Journal of Organometallic Chemistry 695 (2010) 297–303

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

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

An efficient and recyclable water-soluble cyclopalladated complex for aqueous Suzuki reactions under aerial conditions

Jin Zhou [a,b], Xiaoyan Li [a], Hongjian Sun [a,*]

[a] School of Chemistry and Chemical Engineering, Shandong University, Shanda Nanlu 27, 250100 Jinan, People's Republic of China
[b] School of Chemical Engineering, Shandong University of Technology, Zibo 255049, China

ARTICLE INFO

Article history:
Received 6 August 2009
Received in revised form 17 September 2009
Accepted 25 September 2009
Available online 3 October 2009

Keywords:
Cyclopalladated complex
Palladium
Suzuki reaction
Water soluble
Aqueous

ABSTRACT

Several water-soluble cyclopalladated complexes with five- or six-membered rings have been prepared as air-stable solids from Schiff base ligands bearing an N-phenyl sulfonate groups. Cyclopalladated complexes with six-membered rings show high catalytic efficiency for the Suzuki reactions of aryl bromides with phenylboronic acid in aqueous solvents under mild conditions. Palladium complex **1** can be used for five reaction cycles in high conversions for the Suzuki reactions in neat water without additives. The catalytic process for the Suzuki couplings is proved by TEM analysis to proceed on Pd(0) nanoparticles. Surfactant-protected palladium nanoparticles present lower activities and poorer recyclability for the coupling reactions than those generated *in situ* without additives.

1. Introduction

In the past two decades, the palladium-catalyzed Suzuki reaction of aryl halides with arylboronic acids has evolved into one of the most important and powerful methods to form biaryls [1–8]. Under increasing environmental awareness, water is an attractive alternative to traditional organic solvents because it is inexpensive, nonflammable, nontoxic, and environmentally sustainable. Since Casalnuovo's initial report of TPPMS (triphenylphosphine monosulfonate)/$Pd(OAc)_2$ catalyst system for cross coupling reactions in aqueous solvents [9], Suzuki reaction in aqueous phase including neat water and water–organic mixed solvents has been received much more attention [10–15].

Recently, cyclopalladated complexes have attracted much attention as exciting catalyst precursors to cross coupling reactions [16–20]. The first water-soluble cyclopalladated imine complex reported by Ryabov was applied as catalyst for ester hydrolysis [21]. The use of the hydrophilic cyclopalladated complexes in water is expected to perform as a recyclable and highly active catalyst system for the Suzuki reaction in aqueous solvents. There have been several examples of hydrophilic cyclopalladated complexes or Pd pincer complexes (these so-called pincer complexes are usually denoted as Pd-ECE, such as Pd-NCN, Pd-PCN or Pd-SCS-pincer complex, where E is a neutral two-electron donor atom, and C represents the anionic carbon atom) reported as precatalysts for aqueous Suzuki reactions [22–30]. The simple Pd-oximed complexes with a hydroxy substituent on the aromatic rings reported by Nájera are highly active catalysts for Suzuki couplings of aryl bromides, activated aryl chlorides or heteroaromatic chlorides [22,23]. Pd-NCN and Pd-PCN pincer complexes reported by SanMartin and his co-workers were employed as good catalyst for Suzuki couplings in neat water, although these two precatalysts were not exactly water soluble [24,25]. A hydrophilic Pd-CNC pincer complex was proved to be a highly efficient recyclable homogeneous catalyst for Suzuki couplings, and the reaction could be repeated up to five times [26]. Additionally, the polymer-supported SCS-pincer complexes [27,28] and the oximed cyclopalladated complex attached silica [29] were also used as recyclable heterogeneous catalysts for Suzuki couplings, and it was suggested that the nanopalladium generated gradually *in situ* was the active catalytic species for the reactions. Combined with a water-soluble phosphine ligand (t-Bu-Amphos), cyclopalladated imine complex with sulfonate groups could be efficiently used for coupling reaction of 4-bromotoluene with phenylboronic acid in eleven reaction cycles, but those Pd complexes were not efficient precatalysts on their own [30]. As one of the most popular classes of cyclopalladated derivatives, a cyclopalladated imine complex has proved to be efficient for Suzuki reactions in aqueous solvent with TBAB (tetrabutylammonium bromide) additive [31]. However, no cyclopalladated imine complexes have been reported as efficient and recyclable catalytic precursors for Suzuki reaction in neat water without supports or additives.

* Corresponding author. Tel.: +86 0531 88361350; fax: +86 0531 88564464.
E-mail addresses: zhoujin820514@163.com (J. Zhou), hjsun@sdu.edu.cn (H. Sun).

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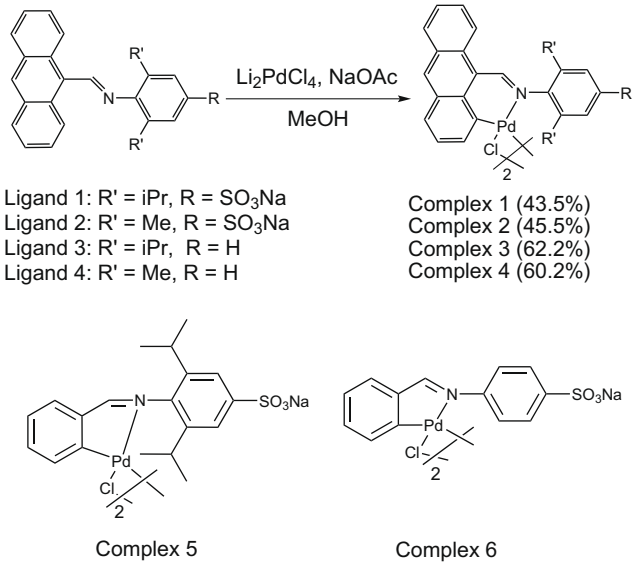
doi:10.1016/j.jorganchem.2009.09.039

Herein, we report several water-soluble cyclopalladated imine complexes and its catalytic performance toward Suzuki reactions in aqueous phase. It was found that the chelated structure of Pd complexes were crucial for the catalytic efficiency. The new complex **1** with six-membered rings is proved to be a highly efficient and recyclable catalyst precursor for the Suzuki reactions of aryl bromides in neat water without additives.

2. Results and discussion

2.1. Preparation of ligands and complexes

Condensation of the sodium salt of 3,5-dialkyl sulfanilic acid (or 2,6-dialkyl aniline) with anthracene-9-carbaldehyde in anhydrous methanol yielded the desired Schiff base ligands. Then the hydrophilic cyclopalladated complexes (**1** and **2**) were prepared by a traditional C–H activation reaction of the sulfonated Schiff base ligands with Li_2PdCl_4 in the presence of sodium acetate in anhydrous methanol (Scheme 1). It has been proved that the weakly coordinating sulfonate anion does not strongly coordinate to palladium, allowing the simple cyclopalladated dimmers to be isolated [30]. The C–H activation in 1-position of the anthracene ring was monitored by the decrease of the ^1H NMR signal intensity. Complexes **1** and **2** are soluble in strongly polar solvents such as water, methanol, dimethyl sulfoxide or others. The corresponding hydrophobic **3** and **4** were prepared by a similar method. IR spectrum reveal a red-shift of $\nu_{C=N}$ from about 1628 cm^{-1} (for Schiff base ligands) to about 1606 cm^{-1} (for complexes). An IR absorption at 1188 cm^{-1} ($\nu_{S=O}$) is displayed for both sulfonated ligands and complexes. Two Shaughnessy-type cyclopalladated complexes (**5** and **6**) were also prepared.



Scheme 1. Complexes **1**–**6.**

The detailed structure of complex **3** was determined by an X-ray diffraction study on orange crystals obtained from a dichloromethane solution [32]. Fig. 1 displays an ORTEP plot of complex **3**. The complex possesses a palladium dimer configuration. In the crystal, each palladium center is in slightly distorted square-planar coordination geometry with nitrogen and carbon donors in *cis*-positions as expected.

2.2. Comparison of catalytic activities of cyclopalladated complexes

The coupling of 4-bromoanisole with phenylboronic acid was selected as a model reaction (Table 1). In a typical experiment, 4-bromoanisole, phenylboronic acid and base in a ratio of 1:1.5:2 were placed in the flask, followed by the addition of the catalyst and the solvent. All instances were carried out under aerial conditions and at appropriate temperature. Evidently, the Pd complexes with six-membered rings (complexes **1** and **2**) are more efficient than Shaughnessy-type Pd complexes with five-membered rings (complexes **5** and **6**). Palladium black was found in the reactions using five-membered Pd complex. The hydrophobic cyclopalladated complexes also gave high conversions in neat water without additives with higher Pd loading of 0.05 mol% at refluxing temperature (Table 1, entries 6 and 7). It appears that the steric hindrance has little influence on catalytic activities of Schiff base ligands (Table 1, entries 1–4). Interestingly, quantitative conversions were achieved for coupling reactions in H_2O/EtOH mixed solvent with either **1** or **5** as catalytic precursor (Table 1, entries 12 and 13), indicating a potential solvent effect.

Today, it is now widely accepted that the cyclopalladated complex operate *via* a traditional Pd(0)–Pd(II) catalytic cycle. These Pd complexes are hypothesized as a source of ligand-free palladium [33]. To know the nature of the catalytic system, TEM analysis

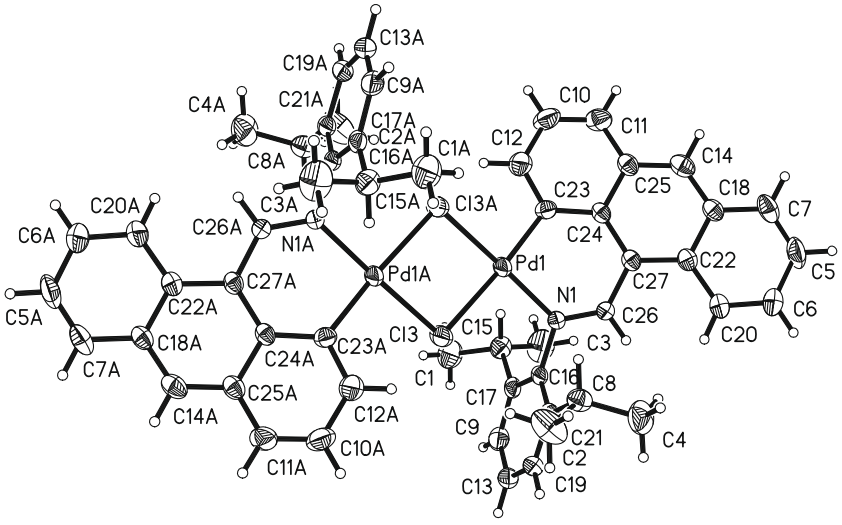


Fig. 1. ORTEP drawing of **3** (drawn with 30% probability ellipsoids).

Table 1
Comparison of catalytic activities of complexes **1**–**6**.[a]

Entry	Complex	[Pd] (mol%)	T (°C)	t (h)	Solvent[b]	Yield (%)[c]
1	**1**	0.01	100	1	H_2O	99
2	**2**	0.01	100	1	H_2O	98
3	**5**	0.01	100	1	H_2O	80[d]
4	**6**	0.01	100	1	H_2O	81[d]
5	**3**	0.05	100	1	H_2O	96
6	**4**	0.05	100	1	H_2O	96
7	**5**	0.1	100	1	H_2O	81[d]
8	**1**	0.01	80	1	H_2O	92
9	**5**	0.01	80	1	H_2O	80
10	**1**	0.1	30	15	H_2O	86
11	**5**	0.1	30	15	H_2O	64[d]
12	**1**	0.05	15	10	H_2O/EtOH[e]	100
13	**5**	0.05	15	10	H_2O/EtOH[e]	100

[a] *Reaction conditions*: 1 mmol of 4-bromoanisole, 1.5 mmol of phenylboronic acid, 2 mol of KOH, solvent.
[b] 10 mL of H_2O.
[c] GC yield based on 4-bromoanisole.
[d] Pd black was found.
[e] H_2O:EtOH = 2 mL:2 mL.

was used to monitor the pathway of the coupling reaction. First, a sample was examined which was activated by refluxing the combination of **1** (or **5**) + phenylboronic acid + KOH in water. The TEM analysis of **1** (Fig. 2a) showed the formation of palladium nanoparticles with a diameter in the range 20–150 nm, while complex **5** (Fig. 2b) aggregated into larger nanoparticles (20–250 nm) with much more nanoparticles over 150 nm than complex **1**. Quantitative conversion was achieved using the above solution of complex **1** for the coupling of 4-bromoanisole and phenylboronic acid, while 80% conversion was achieved for complex **5**, suggesting that the palladium nanoparticles might be the active catalytic species for the coupling reaction. It is likely that the cyclopalladated complex reacted with phenylboronic acid to give the 2-phenyl analogue of the new imine ligand (Scheme 2), and released the palladium nanoparticles [34]. The loose protection due to the weak stabilizing effect of the new ligands towards nanoparticles could prevent the aggregation of nanoparticles into inactive palladium black, and makes these nanoparticles highly active towards the substrates. The fact that the six-membered **1** is more active than the five-membered **5** is due to the size effect of nanopalladium [31,35].

2.3. Suzuki reactions catalyzed by cyclopalladated complexes with six-membered rings

The catalytic performance of the six-membered complexes was studied (Table 2). All reactions proceeded smoothly under aerial conditions. Initially, the coupling reactions were carried out in different solvents. Generally, complex **1** or **3** gave poorer catalytic activities in pure organic solvents (CH_3CN and EtOH), and low conversions were obtained for these reactions (Table 2, entries 1–4). The reaction yields were dramatically improved when water was introduced as a medium (Table 2, entries 5 and 6). KOH gave higher yields than K_2CO_3 or NaOAc (Table 2, entries 6–8). An outstanding coupling reaction could be carried out with quantitative conversion at 15 °C with a loading of 0.05 mol% Pd in H_2O/EtOH mixed solvents (Table 2, entries 9 and 10). Interestingly, the hydrophobic **3** present higher activity in H_2O/EtOH mixed solvent (Table 2, entries 8–10), while the hydrophilic **1** was more efficient in neat water (Table 2, entries 12 and 13). The hydrophilic **1** could smoothly dissolve in either neat water or aqueous solvents, while complex **3** is soluble in H_2O/EtOH mixed solvent and insoluble in neat water. In other words, complex **3** could not deliver high dis-

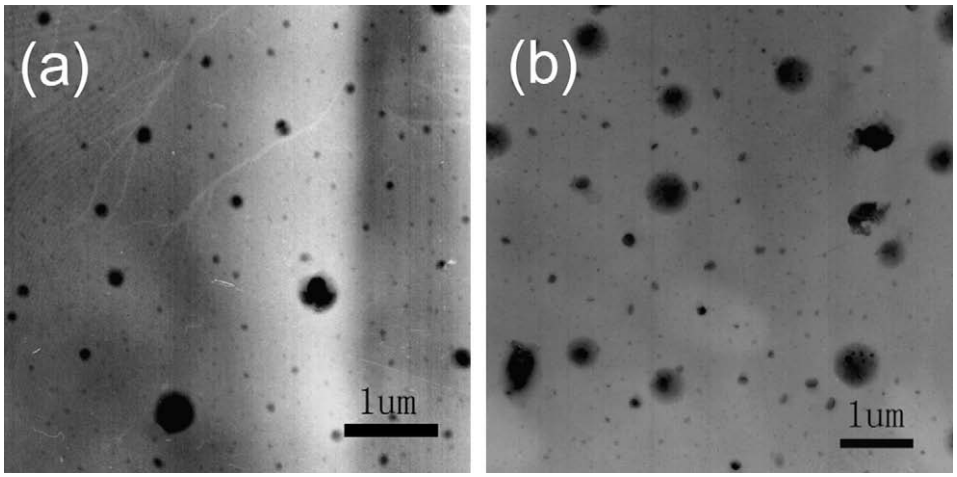
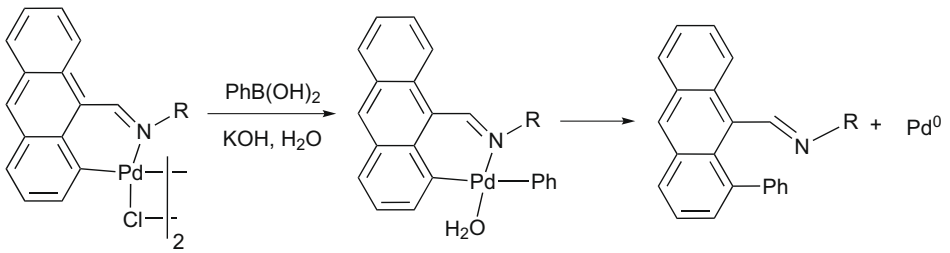


Fig. 2. TEM micrographs of palladium nanoparticles.



Scheme 2. The formation of palladium nanoparticles.

persive and active nanoparticles in neat water due to its insolubility. We suggest that the solubility of substrates and catalyst was crucial for the reactions in neat water (Table 2, entries 12 and 13), while the substituent effect of sulfonate groups may be related to the lower activities of hydrophilic **1** in mixed solvents (Table 2, entries 8 and 10), demonstrating the different performance of **1** and **3**. Thereby it is evident that the hydrophilic **1** is more advantageous for the Suzuki reactions in neat water than the hydrophobic **3**.

Table 2
Catalytic performance of complexes **1** and **3**.[a]

Entry	Complex	[Pd] (mol%)	Solvent[b]	Base	T (°C)	t (h)	Conv.[c] (%)	Yield[d] (%)
1	**1**	1	CH_3CN	K_2CO_3	50	5	Trace	
2	**1**	0.1	DMA	K_2CO_3	30	5	30	
3	**1**	0.05	EtOH	K_2CO_3	15	10	10	
4	**3**	0.05	EtOH	K_2CO_3	15	10	15	
5	**1**	1	H_2O/CH_3CN	K_2CO_3	50	3	30	
6	**1**	0.05	H_2O/EtOH	K_2CO_3	15	4	45	40
7	**1**	0.05	H_2O/EtOH	NaOAc	15	4	20	
8	**1**	0.05	H_2O/EtOH	KOH	15	4	55	50
9	**1**	0.05	H_2O/EtOH	KOH	15	10	100	99
10	**3**	0.05	H_2O/EtOH	KOH	15	5	100	99
11	**1**	0.01	H_2O	KOH	100	1	99	96
12	**1**	0.1	H_2O	KOH	30	4	55	50
13	**3**	0.1	H_2O	KOH	30	4	11	
14	**1**	0.1	H_2O	KOH	30	10	86	82

[a] *Reaction conditions*: 1 mmol of 4-bromoanisole, 1.5 mmol of phenylboronic acid, 2 mmol of base, 10 mL of solvent.
[b] Water:organic solvent = 2 mL:2 mL if necessary.
[c] Determined by GC, average of three runs.
[d] Isolated yield.

Table 3
Suzuki reactions using complex **1** in neat water.[a]

Entry	ArX	[Pd] (mol%)	T (°C)	t (h)	Conv. (%)[b]	Yield (%)[c]
1	p-$MeOC_6H_4Br$	0.01	80	1	92	90
2	p-$MeOC_6H_4Br$	0.01	100	1	99	98
3	p-$MeOC_6H_4Br$	0.01	30	12	25	
4	p-$MeOC_6H_4Br$	0.1	8	12	30	
5	p-$MeOC_6H_4Br$	0.1	30	10	86	82
6	p-$MeOC_6H_4Br$	0.001	100	1	99	96
7	p-$MeOC_6H_4Br$	0.0001	100	5	90	87
8	p-$MeOC_6H_4Br$	0.00001	100	15	93	90
9	p-$NO_2C_6H_4Br$	0.01	100	1	99	95
10	2-MeC_6H_4Br	0.02	100	3	96	90
11	4-MeC_6H_4Br	0.01	100	1.5	93	90
12	2,6-MeC_6H_4Br	0.1	100	5	30	

[a] *Reaction conditions*: 1 mmol of aryl bromides, 1.5 mmol of phenylboronic acid, 2 equiv. of KOH, 15 mL of water, palladacycle **1**.
[b] Determined by GC, average of three runs.
[c] Isolated yield.

The scope of catalytic system using complex **1** was explored with a range of aryl bromides (Table 3). Electron-deficient and electron-rich aryl bromides could be coupled with phenylboronic acid in excellent yields in neat water. A quantitative conversion and excellent yield were obtained at reflux temperature for the coupling of 4-bromoanisole and phenylboronic acid with 0.01 mol% loading of Pd (Table 3, entry 2). The coupling reactions were carried out at different temperatures (Table 3, entries 1–5), and a conversion of 30% could be obtained even at low temperature of 8 °C (the temperature of lab in winter, Table 3, entry 5). A conversion of 93% was reached after 15 h only using 10^{-5} mol% loading of Pd, which corresponded to a TON of 9.3×10^6 (Table 3, entry 8). Reactions in water appear to be sensitive to steric hindrance of the substrate. 2-Bromotoluene gave 96% yield of coupling product with phenylboronic acid using an increased Pd loading (0.02 mol%) and extended reaction time, while 2,6-dimethylbromobenzene gave only 30% yield (Table 3, entries 10 and 12).

2.4. Catalyst recycling

The recyclability of **1** was also investigated for Suzuki reactions in neat water. Three catalyst precursors, including complexes **1**, **5** and Li_2PdCl_4, were explored (Table 4). It was shown that complex **1** could be repeated up to three times in nearly quantitative yield before the efficiency of the catalyst began to degrade, while Li_2PdCl_4 or complex **5** gave dramatically decreased conversions (75% or 50%, respectively) in the second cycle. The six-membered cyclopalladated complexes showed better recyclability than those five-membered complexes. Of interest is that the catalytic system using **1** as precatalyst could be used for five cycles in over 90% yield by extending the reaction time after the third cycle (Table 4, entries 3 and 4).

As shown in Fig. 3, the TEM analysis suggests that a large number of active nanoparticles exist in every run of complex **1** that appears to sustain the catalytic activity. El-Sayed and his co-workers reported that the reactant of phenylboronic acid could act as a stabilizer because the O^- of the deprotonated phenylboronic acid could bind to the surface of the palladium nanoparticles with terminal or bridged binding mode [36,37]. As a result, the Ostwald ripening of nanoparticles could be greatly inhibited, and the nano-

Table 4
Recycling of complex **1.**[a]

Entry	Complex	[Pd]mol%	S (mmol)	Reaction yield by cycle[b]							
				1	2	3	4	5	6	7	8
1	Li_2PdCl_4	0.1		97	75	20					
2[c]	**1**	0.01		99	87	92	62	40	40		
3[d]	**1**	0.1		97	82	98	67	99 [e]	90 [e]		
4[c]	**1**	0.1		99	90	98	85	60	99	37	20
5	**5**	0.01		83	35	10					
6	**5**	0.1		80	50	8					
7[f]	**1**	0.1	TBAB (0.1)	99	80	93	63	60			
8[f]	**1**	0.1	TBAB (1.0)	99	87	86	49	40			
9[f]	**1**	0.1	PVP (0.1)	98	80	60					
10[f]	**1**	0.1	PVP (1.0)	98	60	32	5				

[a] *Reaction conditions*: 1 mmol of 4-bromoanisole, 1.5 mmol of phenylboronic acid, 2 equiv. of KOH, 20 mL of water, Pd complex, 100 °C, 1 h.
[b] GC yield, average of three runs.
[c] 1.5 h for cycles 1–3; 2 h for cycles 4 and 5; 15 h for cycles 6–8.
[d] 1 h for cycles 1–4.
[e] 18 h.
[f] Reaction conditions same to entry 3 except surfactant as additive.

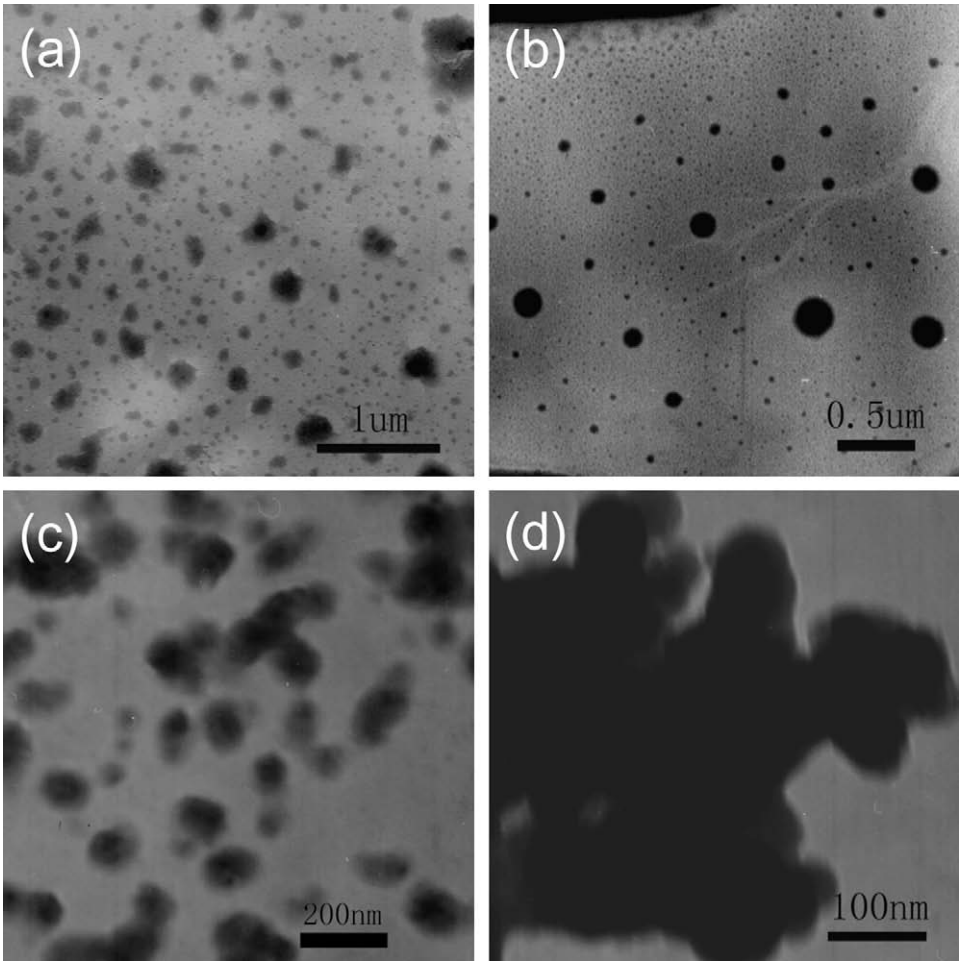


Fig. 3. TEM analysis of catalyst cycles 1–4 (Fig. 3a–d).

particles do not dramatically increase in size. Then, the palladium nanoparticles, which could be considered to be soluble in water because of the ligation of deprotonated phenylboronic acid, could be reused for several cycles. It could be also explained that the degradation of catalytic activity is due to the thermodynamically favored Ostwald ripening process and a greater amount of phenylboronic acid bound to the free active sites of metallic species.

Quaternary ammonium compounds and polymers, such as TBAB and PVP (polyvinylpyrrolidone), are often used as surfactants and stabilizers for nanoparticles. The effects of TBAB and PVP additives were studied. In the presence of 0.1 equiv. of TBAB, the yields were almost same as that without additives for the reaction cycles 1–4, while a lower yield (60%) was obtained for the fifth cycle (Table 4, entry 7). With the increased amount of TBAB (1.0 equiv.), the catalytic system began to lose activity from the third run (Table 4, entry 8), indicating that the excess TBAB could diminish the activity of **1**. Compared with TBAB, PVP additive shows much more diminished effect on catalytic activity of **1** and resulted in lower yields of coupling products (Table 4, entries 9 and 10). Basing on the pathway of palladium nanoparticles, the lower catalytic activity observed could be due to the fact that there are less free metallic surface sites available for the catalysis because many of the free sites are capped by excess surfactant stabilizer.

3. Conclusions

The water-soluble cyclopalladated complex **1** with six-membered rings has been proved to be a highly efficient and recyclable catalyst precursor for Suzuki reactions of aryl bromides in neat water. TEM analysis suggests an active species of Pd(0) nanoparticles for the Suzuki reactions. Surfactants or excess of phenylboronate can occupy active free sites of palladium nanoparticles and result in lower catalytic activity.

4. Experimental

4.1. Materials

Methanol and dichloromethane were purified by standard methods. The sodium salts of 3,5-dialkyl sulfanilic acid [38,39] and the benzaldehyde imine ligands [30] were prepared by modifications of literature procedures. All other reagents were used as received from commercial sources.

4.2. Apparatus

GC yields were determined by comparison to an internal standard. ^{1}H NMR and ^{13}C NMR were recorded on a Bruker 300 MHz. TEM analysis was carried on by a JEM 100-CX II.

4.3. Preparation of ligand *1*

Anthracene-9-carbaldehyde (0.22 g, 1.07 mmol) and sodium salt of 3,5-diisopropyl sulfanilic acids (0.28 g, 1.00 mmol) were dissolved in 5 mL of anhydrous methanol. Two drops of formic acid were added into the solution as catalyst. The mixture was stirred

for 24 h at 40 °C. Ethyl ether (30 mL) was transferred to the reaction mixture, and the crude product was isolated. Recrystallization from methanol/ethyl ether delivered the pure product as a yellow solid (0.27 g, yield in 58%). IR (KBr) 1628 cm^{-1} ($\nu_{C=N}$), 1188 cm^{-1} ($\nu_{S=O}$). ^1H NMR (300 MHz; CD_3OD; Me_4Si) δ 9.54 (1H, s, CH=N), 8.94 (2H, d, ArH), 8.73 (1H, s, ArH), 8.15 (2H, d, ArH), 7.79 (2H, s, ArH), 7.65–7.54 (4H, m, ArH), 3.64–3.50 (2H, m, $CHMe_2$), 1.30 (12H, d, $-CH_3$). ^{13}C NMR (75.5 MHz; CD_3OD) δ 163.3, 151.6, 140.8, 137.7, 133.19, 131.5, 131.4, 130.81, 129.0, 127.4, 125.2, 124.0, 120.8, 28.2, 27.4, 22.5, 21.4, 17.0. Anal. Found (calc. for $C_{27}H_{26}NSO_3Na$): C, 69.13 (69.36); H, 5.78 (5.61); N, 2.74 (3.00)%.

Other Schiff base ligands were prepared by a similar method.

Ligand **2**: yellow solid (65%). IR (KBr): 1629 cm^{-1} ($\nu_{C=N}$), 1181 cm^{-1} ($\nu_{S=O}$). ^1H NMR (300 MHz; DMSO-d_6; Me_4Si) δ 9.56 (1H, s, CH=N), 8.94 (2H, d, ArH), 8.85 (1H, s, ArH), 8.21 (2H, d, ArH), 7.79 (2H, s, ArH), 7.70–7.59 (4H, m, ArH), 2.29 (6H, s, $-CH_3$). ^{13}C NMR (75.5 MHz; DMSO-d_6) δ 163.7, 152.7, 143.9, 131.4, 131.3, 130.5, 129.5, 128.1, 126.7, 126.0, 125.7, 125.1, 19.2. Anal. Found (calc. for $C_{23}H_{18}NSO_3Na$): C, 66.56 (67.14); H, 4.62 (4.41); N, 3.40 (3.58)%.

Ligand **3**: yellow solid (75%). IR (KBr) 1630 cm^{-1} ($\nu_{C=N}$). ^1H NMR (300 MHz; $CDCl_3$; Me_4Si) δ 9.52 (1H, s, CH=N), 8.98 (2H, d, ArH), 8.62 (1H, s, ArH), 8.10 (2H, d, ArH), 7.64–7.52 (4H, m, ArH), 7.31–7.21 (3H, m, ArH), 3.34–3.25 (2H, m, $CHMe_2$), 1.28 (12H, d, $-CH_3$). Anal. Found (calc. for $C_{27}H_{27}N$): C, 88.72 (88.52); H, 7.50 (7.45); N, 3.75 (3.83)%.

Ligand **4**: yellow solid (70%). IR (KBr) 1630 cm^{-1} ($\nu_{C=N}$). ^1H NMR (300 MHz; $CDCl_3$; Me_4Si) δ 9.52 (1H, s, CH=N), 8.98 (2H, d, ArH), 8.62 (1H, s, ArH), 8.10 (2H, d, ArH), 7.64–7.52 (4H, m, ArH), 7.31–7.21 (3H, m, ArH), 2.29 (6H, s, $-CH_3$). Anal. Found (calc. for $C_{23}H_{19}N$): C, 89.20 (89.28); H, 6.22 (6.19); N, 4.69 (4.53)%.

Ligand **5**: white solid (40%). IR (KBr) 1648 cm^{-1} ($\nu_{C=N}$), 1178 cm^{-1} ($\nu_{S=O}$). ^1H NMR (300 MHz; DMSO-d_6; Me_4Si) δ 8.31 (1H, s, CH=N), 7.97 (2H, d, ArH), 7.61–7.55 (3H, m, ArH), 7.40 (2H, s, ArH), 2.91–2.82 (2H, m, $-CHMe_2$), 1.12 (12H, d, $-CH_3$). ^{13}C NMR (75.5 MHz; DMSO-d_6) δ 163.3, 149.8, 143.9, 136.5, 136.0, 132.2, 129.5, 128.9, 120.8, 28.0, 23.6. Anal. Found (calc. for $C_{19}H_{22}NSO_3Na$): C, 61.08 (62.11); H, 6.10 (6.03); N, 3.51 (3.81)%.

Ligand **6**: white solid (42%). IR (KBr); 1647 cm^{-1} ($\nu_{C=N}$), 1188 cm^{-1} ($\nu_{S=O}$). ^1H NMR (300 MHz; D_2O; Me_4Si) δ 9.90 (1H, s, CH=N), 7.93 (2H, d, ArH), 7.79–7.68 (1H, m, ArH), 7.67–7.50 (4H, m, ArH), 6.84 (2H, d, ArH). ^{13}C NMR (75.5 MHz; DMSO-d_6): δ 163.9, 151.4, 145.9, 136.0, 131.5, 128.8, 128.7, 126.6, 120.2. Anal. Found (calc. for $C_{13}H_{10}NSO_3Na$): C, 56.52 (55.12); H, 3.70 (3.56); N, 5.31 (4.94)%.

4.4. General procedure for preparation of cyclopalladated complexes

To a round-bottomed flask with a stir bar was placed Li_2PdCl_4 (130 mg, 0.5 mmol), Schiff base ligands (0.5 mmol) and sodium acetate (41 mg, 0.5 mmol) under nitrogen. Anhydrous methanol (3 mL) was added, and the resulting mixture was stirred at room temperature for 2 days. The reaction mixture was filtered off. The hydrophilic complexes were isolated as orange or yellow solids which were recrystallized from methanol/ethyl ether solution.

Complex **1**: orange solid (75%). IR (KBr) 1606 cm^{-1} ($\nu_{C=N}$), 1188 cm^{-1} ($\nu_{S=O}$). ^1H NMR (CD_3OD, 300 MHz) δ 9.13 (2H, s, CH=N), 8.83 (2H, s, ArH), 8.36 (2H, d, ArH), 8.17 (2H, d, ArH), 7.85 (6H, t, ArH), 7.68 (2H, t, ArH), 7.59–7.50 (4H, m, ArH), 7.34 (2H, s, ArH), 3.72–3.57 (4H, m, $-CHMe_2$), 1.54 (12H, d, $-CH_3$), 1.16 (12H, d, $-CH_3$). ^{13}C NMR (300 MHz; CD_3OD) δ 160.6, 148.2, 144.8, 140.6, 138.5, 131.22, 130.7, 129.6, 128.9, 126.4, 125.2, 121.8, 121.3, 28.5, 23.8, 22.2. Anal. Found (calc. for $C_{54}H_{50}N_2S_2O_6Na_2Pd_2Cl_2$): C, 52.56 (53.30); H, 4.34 (4.14); N, 2.18 (2.30)%.

Complex **2**: orange solid (70%). IR (KBr) 1606 cm^{-1} ($\nu_{C=N}$), 1187 cm^{-1} ($\nu_{S=O}$). ^1H NMR (300 MHz; DMSO-d_6; Me_4Si) δ 9.15 (2H, s, CH=N), 8.95 (2H, s, ArH), 8.20 (4H, t, ArH), 7.88 (2H, d, ArH), 7.70 (2H, t, ArH), 7.60 (4H, t, ArH), 7.44 (4H, s, ArH), 7.27 (2H, t, ArH), 2.51 (12H, s, $-CH_3$). ^{13}C NMR (75.5 MHz; DMSO-d_6) δ 160.1, 149.2, 146.5, 141.7, 137.4, 134.6, 133.7, 131.1, 130.8, 130.5, 129.8, 129.3, 127.2, 126.0, 125.8, 125.5, 124.9, 123.5, 19.2. Anal. Found (calc. for $C_{46}H_{34}N_2S_2O_6Na_2Pd_2Cl_2$): C, 48.69 (50.02); H, 3.15 (3.10); N, 2.69 (2.54)%.

Complex **3**: orange solid (83%). IR (KBr) 1606 cm^{-1} ($\nu_{C=N}$). ^1H NMR (300 MHz; $CDCl_3$; Me_4Si) δ 9.50 (2H, s, CH=N), 8.95 (2H, s, ArH), 8.66 (2H, d, ArH), 7.85–7.70 (4H, m, ArH), 7.63–7.50 (8H, m, ArH), 7.32–7.20 (6H, m, ArH), 3.62–3.47 (4H, m, $-CHMe_2$), 1.27 (12H, d, $-CH_3$), 1.13 (12H, d, $-CH_3$). Anal. Found (calc. for $C_{54}H_{52}N_2Pd_2Cl_2$): C, 64.10 (64.04); H, 5.20 (5.18); N, 2.91 (2.77)%.

Complex **4**: orange solid (86%). IR (KBr) 1606 cm^{-1} ($\nu_{C=N}$). ^1H NMR (300 MHz; $CDCl_3$; Me_4Si) δ 9.52 (2H, s, CH=N), 8.93 (2H, s, ArH), 8.69 (2H, d, ArH), 7.85–7.70 (4H, m, ArH), 7.63–7.50 (8H, m, ArH), 7.36–7.22 (6H, m, ArH), 2.48 (12H, s, $-CH_3$). Anal. Found (calc. for $C_{46}H_{36}N_2Pd_2Cl_2$): C, 61.41 (61.35); H, 3.91 (4.03); N, 3.28 (3.11)%.

Complex **5**: yellow solid (60%). IR (KBr) 1600 m^{-1} ($\nu_{C=N}$), 1187 cm^{-1} ($\nu_{S=O}$). ^1H NMR (DMSO-d_6, 300 MHz) δ 8.26 (2H, s, CH=N), 7.83 (2H, s, ArH), 7.49–7.39 (6H, m, ArH), 7.23–7.11 (4H, m, ArH), 3.29–3.20 (4H, m, $CHMe_2$), 1.27 (12H, d, $-CH_3$), 1.09 (12H, d, $-CH_3$). ^{13}C NMR (DMSO-d_6, 75.5 MHz) δ 147.2, 146.0, 142.2, 140.7, 135.1, 131.0, 130.7, 129.1, 124.4, 120.3, 28.18, 24.57, 22.95. Anal. Found (calc. for $C_{38}H_{42}N_2S_2O_6Na_2Pd_2Cl_2$): C, 42.51 (44.90); H, 4.51 (4.16); N, 3.17 (2.76)%.

Complex **6**: yellow solid (50%). IR (KBr) 1600 cm^{-1} ($\nu_{C=N}$), 1188 cm^{-1} ($\nu_{S=O}$). ^1H NMR (300 MHz; D_2O; Me_4Si) δ 9.97 (2H, s, CH=N), 7.99–7.68 (6H, m, ArH), 7.67–7.52 (4H, m, ArH), 6.88 (8H, d, ArH). Anal. Found (calc. for $C_{26}H_{18}N_2S_2O_6Na_2Pd_2Cl_2$): C, 37.56 (36.81); H, 2.58 (2.14); N, 3.79 (3.30)%.

4.5. General procedure for Suzuki reactions

To a 50 mL round-bottomed flask equipped with condenser were placed Pd complex, aryl bromide (1.0 mmol), base (2.0 mmol), phenylboronic acid (1.5 mmol), and solvent (5 mL). The reaction mixture was stirred and heated at reaction temperature for a given period of time. Upon cooling the reaction mixture was extracted with three portions of CH_2Cl_2 (5 mL). The extract was dried by Na_2SO_4 and concentrated to yield solid material or oil. Reaction conversions were determined by GC analysis using decane as an internal standard. The crude materials were flash chromatographed on a short silica gel column and eluted with a mixture of ethyl acetate and petrol ether. The purified products were identified by ^1H NMR spectra.

4.6. General procedure for catalyst recycling trials

A 50 mL round-bottomed flask was charged with Pd complex (0.1 mol% Pd), KOH (112 mg, 2 mmol), 4-bromoanisole (187 mg, 1 mmol) and phenylboronic acid (180 mg, 1.5 mmol). A certain amount of TBAB or PVP (PVP k17 $(C_{10}H_9NO)_n$ = 8000) was added to the samples. Deionized water (20 mL) was added, and the resulting mixture was stirred at 100 °C for a given period of time. After cooling to room temperature, ethyl ether (15 mL) was added and the mixture was stirred for 1 min. The upper layer was separated and dried by Na_2SO_4. The reaction yields were determined by GC analysis. After removing the volatiles under vacuum, the flask was charged with 4-bromoanisole (1 mmol), phenylboronic acid (1.5 mmol) and KOH (2 mmol). Each time, after cooling and extraction, the reagents and base were added and the reaction was repeated.

4.7. TEM studies

For the test of **1** and **2** (Fig. 2a and b), 1 mmol of **1** or **2**, 2 mmol of KOH, 1.5 mmol of phenylboronic acid were refluxed in 20 mL of water for 1 h. After cooling the reaction mixture, the samples were spotted by placing a drop of the solution onto a copper grid and allowing it to evaporate under infrared in air.

For the test of recycling, a drop of the aqueous layer of every reaction cycle was placed onto a copper grid and allowing it to evaporate under infrared in air.

4.8. Characterization of the coupling products

Biphenyl ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.59–7.57 (4 H m,), 7.45–7.40 (4H, m), 7.35–7.30 (2H, m). m.p.: 69–70 °C.

4-Methoxybiphenyl ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.57–7.52 (4H, m), 7.42 (2H, t), 7.30 (1H, t), 6.98 (2H, d), 3.85 (3H, s). m.p.: 86–88 °C.

2-Methylbiphenyl ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.43–7.35 (2H, m), 7.34–7.27 (3H, m), 7.26–7.18 (4H, m), 2.27 (3H, s).

4-Methylbiphenyl ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.54 (2H, d), 7.45 (2H, d), 7.37 (2H, t), 7.27 (1H, t), 7.19 (2H, d), 2.34 (3H, s). m.p. 69–71 °C.

4-Nitrobiphenyl ^{1}H NMR (300 MHz; $CDCl_3$i): δ 8.27 (2H, m), 7.71 (2H, d), 7.70–7.34 (5H, m).

Acknowledgements

This work was supported by NSFC No. 20372042, Shandong Scientific Plan 032090105 and the Science Foundation of Shandong Y2006B18.

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