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Water-Soluble Palladium Click Chelating Complex: An Efficient and Reusable Precatalyst for Suzuki–Miyaura and Hiyama Reactions in Water

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A water-soluble ionic palladium(II) nitrogen-containing chelating complex, [palladium(II) 1-(4-*N*,*N*′,*N*′′-trimethylbutylammonium)-4-(2-pyridyl)-1*H*-1,2,3-triazole dichloride] chloride (**3**), was prepared through the click reaction of 1-chloro-4-bromobutane, sodium azide, and 2-ethynylpyridine, followed by the quarternization of Me_3N and subsequent reaction with [Pd(cod)Cl_2] (cod = 1,5-cyclooctadiene). The catalytic performances of complex **3** were preliminarily evaluated through Suzuki–Miyaura and Hiyama cross-coupling reactions of aryl bromides; excellent catalytic activity in water was observed. TEM analysis revealed that small palladium nanoparticles (NPs) with a narrow size distribution were formed after the catalytic reaction. The NPs were stabilized by the synergetic effect of coordination and electrostatic interactions from the ionic, bidentate, nitrogen-containing ligand; no palladium black was detected after the aqueous solution of palladium NPs was stored in air for months. The use of **3** as a precursor in the formation of palladium NPs was further explored by using $NaBH_4$ and hydrogen as reductive reagents. The resulting NPs displayed different sizes, surface properties, and catalytic performances in the Suzuki–Miyaura cross-coupling reaction in water.

Introduction

Palladium-catalyzed carbon–carbon cross-coupling reactions of aryl halides are very important routes for the construction of biaryl units in organic synthesis.[1–3] Palladium nanoparticles (NPs) were usually identified as the species formed during cross-coupling reactions when using palladium(II) complexes as the catalytic precursors, in which organic ligands served as stabilizers to prevent the agglomeration of palladium NPs.[3–7] The steric and electronic characteristics of organic ligands may tune the size distribution and surface state of NPs; thus, the optimum balance between stability and activity of NPs can be achieved through the careful choice and modification of organic ligands,[5] which greatly enhances the scope of NPs for different catalytic applications. Various palladium(II) complexes supported by nitrogen-containing,[6] phosphorus-containing,[7] and carbene[8] ligands were selected as NPs precursors, but the preparation and modification of most of ligands required laborious multistep syntheses and/or conditions that did not readily allow the incorporation of useful functional groups. Therefore, the development of new methods for the facile synthesis and modification of organic ligands is very desirable. In this context, the use of readily available building units has been regarded as one ideal strategy.

The click reaction of organic azides and terminal alkynes has attracted considerable attention owing to its superior reliability, mild reaction conditions, wide functional-group tolerance, high yield, and regioselectivity.[9–12] These features have resulted in the extensive use of 1,4-disubstituted 1,2,3-triazolyl as a stable linkage for the connection of two chemical/biological components.[10] The importance of 1,2,3-triazolyl as a potential group for binding metal ions[11] and stabilizing of NPs[12] has been realized, leading to increased interest in the application of catalytic reactions. Recently, we reported a series of click ionic liquids,[13] the steric and electronic properties of which could be easily tuned and modified through variation of substituents at the imidazolium and/or triazolyl rings, that were successfully used as solvents and stabilizers of palladium NPs in carbon–carbon cross-coupling reactions. However, the synthetic complexity and expensive cost limit their further development as reaction media. From an economic and environmental viewpoint, it is more practical and valuable to use water as a reaction medium.

Water is of great interest in organic synthesis and industrial applications because it is inexpensive, readily available, safe, and nontoxic.[14–17] Because the majority of substrates and products in catalytic reactions are insoluble in water, the use of water-soluble catalytic systems contributes to simplify separation, recovery, and recycling of the catalysts. Generally, the smooth implementation of catalytic reactions in water requires precatalysts supported by organic ligands to be soluble in water. Attaching ionic groups, such as sulfonate, carboxylate, and ammonium, to hydrophobic supporting ligands is

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a common method to make metal complexes water soluble.[16] Although a variety of palladium complexes from these water-soluble ionic ligands were used as precatalysts for cross-coupling reactions in water, there were few reports of water-soluble ionic ligands as stabilizers of palladium NPs.[17] Ionic ligands are well known to stabilize palladium NPs through the synergetic effect of coordination and electrostatic interactions, in which coordination atoms bind to the surface of palladium NPs and ionic groups point away from the surface of the NPs. Repulsion interactions between ionic groups may prevent the agglomeration of adjacent NPs, resulting in small sizes and a narrow size distribution of NPs.[18] The synthetic pathways of NPs and the types of reductive reagents have a strong influence on the structures and catalytic activity of NPs.[19] Recent studies demonstrated that the use of discrete metal complexes supported by water-soluble organic ligands was a straightforward and reliable method for the controllable synthesis of metal NPs with a narrow size distribution, but most reports focused on water-soluble, non-ionic ligands, such as 1,3,5-triaza-7-phosphaadamantane (PTA),[7a] polyethylene glycol (PEG)-tagged compounds,[12a] and oxime-derived palladacycles,[20a] whereas palladium NPs stabilized by water-soluble, ionic, nitrogen-containing ligands were seldom explored.[17a] As a continuation of our research into catalytic reactions in environmentally friendly reaction media,[13,17] herein, we report the synthesis and characterization of a water-soluble ionic click ligand, 1-[*N*,*N*′,*N*′′-trimethyl-(4-butyl)ammonium]-4-(2-pyridyl)-1*H*-1,2,3-triazole chloride (**2**), and its palladium complex, [palladium(II) 1-(4-*N*,*N*′,*N*′′-trimethylbutylammonium)-4-(2-pyridyl)-1*H*-1,2,3-triazole dichloride] chloride (**3**). The use of **3** as a precursor in the formation of palladium NPs was explored, and the application of the resulting NPs as a recoverable precatalyst in Suzuki–Miyaura and Hiyama cross-coupling reactions in air and neat water was investigated.

Results and Discussion

The synthetic pathway for water-soluble palladium(II) complex **3** is depicted in Scheme 1. The treatment of 1-chloro-4-bromobutane with sodium azide in H_2O/MeOH at 80 °C overnight, followed by 1,3-dipolar cycloaddition with 2-ethynylpyridine under standard click reaction conditions gave rise to non-ionic, nitrogen-containing chelating ligands **1a** and **1b**. Subsequent quaternization of **1b** with an excess of a 30% aqueous solution of Me_3N in MeCN produced ionic chelating ligand **2**. Reaction of **2** with an equimolar amount of $[Pd(cod)Cl_2]$ in CH_2Cl_2/MeOH produced **3** in almost quantitative yield.

Compounds **1**–**3** are stable in air and can be stored for a long period of time. Compounds **1a** and **1b** possess poor solubility in water, whereas **2** and **3** are soluble in water. The ^1H NMR spectra of **1**–**3** exhibit a typical singlet signal for the proton of the triazolyl ring. The resonance for the proton of the triazolyl ring in **3** was observed at $\delta = 8.89$ ppm, which was downshifted in comparison with that in **2** ($\delta = 8.32$ ppm). A clear shift was also observed for the other signals in the ^1H NMR spectra of **2** and **3**; this suggests coordination of the triazolyl–pyridine rings with palladium(II) in **3**. Thermogravimetric analysis under an atmosphere of N_2 revealed that thermal degradation temperature of **3** (243 °C) was close to that of **2** (231 °C).

It is well known that the triazolyl ring in **2** can in principle bind to a metal center through N2 or N3 atom.[11] To learn the coordination mode of **3**, the single-crystal X-ray structure of **3** was determined. As expected, the pyridyl nitrogen atom and triazolyl N2 atom bind to palladium(II) to generate a five-membered chelating ring (Figure 1). The coordination mode of palladium(II) in **3** is very similar to that of *N*,*N*-chelating ligands.[11a,17a] Palladium(II) is in a slightly distorted square-planar geometry and is coordinated by two chloride atoms and two nitrogen atoms from pyridyl and triazolyl rings, respectively. The bond angle of N1-Pd1-N2 is 80.23(12)°, which is slightly lower than those of other *cis* angles around the Pd1 center. The Pd1–N2 bond length of 1.995(3) Å is shorter than that of the Pd1–N1 bond length of 2.053(3) Å; this can be ascribed to the stronger electron-donating ability of the 1,2,3-triazolyl ring than that of the pyridyl

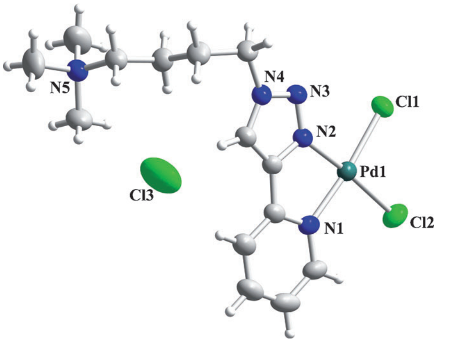
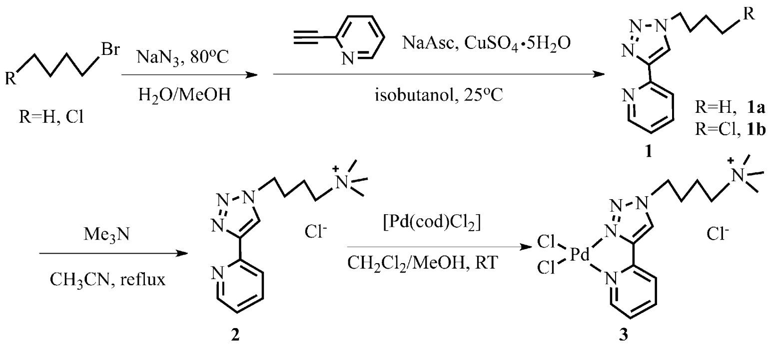


Figure 1. The structure of complex **3** with thermal ellipsoids shown at the 50% probability level.



Scheme 1. The synthesis of water-soluble palladium complex **3**. NaAsc = sodium salt of ascorbic acid, cod = 1,5-cyclooctadiene.

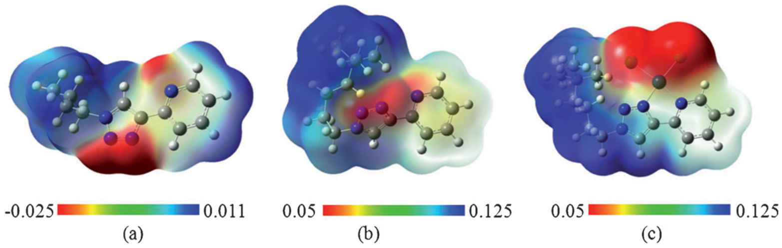


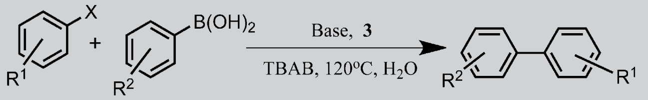
Figure 2. The charge distributions for **1 a** (a) and the cations in **2** (b) and **3** (c).

ring.[11a] The bond length of Pd1–Cl2 *trans* to the coordinated nitrogen atom of the triazolyl ring (2.2922(11) Å) is slightly longer than that of Pd1–Cl1 *trans* to the pyridyl nitrogen atom (2.2767(10) Å); this is consistent with the enhanced *trans* influence of N2 with respect to N1.[17a] It should be mentioned that the triazolyl–pyridyl–$PdCl_2$ parts are almost coplanar with a mean deviation between them of 0.033 Å. The twisting angle between the triazolyl and pyridyl rings is 3.8°. The *N*,*N*′,*N*′′-trimethyl-(4-butyl)ammonium substituent is apparently twisted to minimize steric repulsion. The butyl spacer between the ammonium group and the triazolyl ring exhibits an *anti*–*anti*–*anti* conformation. The torsion angle of the four carbon atoms of the butyl spacer is 3.068°.

To obtain a better understanding of the structures of the nitrogen-containing chelating compounds, the natural bond orbital (NBO) and molecular orbital analyses based on the optimized structures of non-ionic **1 a**, cations of water-soluble ligand **2**, and palladium complex **3** were implemented by using Gaussian 03.[21] As shown in Figure 2 and Table S1 in the Supporting Information, the charge distributions were different in the three compounds, in which the pyridyl nitrogen atom carried the most negative charge. The pyridyl nitrogen atom (N1) in the cation of **2** is more negative (−0.470 e) than that in **1 a** (−0.460 e) and in the cation of **3** (−0.461 e). The charges of the triazolyl N2 atom are similar in **1 a** (−0.258 e) and in the cations of **2** (−0.258 e) and **3** (−0.260 e). Furthermore, N2 carries the most negative charge in the triazolyl ring, indicating that, of the nitrogen atoms of triazolyl the ring, N2 prefers to coordinate with metal ions. Notably, the pyridyl ring in the cations of **2** and **3** possess a positive charge (see Table S2 in the Supporting Information), whereas **1 a** contains a slight negative charge. The triazolyl ring carries most of the negative charge; thus, the binding ability of the triazolyl N2 atom is stronger than that of the pyridyl nitrogen atom. These results are in good agreement with those from the X-ray crystal structure of **3**. As shown in Figure S1 in the Supporting Information, the HOMO and LUMO of **1 a** and the cation of **2** are shared by the triazolyl and pyridyl rings. The HOMO of the cation of **3** predominantly localizes at the Pd and Cl centers,[22] whereas the LUMO is occupied by triazolyl–pyridyl–$PdCl_2$, owing to delocalization over $PdCl_2$ and chelation of the triazolyl–pyridine unit.

Because complex **3** is soluble and stable in water, the Suzuki–Miyaura cross-coupling reaction between aryl bromides and aryl boronic acid was initially tested to evaluate the catalytic performances of **3** in neat water. As shown in Table 1, the

Table 1. Suzuki–Miyaura cross-coupling reaction catalyzed by **3 a**.[a]



Entry	R¹	X	R²	Pd [mol %]	Time	Yield [%][b]
1[c]	4-CH_3CO	Br	H	0.01	20 min	81
2	4-CH_3CO	Br	H	0.01	20 min	98
3[d]	4-CH_3CO	Br	H	0.01	20 min	99
4[e]	4-CH_3CO	Br	H	0.01	20 min	82
5	4-CH_3CO	Br	H	0.001	2 h	91
6	4-CH_3CO	Br	H	0.0001	24 h	43
7	4-CH_3CO	Br	H	0.01	30 min	100 (96)
8	4-NO_2	Br	H	0.01	30 min	98 (93)
9	4-CN	Br	H	0.01	30 min	97 (93)
10	4-MeO	Br	H	0.01	30 min	97
11	4-CH_3	Br	H	0.01	30 min	89
12	3-CH_3	Br	H	0.01	30 min	85
13	2-CH_3	Br	H	0.01	30 min	84
14	2-thiophenyl	Br	H	0.01	30 min	96
15	3-pyridyl	Br	H	0.01	2 h	73
16	4-CH_3CO	Br	4-F	0.01	30 min	99 (98)
17	4-CH_3CO	Br	4-MeO	0.01	30 min	99 (98)
18	4-CH_3CO	Br	4-CH_3	0.01	30 min	99 (97)
19	4-CH_3CO	Br	2-CH_3	0.01	30 min	99 (95)
20	4-CH_3CO	Br	3-CH_3	0.01	30 min	99 (95)
21	4-CH_3CO	Cl	H	0. 1	5 h	80
22	4-CN	Cl	H	0. 1	5 h	100 (93)
23	4-NO_2	Cl	H	0. 1	5 h	100
24	4-NO_2	Cl	2-CH_3	0. 1	5 h	100 (98)
25	4-NO_2	Cl	3-CH_3	0. 1	5 h	98
26	4-NO_2	Cl	4-CH_3	0. 1	5 h	99 (97)
27	4-NO_2	Cl	4-F	0. 1	5 h	100 (93)
28[f]	4-CH_3CO	Br	H	0.01	30 min	89

[a] Reaction conditions: aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2.0 mmol), H_2O (3 mL), tetra-*n*-butylammonium bromide (TBAB; 1.0 mmol). [b] Yields determined by GC; yields of isolated product are given in parentheses. [c] No TBAB was added. [d] KOH was used as a base. [e] NEt_3 was used as a base. [f] The molar ratio of Pd to **1 a** (as a ligand) was 1:1.

cross-coupling reaction between 4-bromoacetophenone and phenylboronic acid gave 4-acetylbiphenyl in 81 % yield, as determined by GC, when K_2CO_3 was used as a base in the presence of 0.01 mol % of **3** in 20 min (Table 1, entry 1). Although the addition of TBAB led to a 98 % yield, as determined by GC, under the same conditions (Table 1, entry 2); this was ascribed to the fact that TBAB served as a phase-transfer catalyst to favor better contact between the substrates and the aqueous catalytic species and accelerate the reaction rate of the Suzuki–Miyaura cross-coupling reaction.[20b] The effect of bases on the cross-coupling reaction was also investigated. Almost quantitative yields were achieved in 20 min when K_2CO_3 or KOH were used as bases (Table 1, entries 2 and 3), whereas NEt_3 was slightly less efficient and gave 82 % yield, as determined by GC, under the same conditions (Table 1, entry 4). Interestingly, when the palladium loading was decreased to 0.001 mol %, 4-acetylbiphenyl was formed in 91 % yield, as determined by GC, after 2 h (Table 1, entry 5). Further reducing the palladium loading to 0.0001 mol % gave the target product in a 43 % yield after 24 h, corresponding to a turnover frequency (TOF) of 18 000 h^{-1} (Table 1, entry 6). Aryl bromides with electron-withdrawing groups, such as –COMe, –CN, and $-NO_2$, provided the desirable products in nearly quantitative yield in 30 min (Table 1, entries 7–9). However, when aryl bromides containing electron-donating groups, such as –MeO and –Me, were selected as substrates under the same conditions, 97 and 89 % yields, as determined by GC, were obtained, respectively (Table 1, entries 10 and 11). These results are consistent with the well-established trends in palladium-catalyzed Suzuki–Miyaura cross-coupling reactions.[12a,20] The reactions between 2-, 3-, or 4-bromotoluene and phenylboronic acid resulted in similar conversion (Table 1, entries 11–13) and no clear steric effect was observed for the substrates. Heteroaryl bromides, such as 2-bromothiophene (Table 1, entry 14) and 3-bromopyridine (Table 1, entry 15), also reacted with phenylboronic acid; the target products were formed in 96 and 73 % yield, as determined by GC, after 0.5 and 2 h, respectively. The cross-coupling reaction with other aryl boronic acids was also performed (Table 1, entries 16–20); the corresponding biaryl products were obtained in almost quantitative yield, regardless of the electronic and steric nature of aryl boronic acids.

Suzuki–Miyaura cross-coupling reactions of aryl chlorides with aryl boronic acid were also performed with **3** as a precatalyst in water. Complete conversion was achieved in the reactions of phenylboronic acid with 4-chlorobenzonitrile and 4-chloronitrobenzene in the presence of 0.1 mol % of **3**, K_2CO_3, and TBAB in 5 h (Table 1, entries 22 and 23), but an 80 % yield, as determined by GC, was obtained when 4-chloroacetophenone was used as a substrate under the same conditions (Table 1, entry 21). The cross-coupling reaction of 4-chloronitrobenzene with various aryl boronic acids was also performed; the corresponding biaryl products were obtained in almost quantitative yields (Table 1, entries 24–27), in which *ortho*, *meta*, and *para* substituents on the aromatic ring of boronic acids had no clear effect on the coupling reactions.

However, when non-ionic **1 a** was used as a supporting ligand for palladium(II), the cross-coupling reaction between 4-bromoacetophenone and phenylboronic acid gave the target product in 89 % yield, as determined by GC (Table 1, entry 28), which was lower than those with **2** as the supporting ligand for palladium under identical conditions (Table 1, entry 7), indicating that the water solubility of the supporting ligands had an important effect on the catalytic activity of the cross-coupling reactions. This effect was further explored by the reaction between 4-bromoanisole and phenylboronic acid in the presence of 0.01 mol % of the precatalyst. As shown in Figure 3, the conversion for both **3** and Pd/**1 a** exhibited sigmoidal-shaped curves. However, Pd/**1 a** has a much longer induction period and lower reaction activity than that of **3** because the insolubility of Pd/**1 a** inhibits the catalytic species from dispersing well in water.

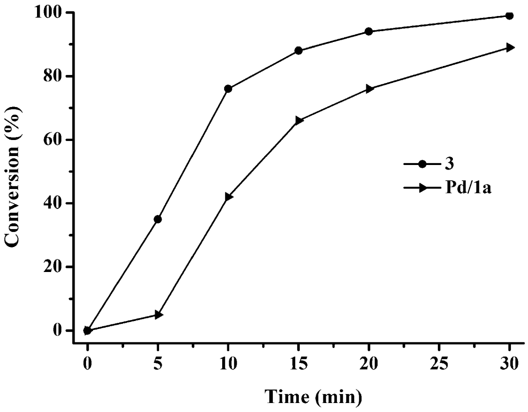


Figure 3. Conversion of 4-bromoanisole as a function of time in the Suzuki–Miyaura reaction when using 0.01 mol % of **3** or Pd/**1 a** as a precatalyst in the presence of K_2CO_3 and TBAB in water at 120 °C.

Catalyst reusability is an important issue from the viewpoints of industrial applications and green chemistry. The reaction between 4-bromoacetophenone and phenylboronic acid was selected as a representative example to test the recyclability of the water-soluble catalytic system. After the reaction was finished, the resulting product was extracted by using ethyl ether. The residual aqueous solution was recharged with the same substrates and one equivalent of base for the next run. The catalytic solution containing the palladium species was used four times; a slight loss of catalytic activity was observed (Figure 4).

The encouraging catalytic performances of **3** in the Suzuki–Miyaura cross-coupling reaction further prompted us to investigate the Hiyama cross-coupling reaction in water. As shown in Table 2, when the reaction of 4-bromoacetophenone and phenyltrimethoxysilane was performed in the presence of 0.5 mol % of **3** and two equivalents of NaOH at 120 °C for 6 h, 4-acetylbiphenyl was formed in 34 % yield, as determined by GC (Table 2, entry 1). However, as determined by GC, 76 % yield was achieved when using phenyltriethoxysilane instead of phenyltrimethoxysilane under identical conditions (Table 2, entry 2). The effect of the amount of arylsiloxane and base on the Hiyama cross-coupling reaction was then investigated. When the equivalent amount of NaOH and phenyltriethoxysi-

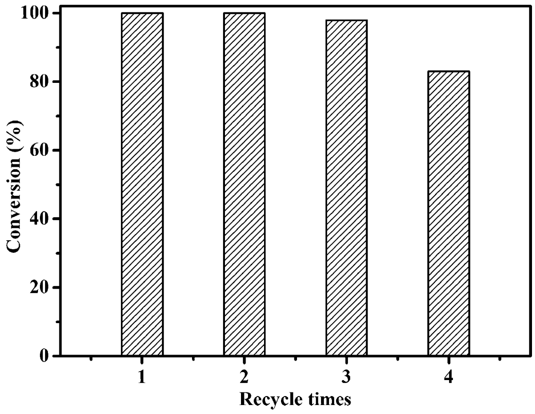
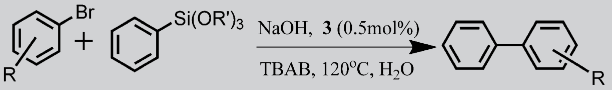


Figure 4. Reusability of **3** in the Suzuki–Miyaura reaction between 4-bromoacetophenone (1.0 mmol) and phenylboronic acid (1.5 mmol) in the presence of K_2CO_3 (2.0 mmol), complex **3** (0.01 mol%), TBAB (1.0 mmol), and H_2O (3 mL) at 120 °C for 0.5 h.

Table 2. Hiyama cross-coupling reaction of aryl bromides with arylsiloxanes catalyzed by **3**.[a]



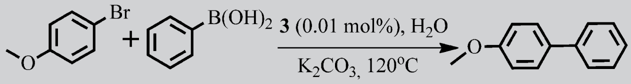
Entry	R	R′	NaOH [equiv]	Additive	Yield [%][b]
1[c]	4-CH_3CO	Me	2	–	34
2[c]	4-CH_3CO	Et	2	–	76
3[c]	4-CH_3CO	Et	2.5	–	93
4	4-CH_3CO	Et	2	–	85
5	4-CH_3CO	Et	5	–	99 (92)
6	4-Me	Et	5	–	58
7	4-Me	Et	5	TBAB	95
8	3-Me	Et	5	TBAB	92
9	2-Me	Et	5	TBAB	91
10	4-MeO	Et	5	TBAB	98
11	4-NO_2	Et	5	TBAB	99
12	4-Cl	Et	5	TBAB	99
13	3-pyridyl	Et	5	TBAB	99
14	2-thiophenyl	Et	5	TBAB	98

[a] Reaction conditions: aryl bromide (1.0 mmol), arylsiloxane (2.0 mmol), NaOH (2 to 5 mmol), TBAB (0 or 1.0 mmol), H_2O (3 mL), 6 h. [b] Yields determined by GC; yields of isolated product are given in parentheses. [c] 1.5 equivalents of arylsiloxane was added.

lane was increased from 2 to 2.5 and from 1.5 to 2 under similar conditions the target product was generated in 93 and 85% yield, as determined by GC, respectively (Table 2, entries 3 and 4). Almost complete conversion was observed when five equivalents of NaOH and two equivalents of phenyltriethoxysilane were used under the same conditions (Table 2, entry 5). However, the reaction between phenyltriethoxysilane and an aryl bromide with an electron-donating methyl group gave 4-methylbiphenyl in 58% yield, as determined by GC, under the same conditions (Table 2, entry 6). When one equivalent of TBAB was added, the yield determined by GC increased to 95% (Table 2, entry 7). Moreover, the steric and electronic properties of the substituents of the aryl bromides had no apparent effect on the reactions; the corresponding biaryl products were obtained in excellent yields as determined by GC (Table 2, entries 7–12). Heteroaryl bromides, such as 3-bromopyridine (Table 2, entry 13) and 2-bromothiophene (Table 2, entry 14), also reacted with phenyltriethoxysilane; the resulting products were obtained in almost quantitative yield, as determined by GC.

It was reported that palladium NPs were usually involved in palladium-catalyzed cross-coupling reactions.[23] The reduction of metal–organic complexes and subsequent stabilization by the supporting ligands have been considered as a simple and reliable approach for the controllable synthesis of palladium NPs with a narrow size distribution. To identify active palladium species from water-soluble complex **3**, poisoning experiments were originally examined in the reaction of 4-bromoanisole and phenylboronic acid with 0.01 mol% of **3** as a precatalyst. As shown in Table 3, when a drop of Hg^0 was added to the reaction mixture before the reaction was performed, no catalytic activity was detected after 30 min (Table 3, entry 1); this is ascribed to the formation of an amalgam on the surface of the palladium NPs, resulting in Pd^0 poisoning. However, nearly quantitative yield was obtained in the absence of mercury under the same conditions (Table 3, entry 3). On the other hand, pyridine and PVPy are known for their good binding ability to palladium, but the insolubility of PVPy in water enables the palladium particles to be removed from water, resulting in an ineffective contact between the catalysts and substrates, as well as extinguishing the active catalytic species.[8a, 23c] As expected, the use of 150 equivalents of pyridine as an additive had no apparent effect on the cross-coupling reaction between 4-bromoanisole and phenylboronic acid (Table 3, entry 2). However, only a trace amount of the product was observed when 150 equivalents PVPy were added to the reaction mixture under the same conditions (Table 3, entry 5). Notably, the presence of 1000 equivalents of pyridine gave 75% yield, as determined by GC (Table 3, entry 3), but almost quantitative yield was observed when the reaction time was extended to 3 h (Table 3, entry 4). If the molar ratio of ligand **2** to palladium was increased from 1 to 6, a slight decrease of conversion was observed (Table 3, entry 6). These re-

Table 3. Summary of poisoning experiments for complex **3**.



Entry	Poisoning additive	Ratio of additive to palladium	Reaction time [h]	Conversion [%]
1[a]	Hg	–	0.5	0
2	pyridine	150	0.5	96
3	pyridine	1000	0.5	75
4	pyridine	1000	3	99
5	PVPy[b]	150	0.5	<2
6	**2**	6	0.5	90

[a] One drop of Hg was added. [b] PVPy = polyvinylpyridine.

sults further revealed the strong chelating ability of the ionic triazolyl–pyridine ligand with palladium in water.

To find more evidence of the formation of palladium(0) NPs, after the Suzuki–Miyaura cross-coupling reaction of 4-bromoanisole and phenylboronic acid with **3** as a precatalyst was finished, the crude mixture was extracted several times with ethyl ether and the aqueous layer containing the active catalytic species was directly analyzed by TEM. The TEM images clearly showed the formation of palladium NPs with a mean diameter of 3.09 nm and a standard deviation of 0.53 (Figure 5 a); the palladium NPs are denoted Pd–Suzuki. The value is smaller than the size of reported palladium NPs dispersed in water.[8a, 24] For example, palladium pincer carbene compounds[8a] and $Na_2[PdCl_4]$/sodium dodecyl sulfate (SDS)[24] generated palladium NPs in situ with average sizes of 6–8 and 5–10 nm, respectively, after the Suzuki–Miyaura reaction in water. Interestingly, these palladium NPs are stable in aqueous solution; no precipitate was observed for months, which contributed to the synergetic immobilization effect of the ionic triazolyl–pyridine ligand. Nitrogen atoms from the triazolyl–pyridine rings bind to the surface of the palladium NPs, while the ionic group points away from the surface of the NPs. The repulsion interactions between the ionic groups prevent agglomeration of the NPs and result in small sizes and good stability of the NPs in water.

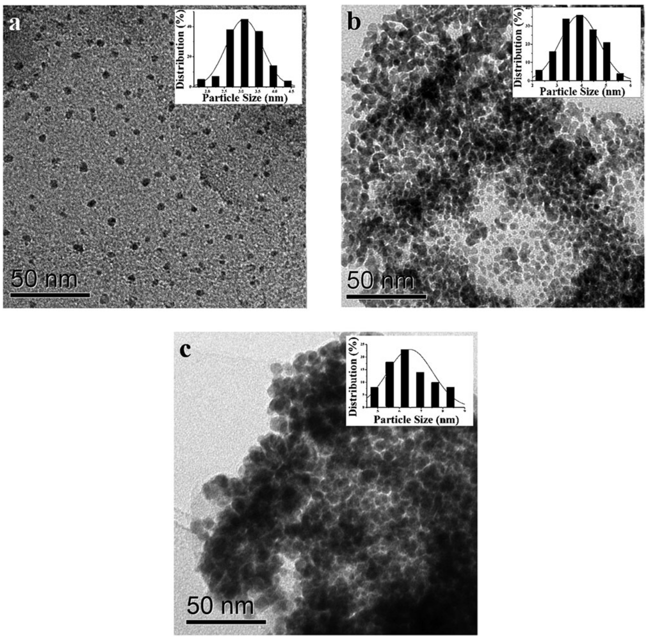


Figure 5. TEM micrographs and size distributions of palladium NPs for a) Pd–Suzuki, b) Pd–$NaBH_4$, and c) Pd–H_2.

X-ray photoelectron spectroscopy (XPS) analysis was performed to gain insight into the surface properties of Pd–Suzuki. As shown in Figure 6 a, the Pd 3d spectrum showed two sets of binding energy peaks, corresponding to two pairs of spin-orbital doublets. The peaks with binding energies at 335.3 (Pd $3d_{5/2}$) and 340.6 eV (Pd $3d_{3/2}$) can be attributed to the fully reduced palladium NPs, whereas the peaks at 336.3 and 341.5 eV indicate the presence of palladium(II) at the surface of the palladium NPs.[25] The molar ratio of Pd^0/Pd^{II} was approximately estimated based on the ratio of peak area for Pd $3d_{5/2}$ of the Pd^0 species to that of the Pd^{II} species.[26] The molar ratio of Pd^0/Pd^{II} at the surface of palladium NPs was 1.34.

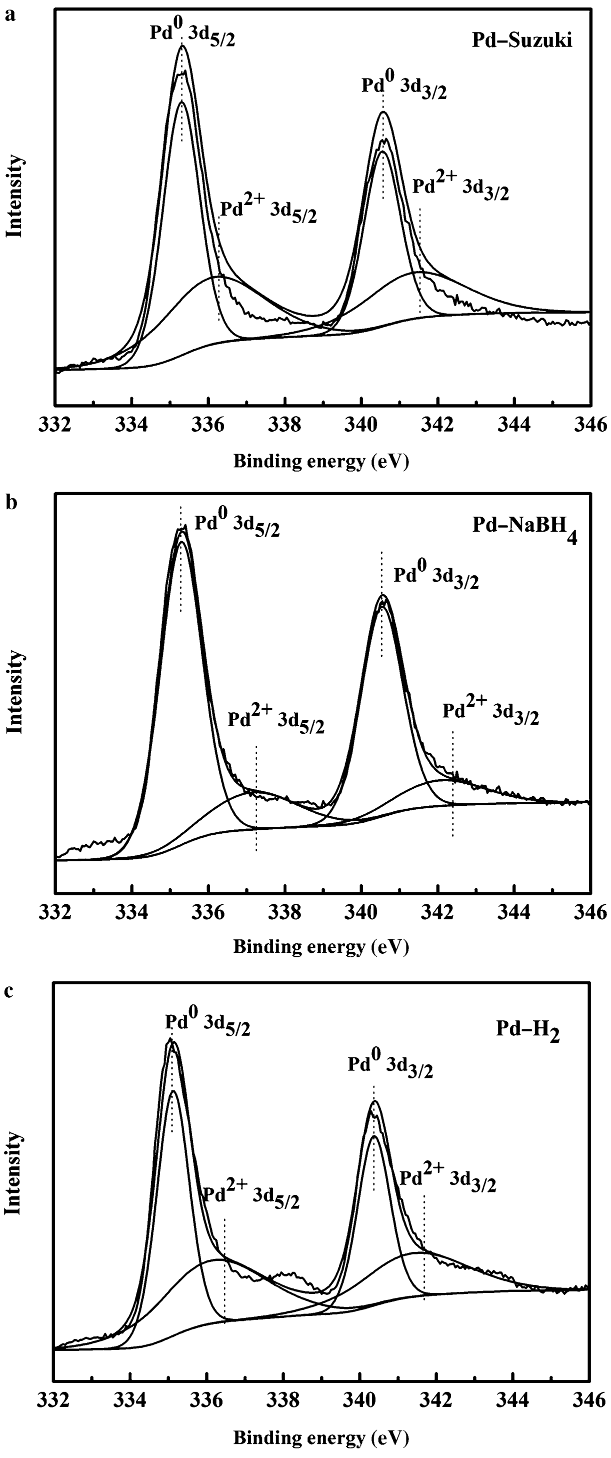


Figure 6. XPS analyses of Pd 3d for a) Pd–Suzuki, b) Pd–$NaBH_4$, and c) Pd–H_2.

For comparison, palladium NPs were also prepared by using $NaBH_4$ and H_2 as reducing reagents and **3** as a precursor; the corresponding palladium NPs were designated Pd–$NaBH_4$ and Pd–H_2, respectively. As shown in Figure 5 b and c, TEM images revealed that the mean diameters of Pd–$NaBH_4$ and Pd–H_2 were (3.92±0.79) and (6.49±1.05) nm, respectively, which were bigger than that of Pd–Suzuki. Moreover, clear aggregation was observed for Pd–H_2. XPS analyses showed that the molar ratio of Pd^0 to Pd^{II} at the surface of Pd–$NaBH_4$ and Pd–H_2 was 3.91 and 1.17, respectively (Table 4, entries 2 and 3). It was known that the properties of the palladium NPs, such as particle size and metal oxidation state, had an important influence on the catalytic activity.[4b, 12a] To further understand the nature of the palladium NPs, the catalytic activity of **3** and the two palladium NPs were evaluated. As shown in Table 4, when using **3** and Pd–$NaBH_4$ as precatalysts, the reaction of 4-bromoanisole and phenylboronic acid in water under identical conditions gave 4-methoxydiphenyl in 70 and 78 % yield, as determined by GC, respectively; the slightly lower catalytic activity in **3** was mainly ascribed to the existence of the induction period at the beginning of the reaction. However, a yield of 8 %, as determined by GC, was achieved by using Pd–H_2 as a precatalyst. These results suggested that the synthetic methods used for palladium NPs and the types of reducing reagents had an important effect on the size and oxidation state of the palladium species, resulting in significant differences in the catalytic performances.

Table 4. Comparison of the performance of palladium NPs.[a]

Entry	Precatalyst	Particle size [nm]	Pd^0/Pd^{II}[b]	Conversion [%]
1	**3**	3.09±0.53	1.34	70
2	Pd–$NaBH_4$	3.92±0.79	3.91	78
3	Pd–H_2	6.49±1.05	1.17	6

[a] Reaction conditions: 4-bromoanisole (1.0 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2.0 mmol), and 0.1 mol % Pd in H_2O (3 mL) at 120 °C for 0.5 h. [b] Oxidation state of the surface Pd defined by XPS.

Conclusion

By using the increasingly popular click reaction, a water-soluble, ionic, triazolyl–pyridine ligand was easily prepared. The crystal structure and theoretical calculation of its palladium(II) complex revealed that palladium(II) was coordinated by the pyridyl nitrogen atom and a triazolyl nitrogen atom to form a stable, five-membered chelating ring, in which the electron-donating ability of 1,2,3-triazolyl ring was stronger than that of the pyridyl ring. Excellent catalytic activity for the palladium-catalyzed Suzuki–Miyaura cross-coupling reaction of aryl bromides and aryl chlorides and the Hiyama cross-coupling reaction of aryl bromides was observed in neat water when the water-soluble palladium complex was used as a precatalyst. Palladium NPs were formed after the catalytic reactions, in which the ionic ligand served as a stabilizer of the NPs. The ionic group is located around the surface of the NPs as a result of nitrogen atoms of the triazolyl–pyridine unit coordinating to the surface of the palladium NPs; repulsion interactions between the ionic groups resulted in a small size and narrow size distribution of the NPs. The structures and catalytic activities of NPs have been influenced by the synthetic routes and types of reducing reagents when **3** was used as a precursor of the NPs.

In summary, this study provides an efficient protocol for the synthesis of water-soluble, ionic, bidentate, nitrogen-containing ligands, the palladium complexes of which may serve as efficient precursors to produce palladium NPs with small sizes and a narrow size distribution. The successful application of these NPs in catalysis not only offers a new strategy for the synthesis of aqueous NPs through the use of ionic, bidentate, nitrogen-containing ligands, but also opens up a green avenue for the development of an environmentally friendly catalytic system.

Experimental Section

General methods

All chemicals were purchased from commercial suppliers and were used without further purification. ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE III NMR spectrometer at 400 and 100 MHz, respectively, using deuterated $CDCl_3$ as a locking solvent except where otherwise indicated. The IR spectra were recorded as KBr pellets by using a PerkinElmer instrument. Thermogravimetric analyses were performed on a Mettler TGA/SDTA 851e analyzer with a heating rate of 10 °C min^{-1} under a nitrogen atmosphere. GC analyses were performed on a Shimadzu GC-2014 instrument equipped with a capillary column (RTX-5, 30 m×0.25 μm) using a flame ionization detector. TEM was performed on a JEOL JEM-2010 microscope operated at 200 kV. XPS was performed on a Thermo ESCALAB 250 spectrometer. Non-monochromatic Al Kα radiation was used as a primary excitation source. The binding energies were referenced to the C 1s line at 284.8 eV from adventitious carbon. Elemental analyses were performed on an Elementar Vario MICRO elemental analyzer.

X-ray crystallography

Data collection for **3** was performed on a Rigaku AFC7R instrument equipped with a graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). The intensity data set was collected by using an ω scan technique and corrected for *Lp* effects. The primitive structures were solved with direct methods and refined on F^2 with full-matrix least-squares methods by using the SHELXS-97 and SHELXL-97 programs, respectively.[27] All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were generated geometrically (C–H bond fixed at 0.96 Å) and allowed to ride on their parent carbon atoms before the final cycle of refinement.

CCDC 910130 contains 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.

Theoretical study

Calculations were performed by using the Gaussian 03 (Revision D.02) suite of programs.[21] The geometric optimization of the structures and frequency analyses were performed by using the B3-LYP method with effective core potentials (ECPs). The all-electron 6-31+G** basis set was used on C, N, Cl, and H atoms, whereas Lanl2dz, developed by Hay and Wadt, was employed to describe the Pd atom.[28] The vibration frequencies were used to characterize the optimized structures for which the energy was at a minimum without imaginary frequencies on the potential energy surface. Scaling factors were neglected in the harmonic vibration frequencies.

Synthesis of 1 a

1-Bromobutane (0.80 g, 6.0 mmol) was added to a solution of NaN_3 (0.32 g, 5.0 mmol) in H_2O (10 mL) and MeOH (10 mL); the mixture was stirred at 80 °C overnight. 2-Ethynylpyridine (0.50 g, 4.8 mmol), the sodium salt of L-ascorbic acid (0.50 g, 2.2 mmol), $CuSO_4{\cdot}5\,H_2O$ (0.20 g, 0.8 mmol), and isobutanol (10 mL) were added to the solution at 0 °C. After the reaction mixture was warmed to 25 °C and stirred overnight, the resulting mixture was extracted with ethyl acetate (3×10 mL). The combined organic layer was washed with H_2O and brine, and dried over anhydrous Na_2SO_4. The solvent was removed in vacuo and the residues were purified by flash column chromatography on silica gel to afford the product as a brown oil (0.77 g, 80%). ^{1}H NMR: $\delta=8.55$ (d, $J=4.16$, 1 H), 8.17 (s, 1 H), 8.14 (d, $J=3.2$, 1 H), 7.78–7.73 (m, 1 H), 7.22–7.19 (m, 1 H), 4.40 (t, $J=7.12$, 2 H), 1.95–1.90 (m, 2 H), 1.41–1.34 (m, 2 H), 0.94 ppm (t, $J=7.32$, 3 H); ^{13}C NMR: $\delta=150.3$, 149.3, 148.3, 137.0, 122.8, 121.8, 120.2, 50.2, 32.2, 19.2, 13.4 ppm.

Synthesis of 1 b

A similar procedure to that for **1 a** was used, except that 1-bromobutane was replaced with 1-bromo-4-chlorobutane to give the product as a white solid (72%). ^{1}H NMR: $\delta=8.58$ (d, $J=3.60$, 1 H), 8.19 (d, $J=7.92$, 1 H), 8.17 (s, 1 H), 7.78 (t, $J=7.52$, 1 H), 7.24 (t, $J=6.20$, 1 H), 4.48 (t, $J=6.88$, 2 H), 3.58 (t, $J=6.28$, 2 H), 2.18–2.10 (m, 2 H), 1.86–1.79 ppm (m, 2 H); ^{13}C NMR: $\delta=150.2$, 149.4, 148.5, 137.0, 122.9, 121.9, 120.3, 49.6, 43.9, 29.2, 27.5 ppm.

Preparation of 2

Compound **1 b** (0.36 g, 1.5 mmol) in acetonitrile (10 mL) was added to a 30% aqueous solution of Me_3N (2 mL); the mixture was heated at reflux overnight. The clear solution was then evaporated under reduced pressure. The residue was washed several times with Et_2O and dried in vacuo to give a white solid in a quantitative yield. ^{1}H NMR (D_2O): $\delta=8.47$ (s, 1 H), 8.32 (s, 1 H), 7.91–7.85 (m, 2 H), 7.37 (t, $J=5.4$, 1 H), 4.53 (t, $J=6.80$, 2 H), 3.33 (t, $J=8.48$, 2 H), 3.06 (s, 9 H), 2.03–1.96 (m, 2 H), 1.82–1.73 ppm (m, 2 H); ^{13}C NMR (D_2O): $\delta=149.0$, 148.0, 147.0, 138.5, 124.0, 123.6, 120.9, 65.6, 52.8, 49.7, 26.1, 19.5 ppm; IR (KBr): $\tilde{\nu}=3410$ (s), 3053 (m), 2964 (w), 1643 (m), 1481 (m), 1392 (w), 1297 (w), 1151 (w), 1051 (w), 972 (w), 922 (w), 788 (m), 660 cm^{-1} (w); elemental analysis calcd (%) for $C_{14}H_{22}ClN_5{\cdot}H_2O$ (313.8): C 53.58, H 7.71, N 22.32; found: C 53.85, H 7.74, N 22.17.

Preparation of 3

A mixture of **2** (31.2 mg, 0.1 mmol) and [Pd(cod)Cl_2] (28.5 mg, 0.1 mmol) in CH_2Cl_2 (10 mL) was stirred for 30 min to form a yellow precipitate. After MeOH (3 mL) was added, the mixture became clear and was stirred for an additional 30 min. The resulting solution was evaporated under reduced pressure and the residue was washed with ethyl ether to give a yellow solid in quantitative yield. ^{1}H NMR (D_2O): $\delta=8.89$ (s, 1 H), 8.36 (d, $J=5.2$, 1 H), 8.02 (t, $J=8.0$, 1 H), 7.94 (d, $J=8.0$, 1 H), 7.33 (d, $J=6.12$, 1 H), 4.64 (t, $J=6.68$, 2 H), 3.41 (t, $J=8.4$, 2 H), 3.12 (s, 9 H), 2.09 (t, $J=7.16$, 2 H), 1.92 ppm (d, $J=6.8$, 2 H); ^{13}C NMR (D_2O): $\delta=149.5$, 148.2, 141.5, 126.0, 125.7, 122.7, 65.5, 58.9, 52.9, 52.1, 25.6, 19.6 ppm; IR (KBr): $\tilde{\nu}=3435$ (s), 2953 (w), 2863 (w), 2353 (m), 1605 (m), 1476 (m), 1224 (w), 1051 (w), 967 (w), 906 (w), 782 cm^{-1} (m); elemental analysis calcd (%) for $C_{14}H_{22}Cl_3N_5Pd{\cdot}2\,H_2O$ (509.2): C 33.02, H 5.15, N 13.75; found: C 33.24, H 4.97, N 13.34. Single crystals suitable for X-ray diffraction were obtained through slow evaporation of a solution of **3** in MeOH at room temperature.

Preparation of Pd–$NaBH_4$

A fresh aqueous solution of $NaBH_4$ (0.1 M, 1.0 mL) was rapidly added to a stirring solution of **3** (5.1 mg, 0.01 mmol) in H_2O (5 mL) at 25 °C. The solution immediately turned dark brown and was stirred at 25 °C for 40 min; the resulting mixture was used for the Suzuki–Miyaura cross-coupling reaction without further purification.

Preparation of Pd–H_2

A solution of **3** (5.1 mg, 0.01 mmol) in H_2O (6 mL) was placed in a 50 mL autoclave and reduced by H_2 (0.3 MPa) at 25 °C for 1 h. After the autoclave was cooled, a black solution was obtained and used directly for the Suzuki–Miyaura cross-coupling reaction.

General procedure for the Suzuki–Miyaura cross-coupling reaction

A 25 mL reactor equipped with a condenser was charged with aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), base (2.0 mmol), TBAB (1.0 mmol), and H_2O (3 mL). An aqueous solution of the appropriate amount of **3** was added to the mixture, which was stirred in a preheated oil bath (120 °C). After an appropriate time, the mixture was cooled with ice-cold water and the product was extracted with hexane or ethyl acetate (3×5 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The crude products were purified by flash column chromatography on silica gel to afford the desired product. The identity of the products was confirmed by comparison with spectroscopic data reported in the literature.

Reuse of the catalytic aqueous solution in the Suzuki–Miyaura cross-coupling reaction

A mixture of 4-bromoacetophenone (1.0 mmol), phenylboronic acid (1.5 mmol), **3** (0.01 mol%), K_2CO_3 (2.0 mmol), and TBAB (1.0 mmol) in H_2O (3.0 mL) was stirred at 120 °C for 0.5 h. After cooling with ice-cold water, the crude product was extracted with diethyl ether (3×5 mL) and the conversion was determined by GC analyses. The aqueous phase containing the catalytic species was evaporated under reduced pressure to remove possible residual diethyl ether. The aqueous catalytic system was recharged with the same substrates and 1.0 mmol base for the next run.

General procedure for the Hiyama cross-coupling reaction

A 25 mL reactor equipped with a condenser was charged with aryl halide (1.0 mmol), arylsiloxane (1.5 or 2.0 mmol), **3** (0.5 mol%), NaOH (2 to 5 mmol), TBAB (1.0 mmol), and H_2O (3 mL). The aqueous solution was stirred in a preheated oil bath (120 °C) for 6 h. After the mixture was cooled with ice-cold water to room temperature, the product was extracted with diethyl ether (3×5 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The crude products were purified by flash column chromatography on silica gel to afford the desired products. The identity of the products was confirmed by comparison with spectroscopic data reported in the literature.

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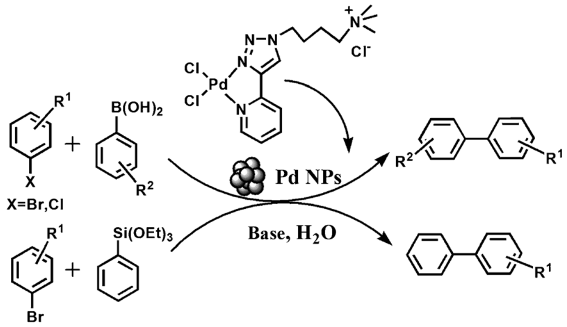

In complete control: A water-soluble palladium(II) click chelating complex serves as an efficient precursor for the formation of palladium nanoparticles (NPs; see picture). Excellent catalytic performances are achieved in Suzuki–Miyaura and Hiyama cross-coupling reactions in water.

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Water-Soluble Palladium Click Chelating Complex: An Efficient and Reusable Precatalyst for Suzuki–Miyaura and Hiyama Reactions in Water