



# Synthesis of silica-supported bidentate arsine palladium complex and its catalytic properties for amidation/butoxycarbonylation of aryl halides

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## Abstract

A silica-supported bidentate arsine palladium complex has been prepared from 4-oxa-6,7-dichloroheptyltriethoxysilane via immobilization on fumed silica, followed by reacting with potassium diphenylarsenide in THF and then the reaction with palladium chloride. This polymeric arsine palladium complex is an efficient catalyst for Heck carbonylation of aryl iodides and activated aryl bromides under atmospheric pressure of carbon monoxide and can be recovered and reused.

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**Keywords:** Supported palladium catalyst; Bidentate arsine palladium complex; Aryl halide; Amidation; Butoxycarbonylation

## 1. Introduction

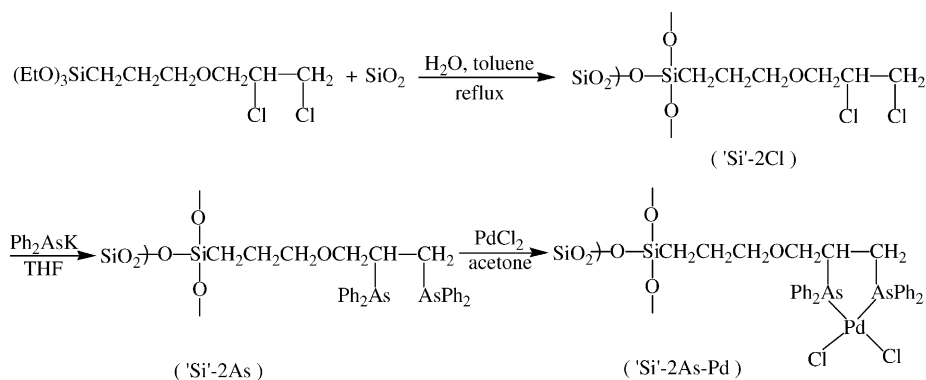
The carbonylation of aryl halides catalyzed by the palladium complex is a very versatile reaction and has found wide applications in organic synthesis because it has the advantage of proceeding smoothly under low pressure of carbon monoxide. For example, the synthesis of carboxylic acids [1], esters [2], amides [3], acid fluorides [4], aldehydes [5] and ketones [6] have been reported to be readily achieved with an atmospheric pressure of CO in good to high yields. In this reaction, homogeneous palladium complexes such as Pd(OAc)<sub>2</sub>, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> are usually used as the catalysts. The amount of catalyst used is about 2 mol% of reactant and it is difficult to recover them from the products. Easy recovery and reuse of the catalytic species make the reaction very attractive commercially.

Polymer-supported organotransition metal catalysts offer several significant advantages in synthetic and industrial chemistry; among these, the ease of separation of catalyst from the desired reaction products and the ease of recovery and reuse of the catalyst are most important. Polymer-supported palladium catalysts have successfully been used for a variety of organic reactions [7].

However, polymer-supported palladium catalysts catalyzed carbonylation of aryl halides has received less attention. Reddy et al. [8] reported that a polystyrene-anchored phosphine palladium complex with a P: Pd ratio of 0.895 catalyzed ethoxycarbonylation of organic halides in ethanol, but the activity of the catalyst was moderate and decreased gradually with repeated use. Recently, we have found that the silica-supported sulfur palladium complex [9], bidentate phosphine palladium complex [10] and selenide palladium complex [11] are efficient catalysts for Heck carbonylation of aryl halides. Study of new types of polymer-bound palladium catalysts which might be suitable for Heck carbonylation has theoretical and practical significance. However, little attention has so far been given to organoarsenium transition metal complexes [12,13]. The Heck reaction catalyzed by palladium acetate in the presence of triphenylarsine ligand has been described in the literature [14]. To our knowledge, no Heck carbonylation of aryl halides catalyzed by an organoarsenium palladium complex has been reported. In this paper we wish to report the synthesis of silica-supported bidentate arsine palladium complex (abbreviation: 'Si'-2As-Pd) and its catalytic properties in the Heck carbonylation of aryl halides. This complex is the first polymer-bound organoarsenium palladium complex and could be easily prepared from 4-oxa-6,7-dichloroheptyltriethoxysilane via immobilization on fumed silica, followed by reacting with potassium

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Scheme 1.

diphenylarsenide and then reaction with palladium chloride (Scheme 1).

## 2. Experimental

All carbonylation products were characterized by comparison of their spectra and physical data with authentic samples. Melting points were taken with a Yanaco micro melting point apparatus and were uncorrected. IR spectra were obtained on a Perkin-Elmer 683 instrument.  $^1\text{H}$  NMR spectra were recorded on a JEOL FX-90 Q (90 MHz) spectrometer with TMS as an internal standard in  $\text{CDCl}_3$  as the solvent. Elemental analyses were measured using a Yanaco MT-3 CHN microelemental analyzer. X-ray photoelectron spectroscopy (XPS) was obtained on a KRATOS XSAM 800 spectrometer.

4-Oxa-6,7-dichloroheptyltriethoxysilane was prepared by a literature method [15]. Aniline,  $n\text{-Bu}_3\text{N}$  and  $n$ -butyl alcohol were distilled before use. Other reagents were used as received without further purification.

### 2.1. Preparation of silica-supported bidentate arsine ligand ('Si'-2As)

A mixture of fumed silica (10.0 g) and 4-oxa-6,7-dichloroheptyltriethoxysilane (7.0 g) in toluene (160 ml) was stirred at  $120^\circ\text{C}$  for 24 h. Distilled water (30 ml) was added and the mixture was refluxed for another 48 h. After being cooled to room temperature, the mixture was filtered, washed with distilled water ( $4 \times 50$  ml) and dried at  $200^\circ\text{C}$  in vacuo for 5 h. The resulting white powder was washed with acetone ( $3 \times 50$  ml), followed by drying under vacuum to give 10.8 g of silica-supported poly-4-oxa-6,7-dichloroheptylsiloxane ('Si'-2Cl). The chlorine content was 1.97 mmol/g.

A mixture of  $\text{AsPh}_3$  (3.62 g, 11.83 mmol) and potassium (0.93 g, 23.66 mmol) in THF (60 ml) was stirred under nitrogen at  $60^\circ\text{C}$  for 16 h. After being cooled to room temperature, the mixture was treated with  $t\text{-BuCl}$  (1.10 g, 11.83 mmol) for 1 h to give a brown solution. Into the re-

sulting solution was added 'Si'-2Cl (5.0 g) and the mixture was stirred at room temperature for 2 h and then refluxed for 24 h. The reaction mixture was cooled to room temperature and treated with  $t\text{-BuCl}$  (2 ml) for 2 h. The mixture was filtered and washed with 95% ethanol ( $4 \times 40$  ml), distilled water ( $5 \times 40$  ml), acetone ( $3 \times 40$  ml) and then dried under vacuum to give 4.97 g of silica-supported bidentate arsine ligand ('Si'-2As). The arsenium content was 1.52 mmol/g.

### 2.2. Preparation of silica-supported bidentate arsine palladium complex ('Si'-2As-Pd)

To a solution of  $\text{PdCl}_2$  (0.156 g) in acetone (40 ml) was added 'Si'-2As (2.01 g). The mixture was refluxed under nitrogen for 48 h. The product was allowed to cool, then filtered. The resulting yellow powder was washed with distilled water ( $3 \times 30$  ml) and acetone ( $3 \times 20$  ml), then dried in vacuo to give 2.02 g of 'Si'-2As-Pd. The arsenium and palladium content was 1.39 mmol/g and 0.41 mmol/g, respectively.

### 2.3. Typical procedure for amidation of aryl halides

To a 50 ml round-bottomed flask, fitted with a gas inlet tube, a magnetic stirrer bar and a reflux condenser, was placed 'Si'-2As-Pd (200 mg, 0.08 mmol Pd). The atmosphere was replaced with carbon monoxide. Iodobenzene (1.02 g, 5 mmol),  $n\text{-Bu}_3\text{N}$  (1.29 g, 7 mmol) and aniline (0.74 g, 8 mmol) were added by syringe and a slow stream of CO was passed into the flask. The mixture was stirred at  $100^\circ\text{C}$  for 8 h. The reaction mixture was cooled and dissolved in diethyl ether (200 ml). The 'Si'-2As-Pd was separated from the mixture by filtration, washed with ether and reused in the next run. The ethereal solution was washed with 20% hydrochloric acid solution ( $2 \times 50$  ml) to remove salts and excess amines. The extracts were washed with distilled water ( $3 \times 50$  ml). The ether layer was decolorized with decolorizing carbon, dried over anhydrous magnesium sulfate and filtered. The solid product formed after concentration of the solution was filtered and air-dried to provide 0.82 g (83% yield) of  $N$ -phenylbenzamide.

#### 2.4. Typical procedure for butoxycarbonylation of aryl halides

Into a 50 ml round-bottomed flask, fitted with a magnetic stirrer, a gas inlet tube and a reflux condenser, was placed 'Si'-2As-Pd (200 mg, 0.08 mmol Pd). The atmosphere was replaced with carbon monoxide. Iodobenzene (1.02 g, 5 mmol), *n*-Bu<sub>3</sub>N (1.29 g, 7 mmol) and *n*-butyl alcohol (4 ml) were added by syringe and a slow stream of CO was passed into the flask. The mixture was stirred at 100 °C for 20 h. The reaction mixture was cooled and dissolved in diethyl ether (80 ml). The 'Si'-2As-Pd was separated from the mixture by filtration, washed with distilled water (2 × 10 ml), ethanol (2 × 10 ml) and ether (2 × 10 ml) and reused in the next run. The ethereal solution was washed with 20% aqueous hydrochloric acid (2 × 20 ml), saturated aqueous sodium hydrogen carbonate (10 ml) and distilled water (3 × 30 ml). The ether layer was dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (light petroleum–ethyl acetate = 19:1) to give 0.79 g (88% yield) of *n*-butyl benzoate.

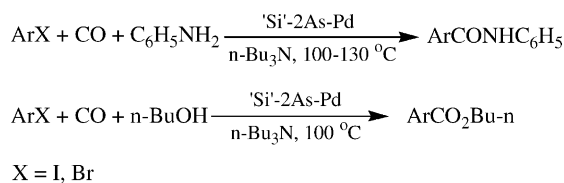
### 3. Results and discussion

A silica-supported bidentate arsine palladium complex, the first polymeric organoarsenic palladium complex, was conveniently prepared from 4-oxa-6,7-dichloroheptyltriethoxysilane via immobilization on fumed silica, followed by reacting with potassium diphenylarsenide and then reaction with palladium chloride (Scheme 1). The X-ray photoelectron spectroscopy has been used to characterize this polymeric palladium catalyst. The XPS data of 'Si'-2As-Pd, 'Si'-2As and PdCl<sub>2</sub> are listed in Table 1. It can be seen that the binding energies of Si(2p) and O(1s) of 'Si'-2As-Pd are similar to those of 'Si'-2As, and the binding energy of

Table 1  
XPS data for 'Si'-2As-Pd, 'Si'-2As and PdCl<sub>2</sub> (in eV)<sup>a</sup>

Sample	Pd <sub>3d<sub>5/2</sub></sub>	As <sub>3d</sub>	Si <sub>2p</sub>	O <sub>1s</sub>	Cl <sub>2p</sub>
'Si'-2As-Pd	336.8	42.6	103.2	532.4	199.0
'Si'-2As		41.7	103.1	532.3	
PdCl <sub>2</sub>	338.3				199.2

<sup>a</sup> The binding energies are referenced to C<sub>1s</sub> (284.6 eV), and the energy differences were determined with an accuracy of ±0.2 eV.



Scheme 2.

Cl(2p) of 'Si'-2As-Pd is similar to that of PdCl<sub>2</sub>. However the difference of As(3d) binding energies between 'Si'-2As-Pd and 'Si'-2As is 0.9 eV, which indicates that the As in the 'Si'-2As-Pd is the electron donor. The difference of Pd<sub>3d<sub>5/2</sub></sub> binding energies between 'Si'-2As-Pd and PdCl<sub>2</sub> is 1.5 eV, which indicates that the Pd in the 'Si'-2As-Pd is the electron acceptor. These results show that a coordination bond between As and Pd is formed.

In order to test the catalytic activity of the novel polymer bound palladium catalyst ('Si'-2As-Pd), the amidation and butoxycarbonylation of aryl halides were studied (Scheme 2). The typical results are summarized in Table 2. The reactions were carried out under conditions similar to those used in the corresponding homogeneous reactions. It was found that this polymeric palladium catalyst showed high activity for the amidation and the butoxycarbonylation of aryl iodides. A variety of substituted *N*-phenylbenzamides and *n*-butyl benzoates were obtained in good to high yields.

Table 2  
Amidation and butoxycarbonylation of aryl halides catalyzed by 'Si'-2As-Pd<sup>a</sup>

Entry	Aryl halide	Amine/alcohol	Temperature (°C)	Time (h)	Product	Yield (%) <sup>b</sup>
1	C <sub>6</sub> H <sub>5</sub> I	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	100	8	C <sub>6</sub> H <sub>5</sub> CONHC <sub>6</sub> H <sub>5</sub>	83
2	4-ClC <sub>6</sub> H <sub>4</sub> I	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	100	8	4-ClC <sub>6</sub> H <sub>4</sub> CONHC <sub>6</sub> H <sub>5</sub>	89
3	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> I	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	100	10	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CONHC <sub>6</sub> H <sub>5</sub>	85
4	4-ClC <sub>6</sub> H <sub>4</sub> Br	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	130	15	4-ClC <sub>6</sub> H <sub>4</sub> CONHC <sub>6</sub> H <sub>5</sub>	74
5	4-CH <sub>3</sub> OCOC <sub>6</sub> H <sub>4</sub> Br	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	130	15	4-CH <sub>3</sub> OCOC <sub>6</sub> H <sub>4</sub> CONHC <sub>6</sub> H <sub>5</sub>	77
6	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> Br	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	130	20	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CONHC <sub>6</sub> H <sub>5</sub>	68
7	C <sub>6</sub> H <sub>5</sub> I	<i>n</i> -BuOH	100	20	C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> Bu- <i>n</i>	88
8	4-ClC <sub>6</sub> H <sub>4</sub> I	<i>n</i> -BuOH	100	20	4-ClC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> Bu- <i>n</i>	84
9	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> I	<i>n</i> -BuOH	100	23	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> Bu- <i>n</i>	89
10	4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> I	<i>n</i> -BuOH	100	20	4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> Bu- <i>n</i>	87
11	4-CH <sub>3</sub> OCOC <sub>6</sub> H <sub>4</sub> Br <sup>c</sup>	<i>n</i> -BuOH	100	30	4-CH <sub>3</sub> OCOC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> Bu- <i>n</i>	68
12	4-ClC <sub>6</sub> H <sub>4</sub> Br <sup>c</sup>	<i>n</i> -BuOH	100	30	4-ClC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> Bu- <i>n</i>	61

<sup>a</sup> Reactions were carried out with 1 atm of CO, 5 mmol of aryl halide, 0.08 mmol of palladium catalyst, 7 mmol of *n*-Bu<sub>3</sub>N and 8 mmol of aniline or 4 ml of *n*-butyl alcohol.

<sup>b</sup> Yields are of isolated, pure products.

<sup>c</sup> PPh<sub>3</sub> (0.1 mmol) was added.

As seen from Table 2, aryl iodides were more reactive than the bromides and the substituent effects in the aryl iodides appeared to be less significant than in the aryl bromides. Amidation of aryl bromides required higher temperature and longer time. Butoxycarbonylation of aryl bromides proceeded very slowly unless they were strongly activated with electron-withdrawing substituents and in the presence of a catalytic amount of  $\text{PPh}_3$ .

In order to compare the activity with the homogeneous arsine palladium complex, we carried out the amidation and butoxycarbonylation reaction of iodobenzene catalyzed by  $\text{Pd}(\text{AsPh}_3)_2\text{Cl}_2$  (1.6 mol%) under the same reaction conditions as Table 2, *N*-phenylbenzamide and *n*-butyl benzoate were obtained in 80 and 86% yield, respectively. This result indicates that the catalytic activity of 'Si'-2As-Pd is slightly higher than that of analogous homogeneous catalyst ( $\text{Pd}(\text{AsPh}_3)_2\text{Cl}_2$ ). This polymeric palladium catalyst can be easily separated from products by a simple filtration and can be reused many times. When 'Si'-2As-Pd was used in five consecutive runs for the amidation reaction of iodobenzene or for the butoxycarbonylation reaction of iodobenzene, *N*-phenylbenzamide was formed in 83, 81, 82, 80 and 79% yield and *n*-butyl benzoate in 88, 86, 84, 85 and 82% yield, respectively. The formation of palladium black was not observed during the carbonylation of aryl halides. The palladium content of the catalyst was determined to be 0.38 mmol/g after five consecutive runs in amidation of iodobenzene and it was found that only 6% of palladium had been lost from the polymer support. In order to determine if the carbonylation reaction of aryl halides catalyzed by the 'Si'-2As-Pd is heterogeneous, after the butoxycarbonylation reaction of iodobenzene proceeded for 10 h, the reaction mixture was filtered at reaction temperature (100 °C) and the filtrate was used as the catalyst to complete the butoxycarbonylation reaction of the left iodobenzene. It was found that the filtrate can not catalyze the butoxycarbonylation reaction of the left iodobenzene. This result suggests that bidentate As is a strong ligand for Pd and the amidation and the butoxycarbonylation of aryl halides catalyzed by the 'Si'-2As-Pd are heterogeneous reactions.

#### 4. Conclusions

We have described a new polymer-bound bidentate arsine palladium complex catalyst whose preparation is simple and convenient. This polymeric palladium catalyst has not only high activity for the amidation and the butoxycarbonylation

of aryl iodides and activated aryl bromides, but offers some practical advantages such as easy handling, separation from the products and reuse.

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