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Amidophosphine-stabilized palladium complexes catalyse Suzuki–Miyaura cross-couplings in aqueous media

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We report a simple and efficient procedure for Suzuki–Miyaura reactions in aqueous media catalysed by amidophosphine-stabilized palladium complexes *trans*-{L^3PPh_2}$_2PdCl_2$ (3), *trans*-{$L^3PPhtBu$}$_2PdCl_2$ (4), [Pd(η^3-C_3H_5)(L^3PPh_2)Cl] (5) and {Pd[2-(Me_2NCH_2)C_6H_4](L^3PPh_2)Cl} (6). The acidity of the NH proton in complexes 3–6 plays an important role in their catalytic activity. In addition, the palladium complexes *cis*-{L^1PPh_2}$_2PdCl_2$ (1) and *trans*-{L^2PPh_2}$_2PdCl_2$ (2) stabilized by phosphines containing Y,C, Y-chelating ligands $L^{1,2}$ have also been found to be useful catalysts for Suzuki–Miyaura reactions in aqueous media. The method can be effectively applied to both activated and deactivated aryl bromides yielding high or moderate conversions. The catalytic activity of couplings performed in pure water increases when utilizing a Pd complex with more acidic NH protons. A decrease of palladium concentration from 1.0 to 0.5 mol% does not lead to a substantial loss of conversion. In addition, Pd complex 1 can be efficiently recovered using two-phase system extraction. Copyright © 2016 John Wiley & Sons, Ltd.

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Keywords: aqueous media; palladium; Suzuki–Miyaura; C C coupling

Introduction

The palladium-catalysed Suzuki–Miyaura cross-coupling reaction between organoboron compounds and organic halides is a very powerful tool for forming carbon–carbon bonds[1–3] and this makes the Suzuki–Miyaura reaction very important not only in academic research but also in industrial synthesis of fine chemicals[4–7] and highly complex pharmaceuticals[8] as well as in the synthesis of functionalized π-conjugated systems.[9] The wide application of the reaction results from the broad functional group tolerance, the commercial availability and low toxicity of the organoborons, and the mild reaction conditions applied.[10] Research in the field of the palladium-catalysed Suzuki–Miyaura cross-coupling reaction is focused on so-called green chemistry, that includes the possibility of using water as a solvent.[11–15] However, an efficient Suzuki–Miyaura protocol in aqueous media is often restricted due to limited solubility and the decreased stability of the catalyst in water.[16–18] Therefore, a way to improve the efficiency of Suzuki–Miyaura catalysis in water is by the employment of hydrophilic ligands.[19–24]

We have recently prepared the Pd complexes *cis*-{L^1PPh_2}$_2PdCl_2$ (**1**) and *trans*-{L^2PPh_2}$_2PdCl_2$ (**2**) containing different Y,C,Y pincer-type ligands L^1 (2,6-(Me_2NCH_2)$_2C_6H_3$)$^-$ and L^2 (2,6-(tBuOCH$_2$)$_2C_6H_3$)$^-$ (Fig. 1).[25] Recently, Baysal and co-workers reported the synthesis of *cis*-{L^3PPh_2}$_2PdCl_2$, where L^3 is (2,6-iPr$_2$(C_6H_3)NH)$^-$ (Fig. 1), and showed its suitability for Suzuki–Miyaura cross-coupling reactions.[26] Ligand L^3 with NH moiety and similarly the presence of the NMe_2 functional group in **1** could be suitable for two-phase system extraction, while **2** contains OtBu group that may render the complex soluble in water.

We therefore decided to expand the number of amidophosphine-stabilized palladium complexes and prepared the following complexes: *trans*-{L^3PPh_2}$_2PdCl_2$ (**3**), *trans*-{L^3PPh(tBu)}$_2PdCl_2$ (**4**), [Pd(η^3-C_3H_5)(L^3PPh_2)Cl] (**5**) and {Pd[2-(Me_2NCH_2)C_6H_4](L^3PPh_2)Cl} (**6**). As the phosphines L^3PPh_2 and $L^3PPh(tBu)$ contain the NH functionality potentially suitable for two-phase system extraction, we started with the testing of all the complexes **1**–**6** in the Suzuki–Miyaura cross-coupling reaction in aqueous media. A decrease of the palladium concentration from 1.0 to 0.5 mol% does not show substantial loss of conversion. Among complexes **3**–**6**, it turns out that the catalytic activity of couplings in water increases when utilizing Pd complex **6** with more acidic NH protons. The possible recovery of **1** from water has also been tested and it is demonstrated that Pd complex **1** can be efficiently recovered by two-phase system extraction to give water-soluble complex **7**.

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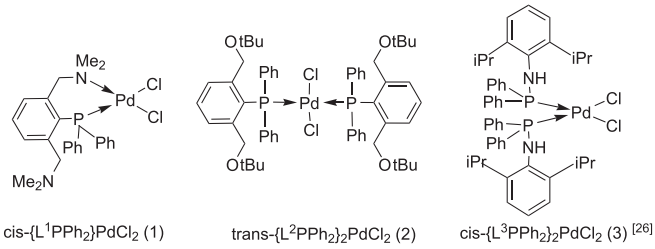


Figure 1. Potentially suitable complexes for two-phase system extraction.

Results and discussion

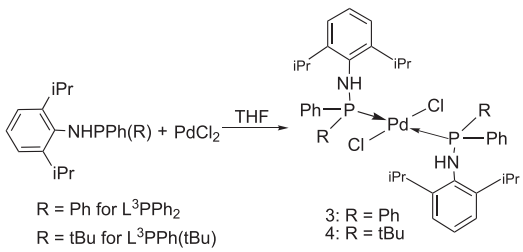
Synthesis and characterization of complexes 1–6

Complexes **1** and **2** were prepared according to the literature.[25] Complexes **3** and **4**, obtained by the reaction of $PdCl_2$ with L^3PPh_2 and $L^3PPh(tBu)$ (Scheme 1) were prepared to study the effect of the steric shielding of the phosphorus atom on the catalytic activity. It is worth mentioning that *cis*-$\{L^3PPh_2\}_2PdCl_2$ has already been prepared by the reaction of L^3PPh_2 with $(cod)PdCl_2$,[26] but the structure of the complex has not been determined so far.

The ^{31}P NMR spectra of **3** and **4** show a signal at 61.8 ppm (**3**) and 69.9 ppm (**4**) that is shifted downfield compared to starting phosphines L^3PPh_2 (45.5 ppm)[26] and $L^3PPh(tBu)$ (54.9 ppm). The ^{31}P NMR signal found for **3** is similar to that of its *cis*-isomer *cis*-$\{L^3PPh_2\}_2PdCl_2$ (64.1 ppm).[26] The ^1H NMR spectra of **3** and **4** show the presence of four doublets at 0.88, 1.03, 1.23 and 1.34 ppm of CH_3 groups of ligand L^3 in **3** (1.01, 1.16, 1.23 and 1.46 ppm for **4**) and two septets of *CH* groups at 3.24 and 3.43 ppm in **3** (3.81 and 3.86 ppm in **4**). The ^1H NMR spectra also reveal the doublet of the P N*H* group of ligand L^3 in **3** at 5.76 ppm (5.57 ppm for **4**) with coupling constant $^2J(^{31}P, ^1H) = 6$ Hz for **3** ($^2J(^{31}P, ^1H) = 5$ Hz for **4**) that is shifted downfield when compare to the value found in free phosphine L^3PPh_2 (3.78 ppm)[26] and $L^3PPh(tBu)$ (4.08 ppm). The data also differ from those found for *cis*-$\{L^3PPh_2\}_2PdCl_2$[26] where one doublet at 1.17 ppm of CH_3 groups, one septet of *CH* groups of the iPr moiety at 3.09 ppm and the doublet of the P N*H* group of ligand L^3 at 6.10 ppm are observed. The data, however, suggest the existence of highly symmetric arrangement of the Pd atom in **3** and **4**. To establish unambiguously the structure of prepared complexes, X-ray structural analysis of complex **3** was carried out.

Single crystals of **3** suitable for X-ray diffraction analysis were obtained from saturated Et_2O–hexane solution. The molecular structure of **3** is shown in Fig. 2. The crystal data and structure refinement are given in Table 1.

The coordination number of the Pd atom in **3** is four with mutually *trans* coordinated phosphines L^3PPh_2 and chlorine atoms Cl1 and Cl1a. The P1-N1 bond distance (1.6901(14) Å) varies between



Scheme 1. Synthesis of complexes *trans*-$\{L^3PPh(R)\}_2PdCl_2$ (R = Ph (**3**); *t*Bu (**4**)).

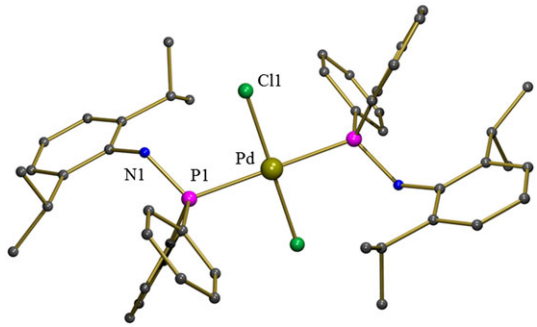


Figure 2. PovRay view of **3**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Pd1–Cl1 2.3014(8), Pd1–P1 2.3124(4), P1–N1 1.6901(14), Cl1–Pd1–P1 89.70(1).

the P-N single bond (Σ_{cov} P,N = 1.73 Å)[27] and P=N double bond (Σ_{cov} P,N = 1.63 Å)[27] and is longer than in $[(Ph_2P\,S)NHC_6H_4$–4-$CH(CH_3)_2]$ (1.6603(18) Å),[26] where lone electron pair of phosphorus atom is used in P=S covalent bond instead of P→Pd donation in **3**. The NH protons are involved in hydrogen bonding with Cl atoms with NH Cl bond distance of 3.193 Å.

Complexes **5** and **6** were prepared by the cleavage reaction of dimeric $[(\eta^3\text{-}C_3H_5)Pd\text{-}(\mu\text{-}Cl)]_2$ and $[\{2\text{-}(Me_2NCH_2)C_6H_4\}Pd\text{-}(\mu\text{-}Cl)]_2$ by phosphine L^3PPh_2 (Scheme 2).

The ^{31}P NMR spectra of **5** and **6** show a signal at 61.5 ppm (**5**) and 71.9 ppm (**6**) that is shifted downfield when compared to the starting phosphine L^3PPh_2 (45.5 ppm).[26] The ^1H NMR spectra of **5** and **6** show the presence of a doublet at 0.91 ppm of CH_3 groups in **5** (0.89 in **6**) and signals of *CH* groups at 3.24 ppm of iPr moiety of ligand L^3 in **5** (3.81 in **6**). The ^1H NMR spectra also reveal the doublet of the P N*H* group of ligand L^3 at 4.33 ppm in **5** (6.40 ppm in **6**) with coupling constant $^2J(^{31}P, ^1H) = 6$ Hz for **5** ($^2J(^{31}P, ^1H) = 7$ Hz for **6**) that is shifted downfield when compared to that found for free phosphine L^3PPh_2 (3.78 ppm).[26] In addition, the signals at 1.14, 2.36, 3.29 and 4.46 ppm define the presence of the $Pd(\eta^3\text{-}C_3H_5)$ group in **5**.

The ^1H NMR data thus provide evidence of different acidity of PN*H* atom in the Pd(II) complexes **3**–**6** and define decreasing acidity of N*H* atom in the sequence **6** > **3** > **4** > **5**. Since complex **2** is partially soluble in water due to the presence of the ethereal O*t*Bu groups and complexes **1**, **3**–**6** contain functional groups potentially suitable for two-phase system extraction, we started with the testing of all the complexes **1**–**6** in Suzuki–Miyaura cross-coupling reactions in aqueous media.

Catalytic activity of 1–6 in Suzuki–Miyaura cross-coupling reactions in aqueous media

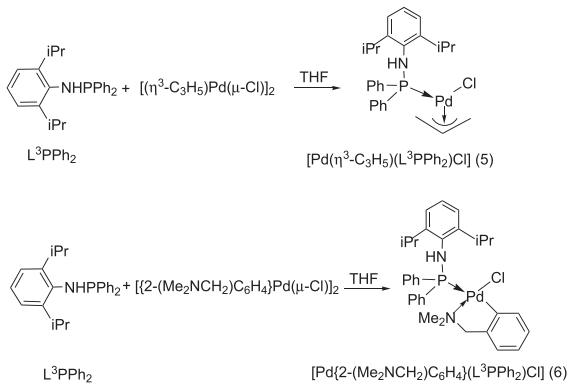
All prepared Pd(II) complexes **1**–**6** were used as catalysts in the Suzuki–Miyaura[28–33] reaction between 4-nitrobenzene bromide and phenylboronic acid (Scheme 3). The cross-coupling reactions were carried out under aqueous conditions (EtOH–water or water) involving Pd(II) catalysts **1**–**6** (1 mol%)/Na_2CO_3 system under argon.[34,35] The reactions were monitored using GC analysis and the results are summarized in Table 2. Commercially available $[(PPh_3)_2PdCl_2]$ was used as a standard.

The systems EtOH–H_2O in 4:1 and 2:1 ratios and pure water were tested as aqueous media. 4-Nitrobiphenyl is detected as a major product in all tested aqueous media. As a general trend, compound **5** with weakly acidic NH group shows lower catalytic activity in pure

Table 1. Crystal data and structure refinement for **3** and **7**·H_2O·0.5EtOH

	3	**7**·H_2O·0.5EtOH
Empirical formula	$C_{48}H_{56}Cl_2N_2P_2Pd$	$C_{24}H_{30}Cl_2N_2PPd·H_2O·0.5C_2H_6O$
Colour	Yellow	Yellow
Crystal system	Triclinic	Triclinic
Space group	P_{-1}	P_{-1}
a (Å)	9.5870(4)	13.7651(12)
b (Å)	11.1420(4)	14.7880(10)
c (Å)	11.7201(5)	15.1400(10)
α (°)	82.641(3)	72.578(5)
β (°)	69.695(4)	74.261(5)
γ (°)	74.079(3)	75.084(4)
Z	1	2
μ (mm^{-1})	0.635	1.037
D_x (Mg m^{-3})	1.325	1.510
Crystal size (mm)	0.48 × 0.33 × 0.21	0.46 × 0.36 × 0.18
Crystal shape	Block	Block
θ range (°)	1.9–27.5	1.4–27.5
T_{min}, T_{max}	0.873, 0.958[a]	0.688, 0.861[a]
No. of reflections measured	22 068	57 780
No. of unique reflections; R_{int}	5162; 0.0356	12 705; 0.0364
No. of observed ref. [$I > 2\sigma(I)$]	4659	10 195
No. of parameters	250	614
Final R^b [$I > 2\sigma(I)$]	0.0232	0.0446
$wR2^b$ (all data)	0.0586	0.1248

[a]Correction by SORTAV program.
[b]Definitions: $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = \left[\sum w\left(F_o^2 - F_c^2\right)^2/\sum w\left(F_o^2\right)^2\right]^{1/2}$, $S = \left[\sum w\left(F_o^2 - F_c^2\right)^2/\left(N_{reflns} - N_{params}\right)\right]^{1/2}$, weighting scheme $w = [\sigma^2(F_o^2) + (w_1P) + w_2P]^{-1}$, $P = [\max(F_o^2, 0) + 2F_c^2]/3$, $R_{int} = \sum\left|F_o^2 - F_o^2(\text{mean})\right|/\sum F_o^2$ (summation is carried out only where more than one symmetry equivalent is averaged).

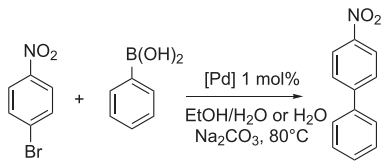


Scheme 2. Synthesis of compounds **5** and **6**.

Table 2. Catalytic activity of **1**–**6** in Suzuki–Miyaura cross-coupling reactions in aqueous media

Catalyst	EtOH–H_2O (4:1)	EtOH–H_2O (2:1)	H_2O
	Conversion (%)[a]		
$[(PPh_3)_2PdCl_2]$	100	97	96
1	95	97	99
2	97	99	99
3	99	95	98
4	99	96	99
5	97	97	76
6	99	99	99

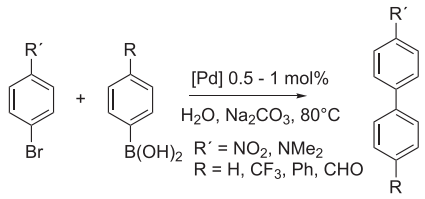
[a]Calculated from GC-MS analysis.



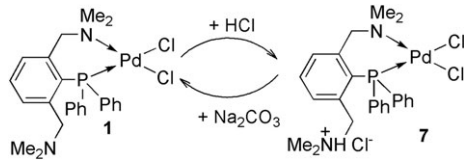
Scheme 3. Suzuki–Miyaura cross-coupling reaction in aqueous media.

water than the other complexes, and, as a result, complex **5** was not tested further.

Therefore, complexes **1**–**4** and **6** were used as the catalysts in the Suzuki–Miyaura reaction[28–33] between 4′-substituted phenyl bromides and 4-substituted phenylboronic acids (Scheme 4). The cross-coupling reactions were carried out in water with 1.0 mol% of the palladium complexes. The reactions were monitored using GC analysis and the results are summarized in Table 3. Commercially available $[(PPh_3)_2PdCl_2]$ was used as a standard (for the results of the Suzuki–Miyaura reaction between 4-chlorobenzonitrile and



Scheme 4. Suzuki–Miyaura cross-coupling reactions in water.



Scheme 5. Synthesis of ionic Pd complex **7** and its regeneration to neutral compound **1**.

phenylboronic acid, see Scheme S1 and Table S1 in the supporting information).

Aryl bromides featuring either electron-donating (NMe_2) or electron-withdrawing (NO_2) substituents were screened. 4,4′-Disubstituted biphenyls are detected as major products in all cases. As a general trend, compounds **1**–**4** and **6** show higher catalytic activities in all examined reactions than commercially available $[(PPh_3)_2PdCl_2]$. Similarly, complex **1** having *cis* arrangement of chlorine atoms shows lower catalytic activities in all examined reactions than complexes **2**–**4** having *trans* arrangement. Complex **4** featuring bulkier phosphine L^3PPh(*t*Bu) shows higher catalytic activity than **3**. As expected, the Suzuki–Miyaura reaction carried out with the electron-rich *N*,*N*-dimethyl-4-bromoaniline affords lower yields of between 62 and 75%, with the highest activity observed for complex **6** where corresponding turnover number (TON) and turnover frequency (TOF) are 75 and 6.3 h^{-1} (0.1 mol% Pd, 75% yield at 80°C for 6 h, see Table S2 in supporting information). Decrease of palladium concentration from 1.0 to 0.5 mol% does not show a substantial loss of conversion (Table 3). Calculated TON (198) and TOF (33 h^{-1}) (0.05 mol% of **1**, 99% yield at 80°C for 6 h, see Table S2 in supporting information) are, however, lower than those reported in Suzuki–Miyaura coupling reactions catalysed by Pd hybrid on graphene oxide.[11,12]

Two-phase separation of 1: synthesis of 7

The possible recovery of **1**-**6** from water was also tested. These attempts were successful for compound **1** only. The aqueous phase was acidified using HCl to pH around 5 after the Suzuki–Miyaura reaction followed by extraction with EtOAc. The organic layers were dried and subjected to GC analysis, while the aqueous phase was evaporated. The residue was dissolved in D_2O and characterized using ^{31}P NMR spectroscopy, where a signal at 18.4 ppm is detected and assigned to complex **7**. Compound **7** can be also prepared by the reaction of **1** with 1 eq. of HCl (Scheme 5) and it was characterized using NMR spectroscopy in D_2O and the structure was determined using X-ray diffraction analysis.

The ^{31}P NMR spectrum of **7** shows a signal at 18.4 ppm which is comparable with the signal found for neutral complex **1** (19.4)[25] but is shifted downfield when compared with the free phosphine L^1PPh_2 (16.5 ppm).[25] The ^{1}H NMR spectrum of **7** reveals an AB spin system (δ_A 3.25, δ_B 3.75) with J_{AB} being 12 Hz and a broad singlet at 4.19 ppm for CH_2N groups and two signals at 2.73 and 2.76 ppm for the CH_3 groups of ligand L^1. In addition, the ^{1}H NMR spectrum also reveals a signal of NH group at 4.28 ppm. This pattern indicates the presence of two inequivalent CH_2NMe_2 moieties. While the first one coordinates the palladium atom to provide P,N-chelating mode of phosphine L^1PPh_2 similar to **1**, the second CH_2NMe_2 group is protonated to give CH_2NHMe_2 moiety in **7**. As a result, the palladium ionic compound **7** consisting of *cis*-{[2-(Me_2NHCH_2)-6-(Me_2NCH_2)C_6H_3]Ph_2P}$PdCl_2$ cation and chloride anion is properly soluble in water.

The molecular structure of **7** was also confirmed using X-ray diffraction techniques and is depicted in Fig. 3 together with selected bond distances and angles. The crystal data and structure refinement are given in Table 1.

The coordination number of Pd(II) is four in **7** with mutual *cis* arrangement of phosphorus P1 and nitrogen N1 of the (k_2NP)-coordinated phosphine L^1PPh_2 and chlorine Cl1 and Cl2 atoms in **7**. The *cis* atoms define angles of P1–Pd1–N1 = 94.14(12)° and Cl1–Pd1–Cl2 = 87.32(4)°, and there is a distortion of ideal square-planar geometry resulting from the ring strain of the six-membered metallacycle Pd1–P1–C1–C2–C7–N1. The Pd1-P1 bond distance in **7** of 2.2522(10) Å is similar to those observed in phosphine and phosphite complexes of Pd(II) (2.2–2.4 Å)[36–49] and in neutral complex **1** (2.2543(9) Å).[25] The value of Pd1-N1 bond length being 2.097(3) Å defines a strong coordination of N to Pd atom and is comparable to those found in similar monomeric N-coordinated Pd complexes (2.073–2.155 Å).[43–55] The second nitrogen atom N2 of L^1PPh_2 is protonated providing palladium cation *cis*-{[2-

Table 3. Catalytic activity of **1**–**4** and **6** in Suzuki–Miyaura cross-coupling reactions in H_2O

Catalyst	R′ = NO_2, R = CF_3	R′ = NO_2, R = Ph	R′ = NO_2, R = CHO	R′ = NO_2, R = H	R′ = NMe_2, R = H	R′ = NO_2, R = H
	Conversion (%)[a]					
$[(PPh_3)_2PdCl_2]$	47	35	34	96	19	46[b]
1	65	72	71	99	62	99[b]
2	88	85	89	99	65	96[b]
3	81	81	89	98	69	90[b]
4	84	88	93	99	67	93[b]
6	83	83	81	99	75	91[b]

[a]Calculated from GC-MS analysis.
[b]0.5 mol% of palladium complex.

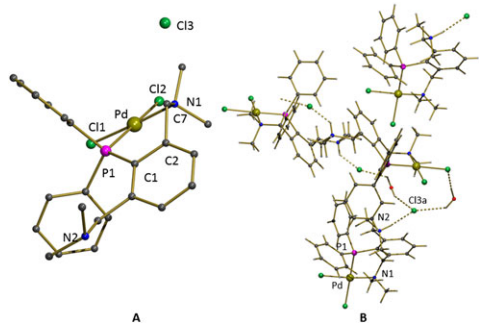


Figure 3. (A) PovRay view of **7**. Hydrogen atoms, H_2O and ethanol molecules are omitted for clarity. Selected bond distances (Å) and angles (°): Pd1–N1 2.097(3), Pd1–P1 2.2522(10), Pd1–Cl1 2.3038(10), Pd1–Cl2 2.3749(11), N1–Pd1–P1 94.14(10), N1–Pd1–Cl1 177.65(10), P1–Pd1–Cl1 86.59(4), N1–Pd1–Cl2 92.00(10), P1–Pd1–Cl2 173.77(4), Cl1–Pd1–Cl2 87.32 (4). (B) Hydrogen bonding in the crystal structure of **7**.

(Me_2NHCH_2)-6-$(Me_2NCH_2)C_6H_3]Ph_2P\}PdCl_2$, that is compensated by Cl^- anion. The Me_2NH atom is also involved in hydrogen bonding with the chloride anion of another molecule of **7** (Fig. 3).

Complex **7** as a water-soluble Pd complex was also tested as a catalyst in the Suzuki–Miyaura reaction between 4′-substituted phenyl bromides and 4-substituted phenylboronic acids (Scheme 4) in water involving Pd(II) catalyst **7** (1%)/Na_2CO_3 system under argon. The reactions were monitored using GC analysis and the results are similar to those for the neutral precursor **1** (Table 3). These results may suggest an easy regeneration of complex **1** from **7** under these conditions (water solution of Na_2CO_3; Scheme 5).

Conclusions

In summary, we report a simple and efficient procedure for Suzuki–Miyaura reactions catalysed by palladium complexes **1**–**6** containing functional groups potentially useful for two-phase system extraction. In this study, aqueous media and green solvents were used instead of toxic organic solvents. It was demonstrated that the NH proton acidity in amidophosphine-stabilized Pd complexes **3**–**6** may tune their catalytic activity (Scheme S3 in supporting information). Complex **4** featuring bulkier phosphine $L^3PPh(tBu)$ showed higher catalytic activities than analogous compound **3** containing phosphine L^3PPh_2. In addition, palladium complexes **1** and **2** stabilized by phosphines containing Y,C,Y-chelating ligands $L^{1,2}$ have also been found to be useful catalysts for Suzuki–Miyaura reaction in aqueous media. The method can be effectively applied to both activated and deactivated aryl bromides yielding high or moderate conversions. Decrease of palladium concentration from 1.0 to 0.5 mol% did not show substantial loss of conversion. The possible recovery of **1**–**6** from water has also been tested. These attempts were successful for compound **1** only. Therefore, the aqueous phase containing complex **1** was acidified by HCl to pH around 5 and the presence of an ionic complex **7** was observed. Compound **7** was quantitatively prepared by the reaction of **1** with 1 eq. of HCl and was characterized using NMR spectroscopy in D_2O and X-ray diffraction analysis. These data provided evidence of the ionic nature of **7** consisting of *cis*-{[2-(Me_2NHCH_2)-6-$(Me_2NCH_2)C_6H_3]Ph_2P\}PdCl_2$ cation and chloride anion. Catalytic activity of **7** is similar to that of its neutral precursor **1** due to an easy regeneration of complex **1** from **7** under basic conditions (water solution of Na_2CO_3). Studies of possible separation of **7** for testing in consecutive runs are of our current interest.

Experimental

General methods

Starting phosphine L^3PPh_2 and compounds **1** and **2** were synthesized according to the literature.[25,26,56] Starting $PdCl_2$, di-μ-chloro-bis(η^3-allyl)dipalladium(II) and di-μ-chloro-bis[2-[(*N*,*N*-dimethylamino)methyl]phenyl-C,N]dipalladium(II) were purchased from Sigma Aldrich and used as received. Starting Ph_2PCl and (*t*Bu)PhPCl were purchased from ABCR and used as received. All reactions were carried out under argon atmosphere, using standard Schlenk techniques. Solvents were dried by standard methods and distilled prior to use. ^1H NMR, ^{13}C NMR and ^{31}P NMR spectra were acquired with a Bruker Avance 500 spectrometer in C_6D_6 or D_2O. Appropriate chemical shifts were calibrated on: ^1H, residual peak of C_6D_6 (7.15 ppm); ^{13}C, residual peak of C_6D_6 (128.00 ppm); ^{31}P, external H_3PO_4 (0.00 ppm).

Preparation of $L^3PPh(tBu)$

An amount of 2.6 ml of 1.6 M *n*-BuLi was added dropwise to an Et_2O (10 ml) solution of L^3H (0.75 g, 4.2 mmol) at −80°C and the solution was stirred for 30 min at room temperature. (*t*Bu)PhPCl (0.80 ml, 4.2 mmol) was added to the resulting Et_2O solution (10 ml) of L^3Li precooled to −80°C and stirred for an additional 3 h. The suspension was filtered and Et_2O solution was evaporated to give a light yellow oil of $L^3PPh(tBu)$. Yield 1.6 g (87%). ^1H NMR (C_6D_6, 500 MHz, δ, ppm): 1.01 (s, 9H, ^tBu), 1.69 (d, 12H, J_{H-H} = 6.8 Hz, $CHCH_3$), 3.58 (m, 2H, $CHCH_3$), 4.08 (d, 1H, N*H*), 6.82 (t, 1H, J_{H-H} = 6.8 Hz, Ar*H*), 6.98–7.25 (m, 4H, Ar*H*), 7.41 (d, 2H, J_{H-H} = 6.8 Hz, Ar*H*), 7.54 (t, 1H, J_{H-H} = 6.8 Hz, Ar*H*); ^{31}P NMR (C_6D_6, 202 MHz, δ, ppm): 54.9. Anal. Calcd for $C_{22}H_{32}NP$ (341.47) (%): C, 77.38; H, 9.45. Found (%): C, 77.42; H, 9.47.

Preparation of *trans*-{$(L^3PPh_2)_2PdCl_2$} (3)

$PdCl_2$ (0.2 g, 1.1 mmol) was added to a solution of L^3PPh_2 (0.79 g, 2.20 mmol) in tetrahydrofuran (THF; 20 ml) and the suspension was stirred for 1 day. The suspension was filtered and the solvent evaporated. The resulting orange solid was washed with hexane (3 ml) to afford a yellow-orange powder of **3**. Yield 0.93 g (94%); m.p. 249–250°C. ^1H NMR (C_6D_6, 500MHz, δ, ppm): 0.88 (d, 3H, J_{H-H} = 6.8 Hz, CH_3), 1.03 (d, 3H, J_{H-H} = 6.8 Hz, CH_3), 1.23 (d, 3H, J_{H-H} = 6.8 Hz, CH_3), 1.34 (d, 3H, J_{H-H} = 6.8 Hz, CH_3), 3.24 (m, 1H, C*H*), 3.43 (m, 1H, C*H*), 5.76 (d, 1H, N*H*, J_{H-P} = 6 Hz), 6.93–7.15 (m, 3H, Ar*H*), 7.21–7.32 (m, 6H, Ar*H*) 7.45–7.58 (m, 4H, Ar*H*). ^{13}C NMR (C_6D_6, 125 MHz, δ, ppm): 23.8 ($CH(CH_3)_2$), 24.3 ($CH(CH_3)_2$), 26.4 ($CH(CH_3)_2$), 28.1 ($CH(CH_3)_2$), 146.5 (C-1), 136.2 (C-2 and C-6), 124.4 (C-3 and C-5), 122.8 (C-4), 136.6 (d, J_{31P13C} = 46.3 Hz, *i*-carbons of phenyls), 133.2 (d, J_{31P13C} = 15.0 Hz, *o*-carbons of phenyls), 131.4 (s, *p*-carbons of phenyls), 125.9 (d, J_{31P13C} = 10.0 Hz, *m*-carbons of phenyls). ^{31}P NMR ($CDCl_3$, 202 MHz, δ, ppm): 61.8. Anal. Calcd for $C_{48}H_{56}N_2Cl_2P_2Pd$ (900.27) (%): C, 64.04; H, 6.27. Found (%): C, 63.49; H, 6.04.

Preparation of *trans*-{[(L^3PPh(tBu)]$_2$PdCl$_2$} (4)

$PdCl_2$ (0.2 g, 1.1 mmol) was added to a solution of L^3PPh(*t*Bu) (0.75 g, 2.20 mmol) in THF (20 ml) and the suspension was stirred for 1 day. The suspension was filtered and the solvent evaporated. The resulting orange solid was washed with hexane (3 ml) to afford an orange powder of **4**. Yield 0.95 g (94%); m.p. 219–220°C. ^{1}H NMR (C_6D_6, 500MHz, δ, ppm): 1.01 (d, 3H, J_{H-H} = 6.6 Hz, CH_3), 1.16 (d, 3H, J_{H-H} = 6.6 Hz, CH_3), 1.23 (d, 3H, J_{H-H} = 6.6 Hz, CH_3), 1.28 (d, 9H, J_{H-P} = 7 Hz, CH_3(^{t}Bu)), 1.46 (d, 3H, J_{H-H} = 6.6 Hz, CH_3), 3.81 (m, 1H, *CH*), 3.86 (m, 1H, *CH*), 5.57 (d, 1H, J_{H-P} = 5 Hz, N*H*), 6.98–7.19 (m, 3H, Ar*H*), 7.21–7.32 (m, 3H, Ar*H*) 7.41–7.56 (m, 2H, Ar*H*). ^{13}C NMR (C_6D_6, 125 MHz, δ, ppm): 23.7 (CH(CH_3)$_2$), 24.3 (CH(CH_3)$_2$), 24.4 (CH(CH_3)$_2$), 28.1 (CH(CH_3)$_2$), 28.4 (C(CH_3)$_3$), 29.7 (d, $C(CH_3)_3$ d, J_{31P13C} = 46.3 Hz), 147.5 (C-1), 135.6 (C-2 and C-6), 123.4 (C-3 and C-5), 126.9 (C-4), 135.6 (d, J_{31P13C} = 42.5 Hz, *i*-carbons of phenyls), 132.2 (d, J_{31P13C} = 10.0 Hz, *o*-carbons of phenyls), 130.4 (s, *p*-carbons of phenyls), 126.9 (d, J_{31P13C} = 11.0 Hz, *m*-carbons of phenyls). ^{31}P NMR (C_6D_6, 202 MHz, δ, ppm): 69.9. Anal. Calcd for $C_{44}H_{64}Cl_2N_2P_2Pd$ (860.26) (%): C, 61.43; H, 7.50. Found (%): C, 61.48; H, 7.54.

Preparation of [Pd(η^3-C_3H_5)(L^3PPh$_2$)Cl] (5)

Di-μ-chlorobis(η^3-allyl)dipalladium(II) (0.23 g, 0.62 mmol) was added to a solution of L^3PPh_2 (0.44 g, 1.23 mmol) in CH_2Cl_2 (15ml) and the mixture was stirred for 1 day. Cloudy solution was filtrated, the solvent was evaporated and the solid residuum was washed with hexane (5 ml) to afford yellow crystals of **5**. Yield 0.60 g (89%); m.p. 139–141°C. ^{1}H NMR (C_6D_6, 500MHz, δ, ppm): 0.91 (d, 12H, J_{H-H} = 6.8 Hz, CH_3), 1.14 (d, 1H, J_{H-H} = 5.5 Hz, CH_2(anti)), 2.36 (d, 1H, J_{H-H} = 5.5 Hz, CH_2(anti)), 3.29 (d, 1H, J_{H-H} = 5.5 Hz, CH_2 (syn)), 3.42 (m, 2H, *CH*), 4.33 (s, 1H, J_{H-P} = 6 Hz, N*H*), 4.46 (d, 1H, J_{H-H} = 5.5 Hz, CH_2(syn)), 4.75–4.81 (m, 1H, *CH* (allyl)), 6.88 (d, 2H, J_{H-H} = 6.8 Hz, Ar*H*), 6.99–7.03 (m, 6H, Ar*H*), 7.15–7.26 (m, 5H, Ar*H*). ^{13}C NMR (C_6D_6, 125 MHz, δ, ppm): 23.9 (CH(CH_3)$_2$), 29.2 (*C*H(CH_3)$_2$), 57.2 (C_{term}(allyl)), 77.2 (C_{term}(allyl)), 110.1 (C_{meso}(allyl)), 147.4 (C-1), 136.9 (C-2 and C-6), 128.3 (C-3 and C-5), 123.5 (C-4), 130.6 (d, J_{31P13C} = 45.3 Hz, *i*-carbons of phenyls), 128.2 (d, J_{31P13C} = 16.0 Hz, *o*-carbons of phenyls), 127.9 (s, *p*-carbons of phenyls), 126.6 (d, J_{31P13C} = 12.0 Hz, *m*-carbons of phenyls). ^{31}P NMR (C_6D_6, 202 MHz, δ, ppm): 61.6. Anal. Calcd for $C_{27}H_{33}ClNPPd$ (544.41) (%): C, 59.57; H, 6.11. Found (%): C, 59.82; H, 6.45.

Preparation of {Pd[2-(Me_2NCH_2)C_6H_4](L^3PPh$_2$)Cl} (6)

Di-μ-chlorobis[2-[(dimethylamino)methyl]phenyl-C,N]dipalladium (II) (0.6 g, 1.1 mmol) was added to a solution of L^3PPh_2 (0.77 g, 2.1 mmol) in CH_2Cl_2 (15 ml) and the mixture was stirred for 1 day. Cloudy solution was filtrated, the solvent was evaporated and the resulting product was washed with pentane (7 ml) to afford yellow crystals of **6**. Yield 1.25 g (92%); m.p. 141.3–143.1°C. ^{1}H NMR (C_6D_6, 500 MHz, 300 K, δ, ppm): 0.89 (d, 12H, J_{H-H} = 6.2 Hz, CH_3), 2.88 (d, 6H, J_{H-P} = 6.8 Hz, NCH_3), 3.39 (m, 2H, *CH*), 4.04 (d, 2H, J_{H-P} = 6.8 Hz, CH_2N), 6.25–6.32 (m, 4H, Ar*H*), 6.40 (s, 1H, J_{H-P} = 7 Hz, N*H*), 6.88–7.04 (m, 5H, Ar*H*), 7.26–7.48 (m, 4H, Ar*H*), 7.72 (dd,4H, J_{H-H} = 6.2 Hz, Ar*H*). ^{13}C NMR (C_6D_6, 125 MHz, δ, ppm): 22.3 (CH(CH_3)$_2$), 29.2 (*C*H(CH_3)$_2$), 50.6 (CH_2NCH_3), 72.7 (CH_2NCH_3), 147.3 (C-1), 136.7 (C-2 and C-6), 127.7 (C-3 and C-5), 123.8 (C-4), 130.8 (d, J_{31P13C} = 47.3 Hz, *i*-carbons of phenyls), 128.1 (d, J_{31P13C} = 12.0 Hz, *o*-carbons of phenyls), 126.3 (s, *p*-carbons of phenyls), 122.9 (d, J_{31P13C} = 12.0 Hz, *m*-carbons of phenyls), 122.6 (C_{ArH}), 126.3 (C_{ArH}), 134.4 (C_{ArH}), 137.2 (C_{ArH}), 148.1 (C_{ArH}), 150.9 (C_{ArH}). ^{31}P NMR (C_6D_6, 202 MHz, δ, ppm): 71.9. Anal. Calcd for $C_{33}H_{40}ClN_3PPd$ (637.53) (%): C, 62.17; H, 6.32. Found (%): C, 62.01; H, 6.35.

Preparation of *cis*-{(2-(Me_2NHCH_2)-6-(Me_2NCH_2)C_6H_3)PPh_2] $PdCl_2$}$^+$ Cl^- (7)

A solution of 36% HCl (0.08 ml, 0.7 mmol) was added to a solution of **1** (0.37 g, 0.68 mmol) in CH_2Cl_2 (5 ml) and the mixture was stirred for 1 h until the precipitation of a yellow solid. Water (30 ml) was added for two-phase extraction. The organic and water fractions were separated. The water was evaporated to yield a yellow solid that was recrystallized from ethanol (10 ml). Slow evaporation of ethanol at room temperature provided yellow crystals of **7** suitable for X-ray diffraction analysis. Yield 0.35 g (85%); m.p. 213–215°C. ^{1}H NMR (D_2O, 400 MHz, δ, ppm): 2.73 (bs, 6H, J_{H-H} = 6.2 Hz, NHCH_3), 2.76 (bs, 6H, NCH_3), 3.50 (AB spin system δ_A 3.25 and δ_B 3.75, 2H, J_{H-H} = 5.8 Hz, CH_2N), 4.19 (bs, 2H, CH_2NH), 4.28 (bs, 1H, N*H*Me_2), 7.37–7.56 (m, 13H, ArH). ^{13}C NMR (D_2O, 100 MHz, δ, ppm): 42.0 (NHCH_3), 42.9 (NCH_3), 59.1 (CH_2N), 61.0 (CH_2NH), 68.0 (CH_2N, J_{31P13C} = 14.0 Hz), 141.7 (C-6), 140.2 (C-2), 132.5 (d, J_{31P13C} = 48.0 Hz, C-1), 131.7 (d, J_{31P13C} = 10.0 Hz, C-3), 130.7 (C-5), 123.0 (C-4), 134.9 (d, J_{31P13C} = 48.3 Hz, *i*-carbons of phenyls), 133.3 (*o*-carbons of phenyls), 130.1 (*p*-carbons of phenyls), 129.2 (*m*-carbons of phenyls). ^{31}P NMR (D_2O, 162 MHz, δ, ppm): 18.4. Anal. Calcd for $C_{24}H_{30}Cl_3N_2PPd$ (590.26) (%): C, 48.84; H, 5.12. Found (%): C, 48.67; H, 5.45.

General procedure for Suzuki–Miyaura reaction

To a degassed solution of starting bromide (0.32 mmol) and boronic acid (0.32 mmol) in aqueous media (10 ml), Pd catalysts **1**–**6** (0.003 mmol or 0.0015 mmol) and Na_2CO_3 (34 mg, 0.32 mmol) were added. The mixture was stirred for 6 h under argon at 80°C, and extracted with EtOAc (2 × 10 ml). The combined organic layers were dried (Na_2SO_4) and subjected to GC analysis (Tables 2 and 3).

Crystallography

Crystals suitable for X-ray analyses were grown from Et_2O–hexane (**3**) or H_2O–EtOH (**7**) solutions at room temperature. Compounds crystallized as the corresponding solvate **7**·H_2O·0.5EtOH. The intensity data for single crystals were measured with a four-circle diffractometer KappaCCD with CCD area detector using monochromatized Mo K_α radiation (λ = 0.71073 Å) at 150(2) K. The crystallographic details are summarized in Table 1, and empirical absorption corrections were applied (multiscan from symmetry-related measurements). Data reductions were performed with DENZO-SMN.[57] The absorption was corrected by integration methods.[58] Structures were solved by direct methods (Sir92) and refined by full matrix least-squares based on F^2 (SHELXL97).[59] Hydrogen atoms were mostly localized on a difference Fourier map and recalculated into idealized positions (riding model) and assigned temperature factors H_{iso}(H) = 1.2U_{eq} (pivot atom) or 1.5U_{eq} for the methyl moiety with C H = 0.96, 0.97 and 0.93 Å for methyl, methylene and hydrogen atoms in aromatic ring moiety, respectively. The structure of **7** contains disordered chloride anion which was split into two positions with occupancy of 52:48; this disorder was modelled according to the position of residual electron density maximum at the Fourier electron density map and treated by standard Shelxl software instructions.[60] The positions of the hydrogen atoms connected to the O1 atom (water molecule) were fixed on places with appropriate hydrogen bond connectivity. CCDC1448889 (for **3**) and 1448890 (for **7**) 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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