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The thermoregulated ligand–palladiumcatalyzed carbonylative Sonogashira coupling of aryl iodides with terminal alkynes in water

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The carbonylative Sonogashira coupling of aryl iodides with terminal alkynes was studied by using thermoregulated ligandpalladium as an efficient and reusable catalyst at 80 °C in water. The corresponding alkynone products were obtained in good to excellent yields under 1 atm of carbon monoxide. The isolation of the products was readily achieved by extraction with ethyl acetate, and the catalyst recovered in water can be reused and recycled up to four times without significant loss in catalytic activity. Copyright © 2015 John Wiley & Sons, Ltd.

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Keywords: alkynones; palladium; carbonylative; Sonogashira coupling; thermoregulated phase-transfer catalysis

Introduction

Alkynones represent an interesting structural motif found in a wide variety of biologically active molecules.^[1–6] Notably, they play a crucial role as key intermediates in the synthesis of many natural products^[7–11] and heterocyclic compounds.^[12–15] A common route to alkynones involves the transition-metal-catalyzed cross-coupling reactions of acid chlorides with terminal alkynes.^[16–20] However, the stability and functional group compatibility of acid chlorides have limited the applications of this methodology. Alternatively, the three-component coupling reaction of terminal alkynes, carbon monoxide and aryl halides, generally known as the carbonylative Sonogashira reaction,^[21] has become one of the most straightforward and convenient processes for the synthesis of alkynones. Over the past few decades, remarkable advancements in this methodology have been achieved, particularly in the substrate scope, functional group tolerance and design of new catalyst systems to make the transformation more efficient and eco-friendly.^[22-29] In most cases, the carbonylative coupling reactions proceed in the presence of palladium-based homogeneous catalysts. Although these palladium catalysts show high activity and good selectivity under mild reaction conditions, the homogeneous catalytic system is limited by the inherent problem of catalyst separation from the products and its recycling. Therefore, the development of a recoverable and recyclable catalyst system that allows for efficient carbonylative Sonogashira coupling of aryl iodides with terminal alkynes is worthwhile.[30-33]

Thermoregulated liquid/liquid catalytic systems offer an attractive alternative approach that can combine the high activity of homogeneous catalysis with the simplicity of catalyst separation.^[34] In our effort to develop efficient aqueous/organic biphasic catalytic systems, a concept of thermoregulated phase-transfer catalysis (TRPTC) has been established based on the cloud point (C_p) of non-ionic alkylpolyoxyethylene surfactants. Alkylpolyoxyethylenemodified phosphine ligands exhibit an inverse temperaturedependent solubility in water; that is, their aqueous solution will undergo a phase separation on heating to C_p and become water soluble again on cooling to a temperature lower than C_p .^[35-38] So far, TRPTC has been successfully applied in hydroformylation,^[38,39] hydrogenation,^[35,40] palladium-catalyzed carbon–carbon cross-coupling reactions,^[41–44] and so on.^[45] In spite of significant advances in this area, there are very few reports of employing TRPTC systems for carbonylative coupling reactions.

In this paper, we report the application of a TRPTC system as an efficient and recyclable catalytic medium for the palladiumcatalyzed carbonylative Sonogashira coupling of aryl iodides with terminal alkynes and carbon monoxide in water. To realize this protocol, the ligand Ph₂P(CH₂CH₂O)_nCH₃ ($n \approx 22$) (**L**), which can be readily prepared^[41,46,47] and possesses a phase-transfer property, was chosen as the thermoregulated ligand. The catalytic process is shown in Fig 1. The thermoregulated ligand-modified palladium catalyst in the aqueous phase is able to transfer into the organic phase (substrate phase) to catalyze the reaction at the elevated reaction temperature, thus allowing the reaction to take place in the organic phase, and the subsequent separation of the catalyst in the aqueous phase, and further reuse, upon cooling to room temperature.

Results and Discussion

The carbonylative Sonogashira coupling of iodobenzene (1a) with phenylacetylene (2a) under a carbon monoxide atmosphere of

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Figure 1. Thermoregulated ligand-palladium-catalyzed carbonylative Sonogashira coupling in water. (Cat., catalyst; Pro., products; Sub., substrate.)

1 atm in water was chosen as the model reaction. The influence of various reaction parameters on the model reaction was examined, and the results obtained are summarized in Table 1. It is observed that the nature of the base is essential to achieve selective formation of the carbonylative product 1,3-diphenylpropynone (**3aa**) without non-carbonylative by-product 1,2-diphenylethyne (**4aa**).

For instance, organic bases such as Et₃N, (*n*Bu)₃N and pyridine result in a significant amount of 4aa, even under higher carbon monoxide pressure (Table 1, entries 1-4). In contrast, inorganic bases such as K₂CO₃, K₃PO₄·3H₂O, Na₂CO₃, NaHCO₃ and NaOAc afford better selectivity to the carbonylative products (Table 1, entries 5-10). Notably, the inexpensive Na₂CO₃ furnishes the highest yield of 3aa (Table 1, entry 7). Among the reaction temperatures screened (Table 1, entries 7, 11 and 12), 80 °C was chosen as the optimum reaction temperature. Then, the effect of the L/Pd molar ratio was studied. The yield of the desired product 3aa increases with increasing L/Pd, and the best result is obtained when the L/Pd ratio reaches 2:1 (Table 1, entries 7 and 13). Further increasing the amount of L results in a decrease in yield, probably due to excess ligand sequestering the active palladium species (Table 1, entries 14 and 15). Thus, the optimized reaction conditions for this carbonylative coupling reaction are the use of PdCl₂/L (molar ratio of 1:2) as catalyst, Na₂CO₃ as base in water at 80 °C under a carbon monoxide atmosphere of 1 atm. In contrast, when using triphenylphosphine (TPP) or tris(3-sulfophenyl)phosphine trisodium salt (TPPTS) as ligand, the reaction does not show competitive results under the conditions mentioned above (Table 1, entries 16 and 17).

Next, the generality and scope of this catalytic system were examined with various aryl iodides and terminal alkynes. As evident from Table 2, most of the carbonylative coupling reactions proceed smoothly, affording good to excellent yields of the desired carbonylative products, and many functional groups are tolerated in these reactions. Generally, the aryl iodides with electron-

Table 2. Carbonylative Sonogashira coupling of anyl halides with termi

Sonogashira coupling of 1a with 2a ^a											
$H_{3}C^{\downarrow}O^{\downarrow}PPh_{2} \qquad O \\ H_{3}C^{\downarrow}O^{\downarrow}PPh_{2} \qquad O \\ L(n \neq 22) \qquad PdCl_{2}/L \qquad O \\ H_{3}C^{\downarrow}O^{\downarrow}Ph \qquad O \\ H_{3}C^{\downarrow}O^{\downarrow}O^{\downarrow}Ph \qquad O \\ H_{3}C^{\downarrow}O^{\downarrow}O^{\downarrow}Ph \qquad O \\ H_{3}C^{\downarrow}O^{\downarrow}O^{\downarrow}Ph \qquad O \\ H_{3}C^{\downarrow}O^{\downarrow}O^{\downarrow}O^{\downarrow}O^{\downarrow}Ph \qquad O \\ H_{3}C^{\downarrow}O^{\downarrow}O^{\downarrow}O^{\downarrow}O^{\downarrow}O^{\downarrow}O^{\downarrow}O^{\downarrow}O$											
Entr	ry Ligand	(mol%)	Base	Temperature	Time	Yield (%) ^b					
				(°C)	(h)	3aa	4aa				
1	L	5	Et₃N	80	3	56	43				
2	L	5	(<i>n</i> Bu)₃ N	80	3	69	16				
3	L	5	pyridine	80	3	38	10				
4 ^c	L	5	Et_3N	80	3	81	15				
5	L	5	K ₂ CO ₃	80	3	85	4				
6	L	5	K ₃ PO ₄ ·3H ₂ O	80	3	77	8				
7	L	5	Na ₂ CO ₃	80	3	92	2				
8	L	5	NaHCO ₃	80	3	78	2				
9	L	5	NaOAc	80	3	26	0				
10	L	5	NaOAc	80	10	68	0				
11	L	5	Na_2CO_3	70	3	68	1				
12	L	5	Na ₂ CO ₃	100	3	90	9				
13	L	2.5	Na ₂ CO ₃	80	3	80	4				
14	L	10	Na_2CO_3	80	3	84	2				
15	L	15	Na ₂ CO ₃	80	3	72	6				
16	TPP	5	Na ₂ CO ₃	80	3	6	1				
17	TPPTS	5	Na_2CO_3	80	3	30	49				

^aReaction conditions: **1a** (1 mmol), **2a** (1.2 mmol), PdCl₂ (2.5 mol%), base (1 mmol), H₂O (6 ml).

^bYield was determined using GC on the basis of iodobenzene with *n*-decane as internal standard.

^cCO pressure of 5 atm.

nal alkynes in water ^a											
$Aryl-I + = R \frac{PdCl_2/L}{CO} Aryl R$											
Entry	Aryl	R	Time (h)	Product	Yield (%) ^b						
1	Ph	Ph	3	3aa	85						
2	4-MeOPh	Ph	3	3ba	91						
3	4-MePh	Ph	3	3ca	88						
4	2-MeOPh	Ph	8	3da	82						
5	2-MePh	Ph	8	3ea	85						
6	4-NO ₂ Ph	Ph	3	3fa	36						
7	4-FPh	Ph	5	3ga	84						
8	4-BrPh	Ph	6	3 ha	75						
9	2-Thienyl	Ph	6	3ia	33/70 ^c						
10	Ph	4-CH₃Ph	5	3ab	80						
11	4-MePh	4-CH₃Ph	6	3ca	81						
12	4-MeOPh	4-CH₃Ph	6	3bb	86						
13	2-MeOPh	4-CH₃Ph	10	3db	83						
14	4-FPh	4-CH₃Ph	5	3gb	78						
15 ^d	Ph	<i>n</i> Bu	12	3 ac	74						
16 ^d	4-MeOPh	<i>n</i> Bu	12	3bc	80						
17 ^d	4-MePh	<i>n</i> Bu	12	3 сс	82						

^aReaction conditions: **1** (1 mmol), **2** (1.2 mmol), PdCl₂ (2.5 mol%), L/ Pd = 2:1 (molar ratio), Na₂CO₃ (1 mmol), H₂O (6 ml), CO (1 atm), 80 °C.

^blsolated yields.

^cCO pressure of 5 atm.

^d1.5 equiv. of **2**.

donating groups, such as methyl and methoxy, react with phenylacetylene to generate the corresponding carbonylative coupling products 3ba-3ea in 82-91% yields (Table 2, entries 2-5). When 4-nitroiodobenzene is used as substrate, dramatically decreased selectivity to the carbonylative coupling product is observed (Table 2, entry 6). Fluoro- and bromo-substituted iodobenzenes give 84 and 75% yields of the desired alkynones 3ga and 3 ha, respectively (Table 2, entries 7 and 8). Moreover, heterocyclic 2-iodothiophene affords 70% yield of the expected product **3ia** under high carbon monoxide pressure (Table 2, entry 9). The reactions between substituted phenylacetylenes such as 4methylphenylacetylene and various aryl iodides also proceed effectively to yield 78-86% of carbonylative products (Table 2, entries 10-14). The reactions of aliphatic alkynes are found to be slower than those of arylacetylenes (Table 2, entries 15–17). Aryl bromides do not show any conversion, even when harsher conditions are applied (CO at 1 MPa; 10 h).

To investigate the efficiency of the catalyst, further testing of the amount of catalyst loading was conducted (Table 3). It is noteworthy that the thermoregulated ligand–palladium catalyst exhibits high activity for the carbonylative Sonogashira coupling of **1a** with **2a** (0.25 mol% of Pd, 90% yield, TON = 360; Table 3, entry 2). On further lowering the Pd loading to 0.1 mol%, an acceptable yield can still be obtained (75% yield, TON = 750; Table 3,



^aReaction conditions: 1 (1 mmol), 2a (1.2 mmol), L/Pd = 2:1 (molar ratio), Na₂CO₃ (1 mmol), H₂O (6 ml), CO (1 atm), 80 °C, 24 h.
 ^bGC yield with the use of *n*-decane as an internal standard.
 ^cTON: turnover number, defined as mmol (product)/mmol (Pd).
 ^d16 h, isolated yield.



Figure 2. Recyclability study of the thermoregulated ligand–palladium catalyst (2.5 mol% of PdCl₂, L/Pd = 4:1 (molar ratio), 1 mmol of iodobenzene, 1.2 mmol of phenylacetylene, 1 mmol of Na₂CO₃, 6 ml of H₂O, 1 atm of CO at 80 °C for 5 h, GC yield).

entry 3). Meanwhile, decreasing the palladium loading to 0.5 mol % in the carbonylative coupling reaction of 4-iodoanisole (**1b**) with **2a** furnishes the corresponding alkynone **3ba** in 86% yield (TON = 172; Table 3, entry 4), whereas for the previously reported PdCl₂/PPh₃/Et₃N/H₂O system to afford **3ba** in 87% yield, the reaction needed to be carried out using 5 mol% of palladium catalyst.^[48]

Encouraged by the results presented above, we subsequently evaluated the reusability of the catalyst. As shown in Fig 2, the thermoregulated ligand–palladium catalyst is found to be effective for up to four consecutive recycles for the model reaction. After fourrun recycling, the total leaching of palladium to the combined ethyl acetate extracts is found to be 2.2 wt% using inductively coupled plasma atomic emission spectroscopic (ICP-AES) analysis. From the comparison of the catalyst activity and the loss of palladium, it can be deduced that there is catalyst deactivation during the reaction together with loss of palladium metal in the organic phase. Efforts to enhance the performance of palladium catalyst recycling for this TRPTC system are currently underway.

Conclusions

An efficient and recyclable system for the thermoregulated ligandpalladium-catalyzed carbonylative Sonogashira coupling of various aryl iodides with terminal alkynes has been developed. The reaction proceeds at low carbon monoxide pressure using water as an environmentally benign solvent. The corresponding alkynones are obtained in moderate to good yields. Catalyst reusability and palladium leaching were also examined, and the catalytic system can be recycled up to four times with satisfactory results.

Experimental

General Information

All aryl halides and alkynes were purchased from Shanghai Aladdin Chemical Reagent Co. Ltd and Alfa Aesar China. Other chemicals were purchased from commercial sources and used without further purification. All carbonylative coupling products are well-known compounds, which were characterized by comparison with literature data. Gas chromatography (GC) was performed with a Techcomp 7890 instrument equipped with an OV-101 capillary column. NMR spectra were recorded with Bruker Advance 400 or Bruker Advance 500 spectrometers with CDCl₃ as the solvent. GC-MS data were recorded using an Agilent 7890 instrument equipped with an Agilent 5975 mass selective detector. ICP-AES analyses of palladium were carried out with an Optima 2000DV (Thermo Elemental, USA).

Synthesis of $Ph_2P(CH_2CH_2O)_nCH_3$ ($n \approx 22$) (L)

The ligand **L**, Ph₂P(CH₂CH₂O)_nCH₃ (C_p = 93 °C), was prepared from Ph₂PLi and CH₃(OCH₂CH₂)_nOSO₂Me ($n \approx 22$) according to a known method.^[41,46,47] **L** was stored under nitrogen atmosphere. ¹H NMR (400 MHz, D₂O, δ , ppm): 2.31 (t, 2H, J = 7.6 Hz, PCH₂), 3.30 (s, 3H, OCH₃), 3.48–3.59 (m, 95H, OCH₂), 7.24–7.43 (m, 10H, Ph). ¹³C NMR (100 MHz, D₂O, δ , ppm): 28.03 (d, ¹ J_{PC} = 13.0 Hz, PCH₂), 58.18 (OCH₃), 68.08 (d, ² J_{PC} = 23.0 Hz, PCH₂CH₂O), 69.58 (small, OCH₂), 69.72 (broad, OCH₂), 71.11 (OCH₂), 128.79 (d, ³ J_{PC} = 7Hz, Ph), 129.03 (Ph), 132.63 (d, ² J_{PC} = 19.0 Hz, Ph), 137.85 (d, ¹ J_{PC} = 13.0 Hz, Ph). ³¹P NMR (162 MHz, D₂O, δ , ppm): –22.12.

General Procedure for Carbonylative Sonogashira Coupling in Water

To completely dissolve PdCl₂ and L in water, the following pretreatment protocol was conducted. PdCl₂ (4.43 mg, 2.5×10^{-2} mmol), L $(58.4 \text{ mg}, 5.0 \times 10^{-2} \text{ mmol})$ and H₂O (6 ml) were placed in a 75 ml stainless steel autoclave with a Teflon liner and Teflon-coated magnetic stir bar. Then, the autoclave was closed, flushed with nitrogen and pressurized to 5 atm with nitrogen, and the mixture was stirred at room temperature for 0.5 h. After the pretreatment, Na₂CO₃ (106 mg, 1 mmol), iodobenzene (113 µl, 1 mmol), phenylacetylene (132 µl, 1.2 mmol) and decane (0.1 ml, GC internal standard) were successively added into the liner. Once sealed, the autoclave was purged several times with CO, then pressurized to 1 atm at room temperature and heated in an oil bath at 80 °C for 3 h with magnetic stirring. After the reaction, the autoclave was cooled to room temperature and then vented to discharge excess CO. The resultant mixture was extracted with ethyl acetate $(3 \times 5 \text{ ml})$. The combined organic layers were dried over MgSO₄, filtered and then evaporated with absorption onto silica gel. The crude product was purified by column chromatography using silica gel (eluent: hexane-ethyl acetate = 40:1).

Catalyst Recycling for the Carbonylative Sonogashira Reaction

When the reaction was completed, the autoclave was cooled to room temperature and vented to discharge excess CO. Next, the resultant mixture was extracted with ethyl acetate $(2 \times 3 \text{ ml})$. The organic layer was analyzed quantitatively with GC using decane as an internal standard. The aqueous phase containing the catalyst without additional treatment was used for the next run with the same substrates as mentioned above.

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