ESI-MS spectra, which finally led to Pd(0) nanoparticles at the end of the catalytic process. Under catalytic reaction conditions, Pd(0) nanoparticles can be solubilized and form catalytically active species.

4. Experimental

The palladium complexes $2\mathbf{a}-\mathbf{c}$ [14,17], $2\mathbf{d}$ [15], $3\mathbf{a}-\mathbf{c}$ [14], and $3\mathbf{d}$ [15] were obtained according to literature methods.

4.1. Trimeric complexes $[Pd_3(\mu_2-Cl)_4\{k^2-P,C-P(OR')(OR)_2\}_2]$ (1a-1d)

Method I. PdCl₂ (1 mmol) was added to the solution of an appropriate phosphite $P(OR)_3$ (0.5 mmol) in toluene (5 mL). The reaction mixture was stirred for 24 h at 130 °C. Next, the solvent was evaporated *in vacuo* and the product was precipitated by the addition of pentane and recrystallized from the CH₂Cl₂/pentane mixture.

Method II. $PdCl_2$ (1 mmol) was added to the solution of an appropriate complex $PdCl_2[P(OR)_3]_2$ (0.5 mmol) in toluene (5 mL). The reaction mixture was stirred for 20 h at 130 °C. Next, the solvent was evaporated *in vacuo* and the product was precipitated



Fig. 5. Results of the Sonogashira reaction catalyzed by the complexes **1a**-**1d** in ionic liquids.



Fig. 6. Kinetic profile of Suzuki–Miyaura reaction catalyzed by $1a,\,2a$ and 3a at 0.1 mol%.

by the addition of pentane and recrystallized from the $CH_2Cl_2/$ pentane mixture.

4.1.1. [Pd3(µ-Cl)4{k2-P,C-P(OC6H4)(OC6H5)2}2], 1a

Yield: 0.20 g, 37%; ¹H NMR (300.1 MHz, CDCl₃): δ 7.8 (d, 2H, H5, orthopalladated ring), 7.3 (t, 10H, H2, J_{H-H} = 8.2 Hz), 7.2 (d, 10H, H1, J_{H-H} = 8.2 Hz), 7.1 (t, 6H, H3, J_{H-H} = 7.4 Hz); ³¹P NMR (202.5 MHz, CDCl₃): 125.4 (*major isomer*), 124.5 (*minor isomer*); ESI-MS(*m*/*z*): 1044 (M - Cl)⁺; found: C 44.08, H 2.87; calcd for C₄₃H₃₆Cl₄O₆P₂Pd₃C: 44.08, H 3.10%.

4.1.2. $[Pd_3(\mu-Cl)_4[k^2-P,C-P(O-m-CH_3C_6H_3)(O-m-CH_3C_6H_4)_2]_2]$, **1b**

Yield: 0.25 g, 43%; ¹H NMR (300.1 MHz, CDCl₃): δ 6.63–7.34 (*m*, 44H, Ph), 2.27 (*s*, 3H, CH₃; *minor isomer*), 2.01 (*s*, 3H, CH₃; *major isomer*); ³¹P NMR (202.5 MHz, CDCl₃): 125.01 (*major isomer*), 122.13 (*minor isomer*); ESI-MS(*m*/*z*): 1128 (M – Cl)⁺; found: C 43.06, H 3.61, Pd 27.4; calcd for C₄₂H₄₀Cl₄O₆P₂Pd₃: C 43.35, H 3.46, Pd 27.9%.

4.1.3. $[Pd_3(\mu-Cl)_4\{k^2-P,C-P(O-o-CH_3C_6H_3)(O-o-CH_3C_6H_4)_2\}_2]$, **1**c

Yield: 0.19 g, 32%; ¹H NMR (300.1 MHz, CDCl₃): δ 6.70–7.40 (*m*, 44H, Ph), 2.30 (s, 3H, CH₃; *major isomer*), 2.25 (s, 3H, CH₃; *minor isomer*) ppm; ³¹P NMR (202.5 MHz, CDCl₃): 121.95 (*major isomer*), 122.89 (*minor isomer*); ESI-MS(*m/z*): 1128 (M – Cl)⁺; found: C 43.51, H 3.49, Pd 27.9; calcd for C₄₂H₄₀Cl₄O₆P₂Pd₃: C 43.35, H 3.46, Pd 28.3%.

 Table 4

 Effect of catalyst concentration in the Suzuki–Miyaura reaction catalyzed by complexes 1a, 2a and 3a.

Catalyst	[2-bromotoluene]/[Pd]	Yield [%]	TON	TOF $[h^{-1}]$
1a	100	96	96	384
	1000	95	950	3800
	2000	88	1760	7040
	10000	64	6400	25600
2a	100	100	100	400
	1000	89	890	3560
	2000	83	1660	6640
	10000	69	6900	27600
3a	100	100	100	400
	1000	86	860	3440
	2000	86	1720	6880
	10000	77	7700	30800
2a 3a	10000 1000 2000 10000 1000 2000 1000 2000 10000	64 100 89 83 69 100 86 86 86 77	100 6400 100 890 1660 6900 100 860 1720 7700	400 3560 6640 27600 400 3440 6880 30800

Reaction conditions: [PhB(OH)₂] 7.5 mmol, [2-bromotoluene] 5 mmol, [Cs₂CO₃] 10 mmol, [ethane-1,2-diol] 10 cm³, 80 $^{\circ}$ C, 15 min.

Table 5

Results of recycling and Hg(0) test in the Suzuki–Miyaura reaction catalyzed by complexes **1a**, **2a**, **3a** and **4a**.

Catalyst/yield %						
	1a	2a	3a	4a		
In air 1st cycle 2nd cycle	98 (97 ^a) 40 (9 ^a)	95 (89 ^a) 62 (2 ^a)	96 (96 ^a) 71 (23 ^a)	93 (95 ^a) 60 (15 ^a)		
<i>In N</i> 2 1st cycle 2nd cycle	98 (95 ^a) 82 (38 ^a)	92 (89 ^a) 69 (68 ^a)	98 (97 ^a) 75 (32 ^a)	100 (100 ^a) 65 (19 ^a)		

Reaction conditions: [Pd] 1 mol%, [PhB(OH)₂] 1.5 mmol, [2-bromotoluene] 1 mmol, [Cs₂CO₃] 2 mmol, [ethane-1,2-diol] 2.5 cm³, 80 °C, 1 h.

^a Yield of product obtained at the presence of Hg(0), [Hg]:[Pd] = 200.

4.1.4. $[Pd_3(\mu-Cl)_4\{k^2-P,C-P(O-2,4-tBu_2C_6H_3)(O-2,4-tBu_2C_6H_4)_2\}_2]$, **1d**

Yield: 0.45 g, 51%; ¹H NMR (300.1 MHz, CDCl₃): (*major isomer*) δ 7.66 (d, ³J_{H-H} = 8.5 Hz, 4H; H6 free ring), 7.53 (d, ⁴J_{H-H} = 8.49 Hz, 2H; H5, orthometallated ring), 7.37 (d, ⁴J_{H-H} 8.49 = Hz, 4H; H3 free ring), 7.33 (br s, 2H; H3, orthometallated ring), 6.89 (dd, ³J_{H-H} = 8.5 Hz, ⁴J_{H-H} 2.5 Hz, 4H; H5 free ring), 1.38 (s, 36H; tBu free ring), 1.33 (s, 18H; tBu orthometallated ring), 1.23 (s, 18H; tBu orthometallated ring); 1.23 (s, 18H; tBu orthometallated ring); 1.23 (s, 18H; tBu orthometallated ring); 1.24 (d, ⁴J_{H-H} = 8.49 Hz, 2H; H5, orthometallated ring); 7.04 (*br* s, 2H; H3, orthometallated ring); 6.95–7.14 (*m*, 12H, Ph, free ring); 1.21 (s, 36H; tBu free ring), 1.18 (s, 36H; tBu free ring), 1.14 (s, 36H; tBu orthometallated ring); ³¹P NMR (202.5 MHz, CDCl₃): 119.27 (*major isomer*), 118.75 (*minor isomer*); found: C 56.63, H 7.26; calcd for C₄₂H₄₀Cl₄O₆P₂Pd₃: C 57.56, H 7.13%.

4.2. Crystallographic data collection and structure determination

Single crystals of **1c**, **2b**, **3b** and **3d** 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-K α radiation ($\lambda = 0.71073$ Å). The structures were subsequently solved using direct methods and developed by full least-squares refinement on F^2 . Structural



Fig. 7. TEM micrograph of the post-reaction mixture after Suzuki–Miyaura reaction with 1a.

Table 6					
Crystallographic data	for 1c ,	2b ,	3b	and	3 d .

	1c	2b	3b	3d
Chemical formula	$C_{42}H_{40}Cl_4O_6P_2Pd_3$	C42H42Cl2O6P2Pd	$C_{42}H_{40}Cl_2O_6P_2Pd_2$	$C_{84}H_{124}Cl_2O_6P_2Pd_2\bullet 3C_7H_8$
Formula Mass	1163.68	882.00	986.38	1851.87
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
a/Å	11.965(4)	12.282(4)	9.464(3)	12.062(4)
b/Å	12.362(4)	12.585(4)	12.294(4)	26.575(8)
c/Å	17.058(5)	15.003(5)	18.036(6)	15.828(5)
$\alpha / ^{\circ}$	70.48(3)	77.86(3)	89.88(3)	90
β/°	69.62(3)	74.21(3)	81.02(3)	96.92(3)
$\gamma/^{\circ}$	77.70(3)	61.95(3)	80.52(3)	90
Unit cell volume/Å ³	2215.8(12)	1960.1(13)	2043.9(12)	5037(3)
Temperature/K	100(2)	100(2)	100(2)	100(2)
Space group	P-1	P-1	P-1	$P2_1/n$
No. of formula units per unit cell, Z	2	2	2	2
Absorption coefficient, μ/mm^{-1}	1.563	0.739	1.135	0.492
No. of reflections measured	20161	24800	25542	48229
No. of independent reflections	10048	8960	9378	11548
No. of parameters	523	484	493	564
R _{int}	0.0489	0.0261	0.0415	0.0310
Final R_1 values $(I > 2\sigma(I))$	0.0442	0.0243	0.0358	0.0277
Final $wR(F^2)$ values $(I > 2\sigma(I))$	0.0831	0.0644	0.0880	0.0701
Final R ₁ values (all data)	0.0855	0.0326	0.0523	0.0361
Final <i>wR</i> (<i>F</i> ²) values (all data)	0.0905	0.0662	0.0923	0.0722
Goodness of fit on F ²	1.037	1.092	1.083	1.038

solution and refinement was carried out using SHELX suite of programs [33]. Analytical absorption corrections were performed with CrysAlis RED [34]. C, 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 [35]. Crystal data and selected details of structure determination are summarized in Table 6.

4.3. Catalytic reactions

4.3.1. Suzuki-Miyaura reaction

Suzuki–Miyaura reactions were carried out in a Schlenk tube with magnetic stirring. Reagents: phenylboronic acid (0.183 g, 1.5 mmol), 2-bromotoluene (0.118 mL, 1 mmol), Cs_2CO_3 (2 mmol), ethane-1,2-diol (2.5 mL) and palladium precatalysts (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 preheated to 80 °C. The reaction was carried out at 80 °C for 2 h and after that time cooled down. The organic products were separated by extraction with hexane (4 mL, 3 mL and 3 mL). The extracts (10 mL) were GC-FID analyzed (Hewlett Packard 5890) with 0.076 mL of dodecane as an internal standard. The products were identified by GC–MS (Hewlett Packard 5971A).

4.3.2. Hiyama reaction

Hiyama reactions were carried out in a Schlenk tube with magnetic stirring. Reagents: triethoxysilane (0.26 mL, 1.1 mmol), 2-bromotoluene (0.118 mL, 1 mmol), NaOH (2 mmol), ethane-1,2-diol (2.5 mL) and palladium precatalysts (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 that time cooled down. The organic products were separated by extraction with hexane (4 mL, 3 mL and 3 mL). The extracts (10 mL) were GC-FID analyzed (Hewlett Packard 5890) with 0.076 mL of dodecane as an internal standard. The products were identified by GC-MS (Hewlett Packard 5971A).

4.3.3. Sonogashira reaction

Sonogashira reactions were carried out in a Schlenk tube with magnetic stirring. Reagents: iodobenzene (0.11 mL, 1 mmol), phenylacetylene (0.11 mL, 1 mmol), Et₃N (0.26 mL, 1.9 mmol), ionic liquid (1.5 mL) and palladium precatalyst (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 that time the Schlenk tube was cooled down. The organic products were separated by extraction with hexane (4 mL, 3 mL and 3 mL). The extracts (10 mL) were GC-FID analyzed (Hewlett Packard 5890) with 0.05 mL of mesitylene as an internal standard. The products were identified by GC–MS (Hewlett Packard 5971A).

Acknowledgment

Financial support of the Polish Ministry of Science and Higher Education (N164/COST/2008) and COST D40 are gratefully acknowledged.

Appendix A. Supplementary material

CCDC 820370, 820371, 820372 and 820373 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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