Dalton Transactions

PAPER

View Article Online

Cite this: DOI: 10.1039/c3dt52970c

The copper-free Sonogashira cross-coupling reaction promoted by palladium complexes of nitrogen-containing chelating ligands in neat water at room temperature[†]

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The commercially available 2,2'-dipyridylamine was used as a supporting ligand in the palladium-catalyzed Sonogashira cross-coupling reaction. The reactions between aryl iodides and terminal alkynes with different steric hindrance can be efficiently performed in the absence of copper in neat water at room temperature. The superior catalytic performance of the catalytic system was attributed to water solubility of the palladium 2,2'-dipyridylamine complex. Palladium nanoparticles with small size and narrow size distribution were formed after the cross-coupling reaction.

Received 22nd October 2013, Accepted 7th November 2013 DOI: 10.1039/c3dt52970c

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Introduction

Transition-metal-catalyzed cross-coupling reactions have been considered as one of the most valuable and straightforward methods for the formation of carbon-carbon or carbon-nitrogen bonds in modern organic synthesis.^{1,2} Among them, the palladium-catalyzed Sonogashira cross-coupling reaction between aryl halides and terminal alkynes is an efficient and convenient approach for the introduction of the acetylenic moiety into many biologically important compounds and the engineered materials.²⁻⁴ Traditionally, smooth accomplishment of the reaction has required the presence of both palladium and copper, which resulted in contamination of the coupling products with metal residues as well as a side reaction of Glaser-type oxidative dimerization of the alkyne substrates. These undesirable by-products are difficult to separate from the target products due to their similar chromatographic mobility.⁴ Considerable effort has been devoted to developing a copper-free Sonogashira cross-coupling reaction under mild conditions, especially for the expensive or commercially unavailable terminal alkynes. However, most of the reactions were performed in organic solvents or mixed organic/aqueous solvents,⁵ and neat water is seldom used as a reaction medium in the Sonogashira cross-coupling reaction.^{6,7}

Organic reactions in water are of highly practical value since most wastes per mass unit product in the chemical industry result from organic solvents.8 Although the reaction rates in water may be slower than those in organic solvents or biphasic aqueous systems, water is regarded as the most environmentally benign and cheap medium. Organic reactions in neat water usually place significant demands on the solubility of substrates and catalysts, and the use of water-soluble coordination complexes is a common route to the development of catalytic systems in water.9 Much effort has been devoted to the design and synthesis of water-soluble ionic compounds containing sulfonate, carboxylate and ammonium to serve as the supporting ligands of palladium in the cross-coupling reactions in neat water.¹⁰⁻¹² Very recently, we have prepared a series of water-soluble palladium nitrogen-containing chelating complexes,¹² which showed high catalytic activity and chemical selectivity in catalysis in neat water in comparison with their hydrophobic analogues. In addition, the catalytic activity and selectivity can be modified and tuned by varying the steric and electronic properties of the nitrogen-containing ligands as well as their coordination ability with metal ions, which greatly enhances the scope of catalysts for different catalytic applications, but they are not encouraging for the Sonogashira cross-coupling reaction in neat water. In our continuous study to explore the environmentally friendly catalytic systems,^{12,13} we found that the palladium 2,2'-dipyridylamine complex is soluble in neat water under ambient conditions, though 2,2'-dipyridylamine and palladium sources are insoluble (Scheme 1). This provides a possibility for development of the catalytic systems in water. Dpa was well known for its remarkable binding ability to transition metal ions. Although dpa has been covalently attached to various inorganic or

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[†]Electronic supplementary information (ESI) available: NMR data of the crosscoupling products and details of theoretical calculations. See DOI: 10.1039/ c3dt52970c



 $\label{eq:Scheme 1} \begin{array}{l} \mbox{The images for (a) $Pd(NH_3)_2Cl_2$ in H_2O; (b) $Pd(NH_3)_2Cl_2$ was oscillated in H_2O for 24 h; (c) $Pd(NH_3)_2Cl_2$ and dpa were oscillated in H_2O for 24 h. } \end{array}$

organic supports to serve as the coordination group of palladium(π) or palladium NPs,¹⁴ dpa is seldom chosen as a single supporting ligand in catalysis despite the crystal structure of its palladium(π) coordination complex being reported.¹⁵ Herein, we use the soluble Pd(NH₃)₂Cl₂-dpa complex as a precatalyst for the Sonogashira cross-coupling reaction in the absence of both copper and organic solvents at room temperature.

Results and discussion

In order to obtain a better understanding of the electronic characteristics of dpa and its palladium(II) complex (Pd-dpa), the charge distributions and molecular orbital analyses of dpa and Pd-dpa based on the optimized structures were implemented using Gaussian 03.16 As shown in Fig. 1 and Table S1 in ESI,[†] the nitrogen atoms in both dpa and Pd-dpa possess a negative charge, in which the pyridyl nitrogen atoms in Pd-dpa are more negative (-0.50062 and -0.50064e) than those in dpa (-0.46162 and -0.46163e) owing to the coordination of palladium(II). However, the amine nitrogen atom in Pd-dpa (-0.61948e) is less negative than that in dpa (-0.64026e). Two Cl⁻ ions possess the same negative charge (-0.52523e) in Pd-dpa, and the positive charge of palladium(II) is 0.70234e, which is close to those in similar palladium chelating complexes.¹² The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) have shown that HOMO and LUMO in dpa are shared owing to the conjugative effect. However, HOMO in Pd-dpa consists primarily of the contribution from the PdCl₂ group, and a delocalization over PdCl₂ and dpa was observed in the LUMO of Pd-dpa (Fig. 2).

Catalytic performances of Pd-dpa were initially evaluated using the Sonogashira cross-coupling reaction between iodobenzene and phenylacetylene. As shown in Table 1, when



Fig. 1 The charge distributions of dpa and Pd-dpa.



Fig. 2 HOMO and LUMO for dpa and Pd-dpa (isovalue = 0.02).

 Table 1
 Screening of reaction conditions in the Sonogashira crosscoupling reaction^a



Entry	Pd source	[Pd] amount (mol%)	Base	$\operatorname{Yield}^{b}(\%)$
1	Pd(NH ₃) ₂ Cl ₂	1	NEt ₃	100
2	$Pd(NH_3)_2Cl_2$	0.1	NEt ₃	95
3	$Pd(NH_3)_2Cl_2$	0.01	NEt ₃	51
4	PdCl ₂	0.1	NEt ₃	87
5	$Pd(cod)Cl_2$	0.1	NEt ₃	76
6	$Pd(OAc)_2$	0.1	NEt ₃	81
7	$Pd(NH_3)_2Cl_2$	0.1	(i-Pr) ₂ NH	26
8	$Pd(NH_3)_2Cl_2$	0.1	$(n-Bu)_3N$	30
9	$Pd(NH_3)_2Cl_2$	0.1	NaOAc	<1
10	$Pd(NH_3)_2Cl_2$	0.1	KOH	<1
11	$Pd(NH_3)_2Cl_2$	0.1	K_3PO_4	5
12	$Pd(NH_3)_2Cl_2$	0.1	Cs_2CO_3	7
13	$Pd(NH_3)_2Cl_2$	0.1	Bu_4NOH	<1
14^c	$Pd(NH_3)_2Cl_2$	0.1	NEt ₃	72

^{*a*} Reaction conditions: iodobenzene (0.50 mmol), phenylacetylene (0.75 mmol), base (1.50 mmol), and H_2O (2.0 mL) at 25 °C for 6 h under N₂; the molar ratio of [Pd]/dpa is 1:1. ^{*b*} GC yield. ^{*c*} No water was added.

the reaction was performed using 1 mol% Pd(NH₃)₂Cl₂ and dpa in the presence of NEt₃ in neat water at 25 °C for 6 h, 1,2diphenylethyne was obtained in a quantitative yield (entry 1), and no side products of diynes or enynes were detected. Decreasing the loading of palladium and dpa to 0.1 and 0.01 mol% under the same conditions gave 95% and 51% GC yields, respectively (entries 2 and 3). This effect was further investigated by the kinetic curve of conversion versus palladium loading (Fig. S1[†]). The variation of palladium loading from 1 to 0.05 mol% has no significant effect on catalytic activity of the reaction system, while a sharp decrement was observed when palladium loading was below 0.05 mol%. The effects of palladium sources and bases on the cross-coupling reaction were also examined. PdCl₂, Pd(cod)Cl₂ and Pd(OAc)₂ have been employed successfully as palladium sources, but lower GC yields were obtained (entries 4-6). Among the bases tested, NEt₃ was found to be the most efficient (entry 2), and

other organic bases, such as $(i-Pr)_2NH$ and $(n-Bu)_3N$, gave rise to 1,2-diphenylethyne in 26 and 30% GC yields, respectively (entries 7 and 8). Inorganic bases, such as NaOAc, KOH, K₃PO₄ and Cs_2CO_3 , were inefficient for the catalysis (entries 9–12). It should be mentioned that aqueous Bu₄NOH was widely used as a base and a reaction medium in catalysis, 1^{2a} but no desirable product was detected when the coupling reaction was run using 55% aqueous Bu₄NOH as a base under identical conditions (entry 13). These results revealed a significant dependence of the cross-coupling reaction on the nature of the bases. Similar situations were also observed in the reported Sonogashira cross-coupling reaction.^{6,7} It was recently proposed that catalytic reactions in neat water occurred in the organic layer, while the water phase may dissolve polar reactants and re-absorb side products.^{9d} Because iodobenzene, phenylacetylene and NEt₃ are liquid, the Sonogashira crosscoupling reaction between iodobenzene and phenylacetylene was performed in the absence of water, and a 72% GC yield was obtained (entry 14).

As a comparison, other bidentate nitrogen-containing chelating ligands were also used as supporting ligands of palladium in the reaction of iodobenzene and phenylacetylene (Scheme 2). As shown in Fig. 3, 2,2'-bipy and phen gave 80 and



Scheme 2 The bidentate nitrogen-containing ligands used in this work



Fig. 3 The conversion of iodobenzene in the reaction of iodobenzene and phenylacetylene using different nitrogen-containing ligands as supporting ligands. Reaction conditions: iodobenzene (0.50 mmol), phenylacetylene (0.75 mmol), Pd(NH₃)₂Cl₂-ligand (0.1 mol%), Et₃N (1.50 mmol), and H₂O (2.0 mL) at 25 °C for 6 h under N₂.

68% GC yields under the same conditions, respectively, which are less efficient than dpa; however, the use of impy and pzpy resulted in even lower GC yields, suggesting that dpa is a good promoter in the palladium-catalyzed Sonogashira crosscoupling reaction in neat water.

To further explore the catalytic efficiency of this system, a more versatile and practical method was applied to cross-coupling reactions between aryl iodides and terminal alkynes by using 0.1 mol% Pd(NH₃)₂Cl₂-dpa as a precatalyst in the presence of NEt₃ in neat water at 25 °C for 6 h (Table 2). The effect of varying aryl iodides in the reaction was initially tested by using phenylacetylene as a substrate, aryl iodides bearing electron-withdrawing and electron-donating groups, such as -Cl, -CF₃, -F, -Me and -OMe, smoothly coupled with

Table 2 The Sonogashira cross-coupling reaction of aryl iodides with terminal alkynes^a

RI	$I + \equiv \swarrow_{R_2} \frac{[Pd]}{R_2}$	l, Et ₃ N , 25 °C R ₁ →	
Entry	R ₁	R_2	$\operatorname{Yield}^{b}(\%)$
1	Н	Н	95 (91)
2	4-Cl	Н	91 (86)
3	$4-CF_3$	Н	91 (83)
1	4-F	Н	83
5	4-Me	Н	81
5	3-Me	Н	86 (82)
7	2-Me	Н	90 (86)
3	3,5-Dimethyl	Н	73
Ð	4-H	4-MeO	94 (89)
10	4-Cl	4-MeO	94 (83)
11	$4-CF_3$	4-MeO	98 (95)
12	4-F	4-MeO	77
13	4-Me	4-MeO	76
14	3-Me	4-MeO	78
15	2-Me	4-MeO	85 (72)
16	Н	4-Me	96 (91)
17	4-Cl	4-Me	95 (86)
18	$4-CF_3$	4-Me	93 (90)
19	4-F	4-Me	81
20	4-Me	4-Me	83
21	3-Me	4-Me	84
22	2-Me	4-Me	86 (77)
23	Н	3-Me	94 (87)
24	4-Cl	3-Me	95 (89)
25	$4-CF_3$	3-Me	95 (90)
26	4-Me	3-Me	80
27	3-Me	3-Me	82
28	2-Me	3-Me	84
29	Н	2-Me	100 (91)
30	4-Cl	2-Me	100 (95)
31	$4-CF_3$	2-Me	100 (92)
32	4-Me	2-Me	93 (87)
33	3-Me	2-Me	98 (90)
34	2-Me	2-Me	94 (83)
35	Н	4-MeCO	67
36	$4-CF_3$	4-MeCO	73
37	4-Me	4-MeCO	59
38	3-Me	4-MeCO	61
39	2-Me	4-MeCO	64

^a Reaction conditions: aryl iodide (0.5 mmol), alkyne (0.75 mmol), Pd- $(NH_3)_2Cl_2$ -dpa (0.1 mol%), Et₃N (1.50 mmol), and H₂O (2.0 mL) under N₂ at 25 °C for 6 h. ^bGC yield; the isolated yield is given in parentheses.

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phenylacetylene (entries 2-7), and the corresponding products were obtained in good to excellent yields, in which 4-chloroiodobenzene and 4-trifluoromethyl-iodobenzene gave slightly higher GC yields than 4-fluoro-iodobenzene (entries 2-4). Unexpectedly, the use of 2-methyl-iodobenzene also resulted in a 90% GC yield (entry 7), which is higher than 4-methyliodobenzene (81%), 3-methyl-iodobenzene (86%) and 4-fluoroiodobenzene (83%) regardless of their steric and electronic characteristics (entries 4-6). It is noteworthy that the reaction of 3,5-dimethyl-iodobenzene with phenylacetylene gave rise to the target product in a 73% GC yield (entry 8). Interestingly, a similar conversion trend was observed for the alkynes bearing -OMe (entries 9-15) and different steric hindrance (entries 16-34), in which ortho-, meta- and para-methyl substituents in the aromatic ring of the alkynes have no obvious effect on the cross-coupling reactions; the resulting products were afforded in 76-100% GC yields. However, the electron-deficient 4-acetylphenylacetylene provided the corresponding products in lower GC yields (59-73%) than electron-rich 4-methyl-phenylacetylene and 4-methoxyl-phenylacetylene (entries 35-39). It is noteworthy that cross-coupling reactions of ortho-, meta- and para-methyl substituted iodobenzene with phenylacetylene gave the desired products in 81, 86 and 90% GC yields, respectively (entries 5-7); however, the same products were obtained in 96, 94 and 100% GC yields in the reactions of iodobenzene with ortho-, meta- and para-methyl substituted phenylacetylene under identical conditions (entries 16, 23 and 29).

It was reported that palladium nanoparticles (NPs) may be formed after the cross-coupling reactions catalyzed by palladium coordination complexes.¹⁷ The process is involved in the reduction of palladium complexes and subsequent stabilization by the supporting ligands, and the resulting NPs usually possess small size and narrow size distribution. To identify palladium active species from the catalytic system, the mercury drop test and poisoning experiments were performed in the cross-coupling reaction of iodobenzene and phenylacetylene using 0.1 mol% $Pd(NH_3)_2Cl_2$ -dpa as a precatalyst in the

Table 3 Summary of the poisoning experiments ^a						
		$[Pd], Et_3N, Additive H_2O, 25 °C $				
Entry	Additive	Ratio of the additive to palladium	Yield ^b (%)			
1 ^{<i>c</i>}	Hg	_	10			
2	PVPy	100	0			
3	Pyridine	100	93			
4	Pyridine	1000	92			
5	Thiophene	1000	68			
6	PPh ₃	100	0			
7	Dpa	11	65			

 a Reaction conditions: iodobenzene (0.50 mmol), phenylacetylene (0.75 mmol), Pd(NH₃)₂Cl₂-dpa (0.1 mol%), Et₃N (1.50 mmol), and H₂O (2.0 mL) at 25 °C for 6 h under N₂. b GC yield. c One drop of Hg was added.

presence of NEt₃. As shown in Table 3, when one drop of Hg(0)was added to the reaction mixture before the reaction was carried out, 1,2-diphenylethyne was formed in a 10% GC yield (entry 1), which is much lower than that under normal conditions, and indicates the formation of Pd(0) active species and subsequent interaction with mercury to form amalgamation, resulting in Pd(0) poisoning and low catalytic activity. On the other hand, pyridine and polyvinylpyridine (PVPy) are well 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 catalysts and substrates as well as the extinguishment of catalytically active species. As expected, when 100 equivalent amount of PVPy was used as an additive in the cross-coupling reaction, no catalytic activity was observed (entry 2). However, the addition of 100 and 1000 equivalent amount of pyridine resulted in 93 and 92% GC yields (entries 3 and 4), respectively, which are close to those under normal conditions (Table 2, entry 1).

The kinetic study further showed that the presence of pyridine resulted in a longer induction period and lower reaction activity than that under normal conditions (Fig. 4). It should be mentioned that the addition of 1000 equivalent amount of thiophene gave a 68% GC yield (entry 5), while no catalytic activity was detected when 100 equivalent amount of PPh₃ was added to the reaction mixture. It should be mentioned that a decrease of conversion from 95 to 68% was observed when the molar ratio of dpa to palladium was increased from 1 to 11 (Table 3, entry 6), suggesting that excess of dpa was coordinated around palladium NPs, inhibiting enough contact of substrates with catalytically active sites.

In order to find more evidence of the formation of palladium NPs, after the Sonogashira cross-coupling reaction of iodobenzene and phenylacetylene under normal conditions was finished, the crude mixture was extracted several times



Fig. 4 The conversion of iodobenzene as a function of time for the Sonogashira cross-coupling reaction of iodobenzene and phenyl-acetylene in neat water at 25 °C: (a) under normal conditions; (b) after 100 equivalent amount of pyridine was added; (c) after 100 equivalent amount of PVPy was added.



Fig. 5 TEM images of palladium NPs after the Sonogashira crosscoupling reaction under normal conditions.

with ethyl ether, to the aqueous layer containing catalytically active species was added ethanol and then centrifuged, and the suspended solid was directly placed as a thin film in a carbon coated copper grid for TEM analysis. The TEM images clearly showed the formation of palladium NPs with a mean diameter of 2.3 nm and a standard deviation of 0.5 (Fig. 5). The size is smaller than those of the reported palladium NPs in situ generated after the cross-coupling reaction in water,¹⁸ which is probably ascribed to the low reaction temperature in the catalytic system. Interestingly, the palladium NPs are stable in aqueous solution, and no precipitate was observed for weeks.

Conclusion

We have developed a non-phosphorus catalytic system for the Sonogashira cross-coupling reaction of aryl iodides with terminal alkynes in neat water at room temperature. The reaction was promoted by 2,2'-dipyridylamine in the absence of copper. Interestingly, both 2,2'-dipyridylamine and commercially available palladium sources are insoluble in neat water, but their mixture can dissolve in water, resulting in superior catalytic performances in the Sonogashira cross-coupling reaction at room temperature. The kinetic study, the mercury drop test, poisoning experiments and TEM analysis revealed that palladium nanoparticles with small size and narrow size distribution were formed after the catalytic reaction. This study has extended the scope of the Sonogashira cross-coupling reaction in water, and provided an environmentally benign route for the synthesis of temperature-sensitive 1,2-disubstituted alkyne compounds. Further investigation to broaden the scope of the catalytic system to other reactions is in progress.

Experimental section

General

The impy¹⁹ and pzpy²⁰ were synthesized according to literature methods. The other chemicals were obtained from commercial suppliers and used without further purification. ¹H and ¹³C NMR spectra were recorded on spectrometers at 400 and

100 MHz, respectively, by using CDCl₃ as a locking solvent except where otherwise indicated. Chemical shifts were reported in ppm relative to TMS for ¹H and ¹³C NMR spectra. Gas chromatography (GC) analyses were performed on a Shimadzu GC-2014 equipped with a capillary column (RTX-5, 30 m \times 0.25 mm) using a flame ionization detector. Transmission electron microscopy (TEM) was performed on a JEOL JEM-2010 microscope and was operated at 200 kV.

Theoretical study

Calculations were carried out using the Gaussian 03 (Revision D.02) suite of programs.²¹ The geometric optimization of the structures and frequency analyses were carried out using the B3-LYP method with effective core potentials (ECPs). The allelectron 6-31+G** basis set was used on C, N, Cl and H atoms while Lanl2dz developed by Hay and Wadt was employed to describe the palladium atom.¹⁹ The vibration frequencies were used to characterize the optimized structures where the energy is minimal without imaginary frequencies on the potential energy surface. The scaling factors are neglected in the harmonic vibration frequencies.

General procedures for preparation of a stock solution Pd-dpa. The commercially available palladium(II) of (0.025 mmol) and 2,2'-dipyridylamine (4.3 mg, 0.025 mmol) were added into distilled water (5.0 mL), and the resulting mixture was oscillated until a yellow solution was formed, which was used as a stock solution for catalysis. The concentration of the stock solution is $C_{\text{Pd}} = 0.005 \text{ mol L}^{-1}$.

General procedures for the palladium-catalyzed Sonogashira cross-coupling reaction. A mixture of the aryl iodide (0.50 mmol), aromatic alkyne (0.75 mmol) and base (1.50 mmol) and an appropriate amount of a stock solution of Pd-dpa in H₂O (2 mL) was stirred under N₂ at 25 °C. After 6 h, the resulting mixture was extracted with ethyl acetate (3 \times 5 mL), the combined organic layer was dried over anhydrous MgSO₄ 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 literature spectroscopic data.

Acknowledgements

This work was financially supported by the 973 Program (2010CB933501 and 2011CBA00502), the Natural Science Foundation of China (21273239), the Natural Science Foundation of Fujian Province (2011J01064) and the "One Hundred Talent Project" from the Chinese Academy of Sciences.

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