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A novel imidazolium-supported palladiumchloroglycine complex: copper- and solventfree high-turnover catalysts for the Sonogashira coupling reaction

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A novel, effective 1-glycyl-3-methyl imidazolium chloride–palladium(II) complex ([Gmim]Cl–Pd(II)) was synthesized and studied as an organocatalyst for the Sonogashira coupling reaction under solvent-free conditions at 25 °C. The hydrophobic group on amino acid favors reagent diffusion toward the chloroglycine moiety, increasing the catalytic activity of supported palladium complex. By this protocol, different aryl halides (Cl, Br and I) were reacted with phenylacetylene in good to excellent yields with turnover number 8.0×10^2 to 9.6×10^2 . The catalyst was recycled for the reaction of bromobenzene with phenylacetylene for eight runs without appreciable loss of its catalytic activity and negligible metal leaching. Copyright © 2012 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

Keywords: Sonogashira coupling; palladium; amino acid; ionic liquid

Introduction

The development of recoverable and recyclable catalysts for industrial applications has become important from both the environmental and economical point of view and has been well reviewed in the literature.^[1] In recent years, metal complex-functionalized ionic liquids have emerged as a set of green solvents with unique properties such as tunable polarity, high thermal stability and immiscibility with a number of organic solvents, negligible vapor pressure and recyclability. Their non-volatile character and thermal stability make the metal complexes potentially attractive alternatives to environmentally unfavorable organic co-solvents, notably chlorinated hydrocarbons. In particular, they show promise as solvents for the immobilization of transition metal catalysts, Lewis acids and enzymes.^[2] As a result of their green credential and potential to enhance reaction rate and selectivities, ionic liquids are finding increasing applications in organic synthesis.

The Sonogashira–Hagihara reaction is important because of valuable applications in both laboratory and industry. The significance of these compounds exists in the organic synthesis, structural units found in natural products, pharmaceuticals, biologically active molecules, liquid crystalline materials, conducting polymers and advanced materials. Moreover, the Sonogashira–Hagihara reaction has emerged as one of the most powerful, attractive and widely utilized methods for the formation of Csp²–Csp bonds. In addition, this reaction exhibits high tolerance to the presence of functional groups as substituents in substrates, mild reaction conditions, possibility of performing the reaction in water and very often also in an air atmosphere.^[3–5]

During the last two years, Chungu Xia et al. described crosslinked polymer supported palladium-catalyzed carbonylative Sonogashira coupling reaction in water.^[6] Vasundhara Singh et al. reported the synthesis and characterization of recyclable and recoverable montmorillonite clay-exchanged ammonium-tagged carbapalladacycle catalyst for Mizoroki-Heck and Sonogashira reactions in ionic liquid media.^[7] Furthermore, Mohammad Bakherad et al. have reported the copper and solvent-free Sonogashira coupling reactions of aryl halides with terminal alkynes catalyzed by 1-phenyl-1,2-propanedione-2-oxime thiosemicarbazone-functionalized polystyrene resin supported Pd(II) complex under aerobic conditions.^[8] Nasser Iranpoor et al. illustrated palladium nanoparticles supported on agarose as an efficient catalyst and bioorganic ligand for C&bond; C bond formation via solventless Mizoroki-Heck reaction and Sonogashira-Hagihara reaction in polyethylene glycol (PEG 400).^[9] Haihong Wu et al. exemplified the ionic liquidfunctionalized phosphine-ligated palladium complex for the Sonogashira reaction under aerobic and Cul-free conditions.^[10] All the above-mentioned methods provide good yields, whereas some of these reactions are sluggish, requiring at least 24 h for reaction completion, lengthy work-up procedure, harsh reaction conditions and absolutely dry and inert media. The use

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of an eco-friendly reaction medium, minimization of steps, better yields and faster reaction remained constant challenges in the context of green chemistry. Herein, we report a protocol based on palladium-functionalized 1-glycyl-3-methyl imidazolium chloride (Fig. 1), which proved to be highly efficient at 25 °C for C&bond;C bond formation.

However, recovery and leaching can occur in the extractive workup, leading to a loss of the catalyst in the reaction mixture and requiring additional effort to purify the extracted product. To overcome such problems, a novel palladium complex was developed^[11] by covalent linking of the organocatalytic unit with an ionic liquid moiety (often chloroglycine). This imparts a low solubility of catalyst in the solvents used for extraction of the product on one hand and high solubility in the reaction medium on the other.^[12] This strategy was applied to the Sonogashira coupling reaction, providing high yield and good recyclability of the organocatalyst.

Thus the present study focuses on the development of an efficient synthetic methodology for facile conversion using the Sonogashira coupling reaction. The developed method offers



Figure 1. 1-Glycyl-3-methyl imidazolium chloride–palladium(II) complex [Gmim]Cl–Pd(II)

many advantages, including high conversion, short duration and use of non-toxic reagents.

Experimental

General Methods

All solvents and chemicals were commercially available and used without further purification unless otherwise stated. The 1-glycyl-3-methyl imidazolium chloride-palladium(II) ([Gmim]Cl-Pd(II)) complex was characterized by powder X-ray diffraction (P-XRD) diffractometry with a Bruker D8 (advance model, Germany) and lynx eye detector operating with nickel-filtered Cu-K radiation. ¹ H NMR spectra were recorded on a Bruker 500 MHz instrument using CDCl₃-DMSO-d₆ as the solvent and mass spectra were recorded on JEOL GC-Mate II HRMS (EI) spectrometer. FT-IR spectra were recorded on an Avatar 330 spectrometer with deuterated triglycine sulfate detector. Column chromatography was performed on silica gel (200-300 mesh). Analytical thin-layer chromatography (TLC) was carried out on pre-coated silica gel GF-254 plates. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) were performed using a Nano Surf Easy Scan-2 (Switzerland) and a Carl Zeiss EVO MA 15 instrument, respectively.

Preparation of [Gmim]Cl-Pd(II) Complex

The [Gmim]Cl-Pd(II) complex was synthesized as previously reported and structural conformation available in Supporting

Table 1. Effect of the base and time on Sonogashira coupling reaction ^a							
$Br + = - \sqrt{\frac{[Gmim]Cl-Pd}{25^{O}C/Base}} \sqrt{-} \sqrt{-}$							
Entry	Base	Time (h)	Yield ^b (%)	TON ^c	TOF ^c		
1	_	24	Trace	_	_		
2	Ру	24	_	_	—		
3	Imidazole	24	—	_	—		
4	K ₂ CO ₃	24	25	250	10.41		
5	КОН	24	46	460	19.16		
6	NaOH	24	52	520	21.66		
7	Et ₃ N	24	96	960	40.00		
8	Et ₃ N	20	96	960	48.00		
9	Et ₃ N	18	96	960	53.33		
10	Et ₃ N	12	96	960	80.00		
11	Et ₃ N	6	96	960	160.00		
12	Et ₃ N	3	96	960	320.00		
13	Et ₃ N	1	96	960	960.00		
14	Et ₃ N	0.75	88	880	1173.33		
15	Et₃N	0.50	85	850	1700.00		
16	Et ₃ N	0.25	80	800	3200.00		

^aReaction conditions: bromobenzene (1 mmol), phenylacetylene (1.2 mmol), different base (1 mmol) and [Gmim]Cl–Pd(II) (0.1 mol%), with stirring at 25 °C.

^bYield determined by HPLC.

^cTON, turnover number; TOF, turnover frequency (mol product mol⁻¹ catalyst h⁻¹).

 Table 2. Effect of the solvent on the Sonogashira coupling reaction^a



Entry	Solvent	Temp. (°C)	Time (h)	Yield ^b (%)	TON ^c	TOF ^c
1	CH₃CN	60	24	40	400	16.66
2	DMF	130	24	53	530	22.08
3	DCM	35	24	Trace		_
4	CHCl₃	50	24	Trace		_
5	THF	50	24	Trace	_	_
6	Methanol	50	24	Trace		_
7	Ethanol	65	24	Trace		_
8	Solvent free	25	1	96	960	960.00
9	Solvent free	20	1	90	900	900.00
10	Solvent free	35	1	97	970	970.00
11	Water (5 ml)	90	24	50	500	20.83

^aReaction conditions: bromobenzene (1 mmol), phenylacetylene (1.2 mmol), solvent (5 ml), Et₃N (1 mmol) and [Gmim]Cl–Pd(II) (0.1 mol%), with stirring at different temperatures (see Table 2).

^bYield determined by HPLC.

^cTON, turnover number; TOF, turnover frequency (mol product mol⁻¹ catalyst h⁻¹).

Table 3. Effect of the various catalysts on Sonogashira coupling reaction ^a						
	Br +	$- \underbrace{ \begin{array}{c} \\ \hline \\ $				
Entry	Catalyst	Time (h)	Yield ^b	TON ^c	TOF ^c	
1	∟-Glycine	24	Trace	_	_	
2	Chloroglycine [Cl-gly]	24	Trace	_	—	
3	PdCl ₂ /[Cemim] Br	24	65	650	27.08	
4	PdCl ₂ /[Aemim] Br	24	70	700	29.16	
5	PdCl ₂ /[Gmim]Cl	24	75	750	31.25	
6	[Gmim]Cl–Pd(II)	1	96	960	960.00	
7	[Gmim]Cl–Pd(II) ^d	2	97	970	485.00	

^aReaction conditions: bromobenzene (1 mmol), phenylacetylene (1.2 mmol), triethylamine (1 mmol) and catalyst (0.1 mol%), with stirring at 25 °C. ^bYield determined by HPLC.

^cTON, turnover number; TOF, turnover frequency (mol product mol⁻¹ catalyst h⁻¹).

^dReaction duration 2 h.

information,^[2] and the other ionic liquids were synthesized using the literature procedure reported elsewhere.^[13]

General Experimental Procedure for the Sonogashira Coupling Reaction

A mixture of aryl halide (1 mmol), phenylacetylene (1.2 mmol), triethylamine (1 mmol) and [Gmim]Cl-Pd(II) (0.1 mol%) was placed in a 50 ml conical flask and stirred at 25 °C for a period as indicated in Table 5 (the reaction was monitored by high-performance liquid chromatography (HPLC) and TLC). The resulting heterogeneous mixture was extracted with ethyl

acetate or diethyl ether (3 \times 5 ml). The organic phase was separated, dried over anhydrous Na₂SO₄ and evaporated. A crude residue was obtained as the product, which was further purified by column chromatography (EtOAc–*n*-hexane) to obtain the desired coupling product in 80–96% isolated yield.

Recycling of the Catalyst for the Model Reaction of Bromobenzene with Phenylacetylene using [Gmim]Cl-Pd(II)

Bromobenzene (1 mmol) was reacted with phenylacetylene (1.2 mmol) in the presence of [Gmim]Cl-Pd(II) (0.1 mol%) and triethylamine (1 mmol) at 25 °C. After completion of the reaction

 Table 4. Effect of catalyst loading on Sonogashira coupling reaction^a

Entry	[Gmim]Cl–Pd(II) mol%	Time (h)	Yield ^b	TON ^c	TOF ^c
1	_	48	_	_	_
2	0.025	24	50	500	20.83
3	0.050	24	62	620	25.83
4	0.075	24	75	750	31.25
5	0.1	24	96	960	40.00
6	0.1	18	96	960	53.33
7	0.1	12	96	960	80.00
8	0.1	б	96	960	160.00
9	0.1	3	96	960	320.00
10	0.1	1	96	960	960.00
11	0.125	1	97	970	970.00
12	0.150	1	97	970	970.00

^aReaction conditions: bromobenzene (1 mmol), phenylacetylene (1.2 mmol), triethylamine (1 mmol) and [Gmim]Cl–Pd(II) (0.1 mol%), with stirring at 25 °C.

^bYield determined by HPLC.

^cTON, turnover number; TOF, turnover frequency (mol product mol⁻¹ catalyst h⁻¹).

(TLC/ HPLC), the product was extracted as stated above ('General Methods'). The white solid [Gmim]Cl–Pd(II) was isolated by centrifugation. Further, the recovered complex was washed with diethyl ether and dried in air. The resulting catalyst was charged to another batch of a similar reaction. This was repeated for eight runs to complete the reaction in 1 h, to give the desired product with 86–96% yield (Table 6).

Results and Discussion

The palladium complex-catalyzed Sonogashira coupling reaction was carried out using phenylacetylene and bromobenzene as a model reaction to investigate different parameters such as effect of solvent and duration, diverse bases, catalysts and their concentration. Initially, the influence of different bases on the model reaction was studied; these results are summarized in Table 1. It was observed that organic bases showed maximum conversion over the inorganic bases. Moreover, this reaction was unsuccessful in the absence of base (Table 1, entry 1). However, there was no product formation between phenylacetylene and bromobenzene in the presence of pyridine and imidazole (Table 1, entries 2 and 3). Furthermore, when the Sonogashira coupling reaction was carried out using K₂CO₃, KOH, NaOH and Et₃N the formation of biphenyl increased from 25% to 96% (Table 1, entries 4-7). After finding the best catalyst systems, we further optimized the reaction conditions in the presence of Et₃N. The experiments showed that on decreasing the time from 20 h to 1 h, the same results were obtained, with full conversion and 96% yield of biphenyl (Table 1, entries 8-13). However, the yields dropped appreciably on decreasing the time from 1 h to 0.25 h (Table 1, entries 14-16). From all these experimental results and discussion it was concluded that 1 mmol Et₃N is sufficient to achieve the complete Sonogashira coupling reaction in 1 h at 25 °C.

Subsequently, in order to find a suitable solvent for the reaction, the coupling of bromobenzene and phenylacetylene was carried out with different solvents and Et₃N. According to publications from Chungu Xia and co-workers,^[6] Lei Wang,^[14] Habib Firouzabadi^[15] and Mohammad Bakherad,^[8] polar, aprotic solvents tend to give the best results for the Sonogashira coupling reaction, while Vasundhara Singh^[7] and Haihong Wu^[10] obtained high activity of catalysts in ionic liquids. We also employed several solvents in the model reaction. Among the previous reports, reaction under solvent-free conditions was the most productive as compared with the polar and non-polar solvents. The catalyst was easily coordinated with organic co-solvents. It has also been reported that H₂O molecule is required in some cases to activate the Pd(II) catalyst. In our case, carrying out the reaction in H₂O (5 ml) at 90 °C produced a negative effect on the product yield in comparison with solvent-free conditions and this lower yield could be due to delocalization of the complex under aqueous conditions (Table 2).

Next, in order to optimize the reaction conditions for a particular catalyst the coupling reaction of bromobenzene and phenylacetylene was executed in the presence of Et_3N using different catalysts and the results are given in Table 3. When the reaction was carried out using various catalysts such as L-glycine, chloroglycine, PdCl₂–1-carboxyethyl-3-methylimidazoliumbromide [Cemim] Br, PdCl₂/ 1-aminoethyl-3-methylimidazoliumbromide [Aemim]Br and PdCl₂–[Gmim]Cl with Et_3N , it yielded trace amounts to 75% of product respectively (Table 3, entries 1–5). However, when the same reaction was conducted with [Gmim] Cl–Pd(II) as a catalyst it yielded a remarkable yield of product within a short duration (Table 3, entry 6). An almost similar yield was obtained when increasing the duration of reaction (Table 3, entry 7).

The catalytic reactions which can be carried out with a small amount of expensive complexes are the most useful feature of

Table 5. Sonogashira coupling reaction of different aryl halides with phenylacetylene in the presence of [Gmim]Cl-Pd(II) and Et ₃ N as base ^{a,c}						
	R B	$f + = \sqrt{\frac{[Gmim]Cl-Pd}{25^{\circ}C/1-3h/Et_{3}N}}$				
Entry	Aryl halides	Product	Time (h)	Yield ^b (%)	TON	TOF ^c
1	Ph-Br	✓5a	1	96	960	960.00
2	p-NO ₂ Ph-Br	0 ₂ N-{5b	1.5	94	940	626.66
3	p-OMePh-Br	`o⟨}-=-⟨] _{5c}	1.5	92	920	613.33
4	p-MeCOPh-Br		2	93	930	465.00
5	1-Bromonaphthalene		1.5	90	900	600.00
6	Ph-Cl	5f	2	86	860	430.00
7	p-NO ₂ Ph-Cl	0 ₂ N	3	83	830	276.66
8	p-OMePh-Cl	℃{}5h	3	82	820	273.33
9	p-MeCOPh-Cl		3	80	800	266.66
10	Ph-I	5j	1	96	960	960.00
11	p-NO ₂ Ph-I	0 ₂ N-{5k	1.5	94	940	626.66

(Continues)

Table 5. (Continued)



synthetic reactions involving palladium complex. According to the literature, Mohammad Bakherad^[8] and co-workers obtained a good yield in the Sonogashira coupling reaction of aryl halide with phenylacetylene using 1-phenyl-1,2-propanedione-2-oximethiosemi-carbazone-functionalized polystyrene resin-

supported Pd(II) complex (0.01 mmol) stirred at room temperature

for 3 h under aerobic conditions. Using ionic liquid-functionalized

phosphine-ligated palladium complex in the range between

0.01 and 0.02 mmol, Haihong Wu et al. observed an acceptable

rate in the Sonogashira coupling reaction.[10] Among the

previous reports, increasing the quantity of the catalyst can improve the reaction yield and shorten reaction time. Initially, when C&bond;C formation was carried out in the absence of catalyst at ambient temperature, no product formed even after 48 h (Table 4, entry 1). Further, when the amount of catalyst was increased from 0.025 to 0.075 mol%, the yield was increased 50–75% (Table 4, entries 2–4). However using 0.1 mol% of [Gmim]Cl–Pd(II), biphenyl was obtained with 96% yield in 1 h (Table 4, entries 5–10). A similar yield was achieved when increasing the catalyst amount from 0.1% to 0.15 mol% (Table 4, entries 11



^aReaction conditions: bromobenzene (1 mmol), phenylacetylene (1.2 mmol), triethylamine (1 mmol) and [Gmim]Cl–Pd(II) (0.1 mol%), with stirring at 25 °C.

^bYield determined by HPLC.



Figure 2. Powder X-ray diffraction patterns of the [Gmim]Cl–Pd(II) complex: (a) before reaction; (b) after reaction (eighth run)

and 12). Therefore, the Sonogashira coupling reaction was carried out at a molar radio of bromobenzene, phenylacetylene, triethylamine and [Gmim]Cl–Pd(II) of 1:1.2:1:0.001 mmol at 25 $^{\circ}$ C.

The heterogeneous green catalytic copper-free Sonogashira coupling was examined with a variety of haloarenes under the reaction conditions identified above and exhibited wide substrate tolerance. Representative results are summarized in Table 5. It can be noted that a wide range of aromatic halides can efficiently contribute in the Sonogashira coupling reaction. However, both electron-rich and electron-poor aryl halides could be successfully converted to the desired products in 1–3 h at room temperature. On the other hand, the reaction of aryl chlorides with phenylacetylene is usually very slow with modulator yields. Isolation of the heterogeneous catalyst was easily performed by extraction or centrifugation. The isolated catalyst was washed with diethyl ether and dried in air. The regenerated catalyst was used for the reaction of bromobenzene with phenylacetylene for eight runs to afford 1,2-diphenylethyne with 96–86% isolated yields (Table 6).

For practical application in the Sonogashira coupling reaction, the lifetime of the heterogeneous catalysts and their reusability are very important factors. For the comparative study, Sonogashira coupling reaction was carried out with the model reaction under optimized conditions in the presence of Pd/C catalyst. However, a significant difference in Pd leaching was observed. Without exclusion of air about 34% of the total palladium amount was lost from the Pd/C and found in solution Atomic absorption spectroscopy (AAS) compared to [Gmim]Cl–Pd(II), where no leaching was detected.

For those conformations, the [Gmim]Cl-Pd(II) catalyst was collected after completion of the reaction and analyzed by the P-XRD method; the diffraction patterns are given in Fig. 2. The analysis specifies that [Gmim]Cl-Pd(II) does not undergo any chemical and structural changes, thus proving its surface catalytic activity towards the coupling reaction of bromobenzene with phenylacetylene. On the other hand, presence of peaks due to metallic palladium is noted in the P-XRD pattern of the complex in the case of 'Pd(II); (Fig. 2). Moreover, surface and size of the reused catalyst were captured by AFM. The surface of reused palladium complex evidenced a rough topography and reduced particle size (755 nm) (Fig. 3). However, the extracted product was analyzed by P-XRD, which indicates the presence of a peak at 38.81 that provided evidence for 'no leaching' of the complex. Furthermore, Pd leaching was also studied by inductively coupled plasma-atomic emission spectroscopy (ICP-AES), indicating that the mixture contains less palladium than the limit of detection, accounting for 0.1 mol% of the initially added amount of Pd. From those three experimental results, we believe that the absence of Pd leaching observed in the Sonogashira coupling reaction is due to immobilized palladium in the amino acid-functionalized ionic liquid binding site located on the surface, which acts as a ligand through metal-ligand interaction. The anchoring of Pd species by amino acid sites supported on ionic liquid minimizes catalyst deterioration and no metal leaching and therefore allows efficient catalyst recycling. The precise mechanism of the catalytic reaction needs to be elucidated, but it is noticeable that the mechanism is strongly modified depending of the halobenzene employed, obtaining 1,2-diphenylethyne as the main product (Scheme 1).

Conclusion

In this study, for the first time we have introduced [Gmim]Cl–Pd (II) as a catalyst for the Sonogashira coupling reaction with Et_3N in the absence of an organic co-solvent. Arylbromides and iodides reacted efficiently with phenylacetylene at ambient



Figure 3. AFM image of 3-(amino(carboxy)methyl)-1-methyl-1 H-imidazol-3-ium chloride-supported palladium complex after eighth run



Scheme 1. Proposed catalytic mechanism

temperature in the presence of our catalyst. The procedure is easy and does not require special precautions. All the reactions were conducted in air without the use of an organic co-solvent. The [Gmim]Cl–Pd(II) complex was shown to be superior to most of the reported catalysts, with many advantages: facile synthesis, thermal stability and structural versatility, easy handling, catalytic performance in air at 25 °C, without any additives, inert atmosphere not required and without leaching of catalyst. Moreover, the catalyst could be reused for seven consecutive cycles without significant loss of its catalytic activity. These advantages make the process highly valuable from the synthetic and environmental points of view. Further investigation on the application of this kind of catalyst is in progress in our laboratory.

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