

# Heterogeneous Heck reaction catalyzed by a series of amine–palladium(0) complexes

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## Abstract

A series of polymeric amine–palladium(0) complexes have been prepared from organic silica via immobilization on fumed silica, followed by treatment with palladium chloride in ethanol and then the reduction with  $\text{KBH}_4$  in ethanol. The effects of amine ligands and solvent on catalytic properties of silica supported amine–palladium(0) complexes were studied. They are efficient catalysts for Heck arylation of aryl iodides with alkene and can be recovered and reused.

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**Keywords:** Organic silica; Palladium complex; Heck reaction

## 1. Introduction

Palladium-catalyzed carbon-carbon bond forming reactions have contributed remarkably to synthetic organic chemistry [1]. Palladium catalyzed coupling of haloarenes and haloalkenes with alkenes is one of most important C–C coupling reaction in organic synthesis [2–4]. In view of the economy of the reaction, the recovery as well as recycling of the expensive Pd catalyst is required. However, metal Pd is usually precipitated from the solution, and recycling or recovery of an active Pd catalyst is difficult. Heterogeneous catalysts would be much better from such a viewpoint. Clays and cation-exchanged montmorillonite K10 clay, clay-supported reagents, MCM-41 material and pillared clays have been extensively applied in organic synthesis under relatively mild reaction condition [5–8].

Our interest in modified silica materials and their application in organic functional group conversion prompt us to explore the arylation of define using new silica-based catalyst system. In this paper, we wish to report the synthesis of a series of amine–palladium(0) complexes and their catalytic performances in the Heck arylation. It is found that these complexes are highly active and stereoselective for the

arylation of aryl iodides with styrene, acrylic acid at 90 °C, and can be reused by washing without loss in activity.

## 2. Experimental

### 2.1. Preparation of polymeric amine–palladium(0) complexes

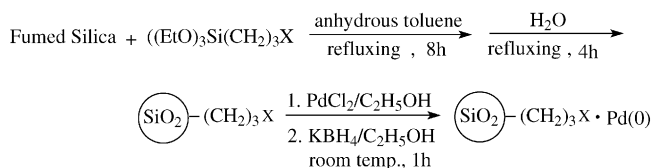
These polymeric palladium(0) complexes could be easily prepared from organic silica and fumed silica, followed by treatment with palladium chloride in ethanol and then the reduction with  $\text{KBH}_4$  in ethanol (Scheme 1).

In a typical surface modification process, a mixture of fumed silica (6 g), anhydrous toluene (140 ml) and  $\gamma$ -aminopropyl trimethoxysilica (4.65 g) was refluxed for 8 h, then 20 ml  $\text{H}_2\text{O}$  was added. The mixture was stirred again for 4 h. The organic silica (“Si”– $\text{NH}_2$ ) was filtered, and then dried in vacuum at 200 °C for 5 h.

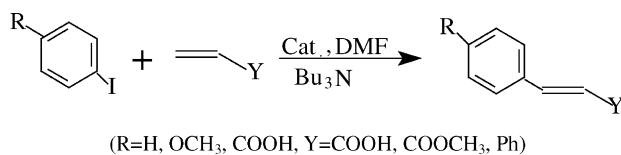
A mixture of  $\text{PdCl}_2$  (0.021 g), “Si”– $\text{NH}_2$  (0.5 g) and ethanol (32 ml) was stirred at room temperature for 1 h. The product was filtered, washed with ethanol, and treated with  $\text{KBH}_4$  (20 mg) in ethanol (28 ml) at room temperature for 1 h, and dried in air. The palladium contents in “Si”– $\text{NH}_2$ ·Pd(0), “Si”– $\text{NEt}_2$ ·Pd(0) and “Si”– $\text{NHBu}$ ·Pd(0) catalysts were measured by ICP instrument, to be  $2.51 \times 10^{-2}$ ,  $2.51 \times 10^{-2}$ , and  $1.01 \times 10^{-2}$  g/g

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Scheme 1.



1	a	b	c	2	a	b	c
R	H	OCH <sub>3</sub>	COOH	Y	COOH	COOMe	Ph

Scheme 2.

catalyst, respectively. The nitrogen contents in the catalysts were to be  $3.2 \times 10^{-2}$ ,  $0.41 \times 10^{-2}$ , and  $0.47 \times 10^{-2}$  g/g catalyst, respectively.

### 2.2. Typical procedure for Heck acrylation

In a typical Heck reaction, a mixture of tri-*n*-butylation (11 mmol), acrylic acid (5.5 mmol), iodobenzene (5 mmol), DMF (3 ml) and polymeric amine-palladium(0) complex ( $1.175 \times 10^{-2}$  mmol Pd) was stirred at 90 °C (Scheme 2). The reaction progress was monitored by TLC. After the reaction, the catalyst was separated from the mixture by filtration. The filtrate was poured into 2% HCl solution. On cooling to 0 °C, a white precipitate was formed. The precipitate was filtered, washed with H<sub>2</sub>O and dried to give the product. The selectivity of *trans*-product was ~100% and no *cis*-product was observed.

## 3. Results

### 3.1. UV-Vis diffuse reflectance spectra

The efficiency of Pd complexation with group -X in organic silica ("Si"-X) is illustrated by UV-Vis Diffuse reflectance spectroscopy. Fig. 1 shows the UV-Vis absorption spectra of organic silica before and after Pd complexation in the range of 190–800 nm. It is found that there are two significant absorption peaks at about 220 and 424 nm for "Si"-NH<sub>2</sub>·PdCl<sub>2</sub>, and no absorption peak for "Si"-NH<sub>2</sub> in the range of 190–800 nm. For "Si"-NEt<sub>2</sub>·PdCl<sub>2</sub> and "Si"-NHBu·PdCl<sub>2</sub>, though no new absorption peaks appear, the absorption peaks slightly shift to long wavelength, such as the peaks at 212, 316 and 408 nm shift to 244, 330 and 433 nm for "Si"-NEt<sub>2</sub>·PdCl<sub>2</sub>, respectively. The results revealed that between the group -X in "Si"-X and Pd occurs

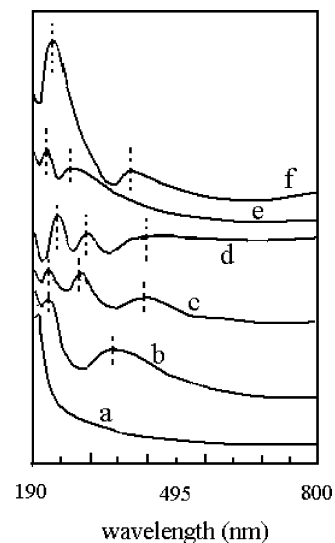
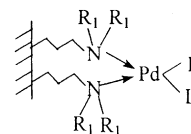


Fig. 1. UV-Vis diffuse reflectance spectra of "Si"-X·PdCl<sub>2</sub> catalysts (a) "Si"-NH<sub>2</sub>; (b) "Si"-NH<sub>2</sub>·PdCl<sub>2</sub>; (c) "Si"-NEt<sub>2</sub>; (d) "Si"-NEt<sub>2</sub>·PdCl<sub>2</sub>; (e) "Si"-NHBu; (f) "Si"-NHBu·PdCl<sub>2</sub>.

the charge transfer. We think that the probable structure is



(R<sub>1</sub> = -H-Et or -Bu; L = Cl)

### 3.2. FT-IR spectra

FT-IR spectra of "Si"-X·Pd(0) and PdCl<sub>2</sub> are showed in Fig. 2. As can be seen, characteristic transmission peaks of pure PdCl<sub>2</sub> appear at 345 and 340 cm<sup>-1</sup>, and the characteristic peaks of Pd-Cl in Si<sup>i</sup>X·PdCl<sub>2</sub> shift to low wavelength. After the reaction, the Pd-Cl is disappear, that is to say the active Pd species is Pd(0).

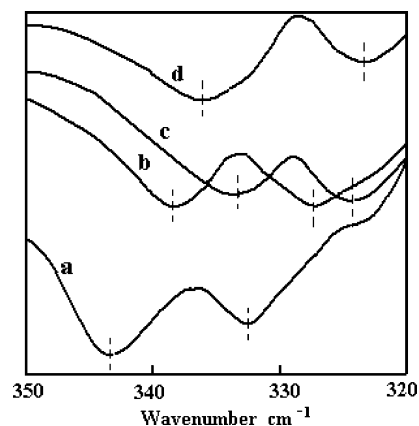


Fig. 2. the FT-IR spectra of "Si"-X·Pd Cl<sub>2</sub> and PdCl<sub>2</sub> (a) PdCl<sub>2</sub>; (b) "Si"-NEt<sub>2</sub>·PdCl<sub>2</sub>; (c) "Si"-NH<sub>2</sub>·PdCl<sub>2</sub>; (d) "Si"-NHBu·PdCl<sub>2</sub>.

Table 1  
Data of XPS for “Si”–X and “Si”–X·PdCl<sub>2</sub>

Sample	XPS data (Binding energy in eV <sup>a</sup> )	
	Pd <sub>3d5/2</sub>	N <sub>1s</sub>
Metal Pd	334.89	
Pure PdCl <sub>2</sub>	337.45	
“Si”–NH <sub>2</sub>		399.72
“Si”–NH <sub>2</sub> ·PdCl <sub>2</sub>	337.16	399.73
“Si”–NEt <sub>2</sub>		399.2
“Si”–NEt <sub>2</sub> ·PdCl <sub>2</sub>	334.98	402.4
“Si”–NHBu		399.8
“Si”–NHBu·PdCl <sub>2</sub>	335.01	401.7

<sup>a</sup> All relative to C<sub>1s</sub> is 285.0 eV.

### 3.3. Data of XPS

XPS has been widely used to investigate metal deposited on solid supports. The binding energy of Pd<sub>3d5/2</sub> and N<sub>1s</sub> in “Si”–X·PdCl<sub>2</sub> has been measured, the results list in Table 1. It is found that the binding energy of Pd<sub>3d5/2</sub> except “Si”–NH<sub>2</sub>·PdCl<sub>2</sub> decreases and the binding energy of N<sub>1s</sub> increases remarkably after Pd complexation with “Si”–X, which shows that Pd receives electron from N atom. The binding energy of Pd<sub>3d5/2</sub> and N<sub>1s</sub> in “Si”–NEt<sub>2</sub>·PdCl<sub>2</sub> and “Si”–NHBu·PdCl<sub>2</sub> catalysts changes obviously before and after Pd complexation with “Si”–X. We suggested that it is duo to that the group –Et and –Bu can offer electrons to N atom, and increase its electron density.

## 4. Discussion

In order to test the catalytic activities of the polymeric amine–palladium(0) complexes, the Heck reactions of aryl iodides with alkene catalyzed by the catalysts were studied. The results are summarized in Table 2. As can be seen, these catalysts have high activity for Heck arylation of aryl iodides

Table 2  
Properties of various polymeric amine–palladium(0) complexes<sup>a</sup>

Aryl iodide	Alkene	Product	Isolated yield <sup>b</sup> %		
			“Si”–NH <sub>2</sub> ·Pd	“Si”–NEt <sub>2</sub> ·Pd	“Si”–NHBu·Pd
1a	2a	3a	97.1	97.4	90.3
1a	2b	3b	88.7	65.1	69.2
1a	2c	3c	89.4	92.4	96.5
1b	2a	3d	95.6	96.7	94.7
1b	2b	3e	97.0	86.7	79.2
1b	2c	3f	98.9	96.4	91.9
1c	2a	3g	100.0	95.0	98.4
1c	2b	3h	92.2	98.1	89.2
1c	2c	3i	97.8	97.1	95.5

<sup>a</sup> All reaction are carried out at 90 °C, 3 ml DMF, 2.03 g Bu<sub>3</sub>N, 1.175 × 10<sup>–2</sup> mmol Pd(0), 5 mmol aryl iodide and 5.5 mmol alkene were used. Reaction time was 12 h.

<sup>b</sup> Isolated yield based on aryl iodide.

Table 3  
Recycling and reuse of catalysts in the Heck reaction<sup>a</sup>

Catalyst	Yield <sup>b</sup> (time, h) %		
	Fresh	First cycle	Second cycle
“Si”–NH <sub>2</sub> ·Pd	99.1 (3.0)	98.4 (4.0)	97.0 (4.0)
“Si”–NEt <sub>2</sub> ·Pd	99.4 (1.0)	96.3 (1.25)	93.1 (2.5)
“Si”–NHBu·Pd	92.3 (1.0)	91.5 (1.0)	89.7 (1.0)

<sup>a</sup> All reaction are carried out at 90 °C, 3 ml DMF, 2.03 g Bu<sub>3</sub>N, 1.175 × 10<sup>–2</sup> mmol Pd(0), 5 mmol iodobenzene and 5.5 mmol acrylic acid were used.

<sup>b</sup> Isolated yield based on iodobenzene.

and conjugated alkenes except the reaction of iodobenzene with methyl acrylate. A variety of substituted products were obtained in high yields with “Si”–NH<sub>2</sub>·Pd catalyst. All the olefins gave >88.7% yield. As for the arylation reaction of acrylic acid with iodobenzene, the TOFs (mol product per mol Pd per hour) of 420 for “Si”–NHBu·Pd(0) and 677 for “Si”–NHBu·Pd(0) catalysts at 90 °C are larger than that of 230 at 100 °C in corresponding Heck reaction reported by Cai and Song [9].

Recycling studies were also carried out on these catalysts. In the recycling experiment, two recycles were carried out for the reaction of iodobenzene with acrylic acid. The results are listed in Table 3. It is found that the activity of the catalysts decreased very slightly after two recycles, and which gave >91% yield in the first recycle, and >89% yield in the second recycle. We also test the Pd content in the used catalysts, such as “Si”–NH<sub>2</sub>·Pd(0) catalyst, the Pd content of fresh, first cycle and second recycle is 2.53, 1.57 and 1.4%, respectively. The results show that the Pd leach is main reason of the decrease of catalytic activity in first cycle reaction.

The effect of the solvent on catalytic performance was also investigated for the arylation reaction of iodobenzene with acrylic acid. The results are showed in Table 4. It is found that the catalysts gave high yield of the substituted product with all the solvents. This indicated that the influence of the polarity of solvent is not obvious to the Heck reaction with the polymeric amine–palladium(0) catalysts. But as a whole, the polar solvent is better than non-polar solvent because the Heck reaction required longer hours using non-polar solvent C<sub>6</sub>H<sub>12</sub>.

Table 4  
The effect of solvent on catalytic performance<sup>a</sup>

Agent	Isolated yield <sup>b</sup> (time, h), %		
	“Si”–NH <sub>2</sub> ·Pd	“Si”–NEt <sub>2</sub> ·Pd	“Si”–NHBu·Pd
DMF	99.1 (3.0)	99.4 (1.0)	92.3 (1.0)
C <sub>2</sub> H <sub>5</sub> OH	90.5 (5.0)	86.0 (4.0)	87.2 (2.5)
CH <sub>3</sub> CN	88.9 (4.7)	82.9 (4.0)	91.4 (3.5)
C <sub>6</sub> H <sub>12</sub>	83.2 (6.0)	91.9 (7.0)	90.7 (3.5)

<sup>a</sup> All reaction are carried out at 90 °C, 3 ml DMF, 2.03 g Bu<sub>3</sub>N, 1.175 × 10<sup>–2</sup> mmol Pd(0), 5 mmol iodobenzene and 5.5 mmol acrylic acid were used.

<sup>b</sup> Isolated yield based on iodobenzene.

The arylation of conjugated alkenes was not effective using bromobenzene or chlorobenzene as arylating agent in the present studies. Similar results have been also observed by Cai and Song [9] Choudary et al. [10].

## 5. Conclusions

We have described a series of amine–palladium(0) complexes whose preparation are simple and convenient. These complexes have not only high activity for Heck reaction, but also offer practical advantages, such as handling, separation from the product and reuse. The most important point is that it provides an economic way to synthesis unsymmetrical *trans*-stilbenes.

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