

Synthesis of silica-supported poly- γ -diphenylarsinopropylsiloxane palladium complex and its catalytic behavior for Heck carbonylation of aryl halides

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Abstract

A silica-supported poly- γ -diphenylarsinopropylsiloxane palladium complex has been prepared from γ -chloropropyltriethoxysilane via immobilization on fumed silica, followed by reacting with potassium diphenylarsenide in THF and then the reaction with palladium chloride. It is an efficient catalyst for Heck carbonylation of aryl halides under atmospheric pressure of carbon monoxide. This polymeric palladium catalyst can be recovered and reused.

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1. Introduction

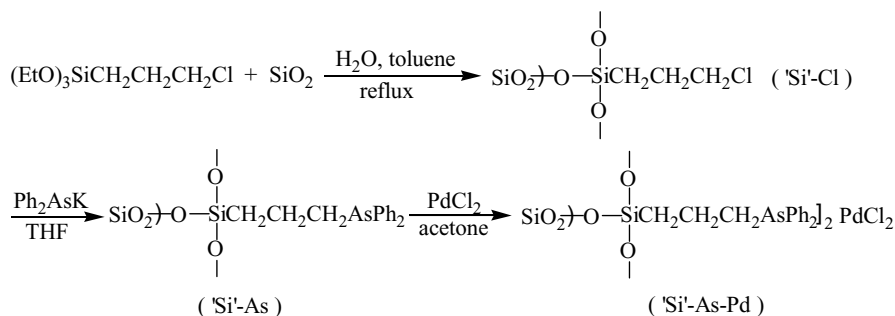
The palladium-catalyzed carbonylation of aryl halides is a very versatile reaction and has found wide application in organic synthesis because it has the advantage of proceeding smoothly under low pressure of carbon monoxide. For example, the synthesis of carboxylic acids [1,2], esters [3], amides [4], acid fluorides [5], aldehydes [6] and ketones [7] have been reported to be readily achieved with an atmospheric pressure of CO in good to high yields. In this reaction, homogeneous catalytic systems have been proven to be highly efficient and palladium complexes such as Pd(OAc)₂ or Pd(PPh₃)₂Cl₂ are usually used as the catalyst. 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.

In order to make homogeneous catalysts generally more attractive from an industrial point of view, the technique of complex immobilization have been developed [8], and polystyrene-supported palladium catalysts have successfully

been used for a variety of organic reactions [9]. However, polymer-supported palladium catalyst catalyzed carbonylation of aryl halides has received less attention. Reddy et al. [10] 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. We reported the amidation of aryl halides catalyzed by a silica-supported bidentate phosphine palladium complex and the butoxycarbonylation of aryl halides catalyzed by a silica-supported sulfur palladium complex [11,12]. Recently, we have described the synthesis of a silica-supported selenide palladium complex and its catalytic properties in the Heck carbonylation of aryl halides [13]. 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 [14,15]. 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 poly- γ -diphenylarsinopropylsiloxane palladium complex (abbreviation: 'Si'-As-Pd) and its catalytic properties in the Heck carbonylation of aryl halides. This complex is the first

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Scheme 1.

polymer-bound organoarsenic palladium complex and could be easily prepared from γ -chloropropyltriethoxysilane via immobilization on fumed silica, followed by reacting with potassium diphenylarsenide and then reaction with palladium chloride (Scheme 1).

2. Experimental

Melting points were taken with a Yanaco micro melting point apparatus and were uncorrected. IR spectra were obtained using a Shimadzu IR-435 grating spectrophotometer. ^1H NMR spectra were recorded on a JEOL FX-90Q (90 MHz) instrument with TMS as an internal standard in CDCl_3 as the solvent. Elemental analyses were performed on a Perkin-Elmer 240 elemental analysis instrument. X-ray photoelectron spectroscopy (XPS) was obtained on a KRATOS XSAM800 spectrometer. All carbonylation products were characterized by comparison of their spectra and physical data with authentic samples.

Aniline, *n*- Bu_3N and *n*-butyl alcohol were distilled before use. Other reagents were used as received without further purification.

2.1. Preparation of silica-supported poly- γ -diphenylarsinopropylsiloxane ('Si'-As)

A mixture of fumed silica (6.0 g) and γ -chloropropyltriethoxysilane (5.0 g) in toluene (140 ml) was stirred at 120°C for 24 h. Distilled water (20 ml) and 10% hydrochloric acid (0.2 ml) were added and the mixture was refluxed for another 48 h. After being cooled to room temperature, the mixture was filtered, washed with distilled water (4×50 ml) and dried at 220°C in vacuo for 5 h. The resulting white powder was washed with acetone (3×50 ml), followed by drying to afford 7.2 g of silica-supported poly- γ -chloropropylsiloxane ('Si'-Cl). The chlorine content was 2.08 mmol/g.

A mixture of Ph_3As (2.90 g, 9.5 mmol) and potassium (0.74 g, 19 mmol) in THF (50 ml) was stirred under nitrogen at 60°C for 16 h. After being cooled to room temperature, the mixture was treated with *t*-BuCl (0.88 g, 9.5 mmol) for

1 h to give a brown solution. Into the resulting solution was added 'Si'-Cl (4.10 g) and the mixture was stirred at room temperature for 2 h and then refluxed for 24 h. The mixture was cooled to room temperature and treated with *t*-BuCl (2 ml) for 2 h. The mixture was filtered and washed with 95% ethanol (4×30 ml), distilled water (5×30 ml), acetone (3×30 ml) and then dried under vacuum to give 3.98 g of silica-supported poly- γ -diphenylarsinopropylsiloxane ('Si'-As). The arsenic content was 1.58 mmol/g.

2.2. Preparation of silica-supported poly- γ -diphenylarsinopropylsiloxane palladium complex ('Si'-As-Pd)

To a solution of PdCl_2 (0.156 g) in acetone (40 ml) was added 'Si'-As (2.02 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 (3×20 ml) and acetone (3×20 ml), then dried in vacuo to afford 2.04 g of 'Si'-As-Pd. The arsenic and palladium content was 1.41 and 0.39 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'-As-Pd (200 mg, 7.8×10^{-2} mmol Pd). The atmosphere was replaced with carbon monoxide. Iodobenzene (1.02 g, 5 mmol), *n*- Bu_3N (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°C for 8 h. The reaction mixture was cooled and dissolved in diethyl ether (200 ml). The 'Si'-As-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 (2×50 ml) to remove salts and excess amines. The extracts were washed with distilled water (3×50 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 0.81 g (82% 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'-As-Pd (200 mg, 7.8×10^{-2} mmol Pd). The atmosphere was replaced with carbon monoxide. Iodobenzene (1.02 g, 5 mmol), *n*-Bu₃N (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'-As-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 0.75 g (84% yield) of *n*-butyl benzoate.

3. Results and discussion

A silica-supported poly- γ -diphenylarsinopropylsiloxane palladium complex, the first polymeric organoarsenic palladium complex, was conveniently prepared from γ -chloropropyltriethoxysilane 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

Table 1

XPS data for 'Si'-As-Pd, 'Si'-As and PdCl₂ (in eV)^a

Sample	Pd 3d _{5/2}	As 3d	Si 2p	O 1s	Cl 2p
'Si'-As-Pd	336.7	42.5	103.1	532.4	199.1
'Si'-As		41.6	103.0	532.3	
PdCl ₂	338.3				199.2

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

of 'Si'-As-Pd, 'Si'-As and PdCl₂ are listed in Table 1. It can be seen that the binding energies of Si 2p and O 1s of 'Si'-As-Pd are similar to those of 'Si'-As, and the binding energy of Cl 2p of 'Si'-As-Pd is similar to that of PdCl₂. However, the difference of As 3d binding energies between 'Si'-As-Pd and 'Si'-As is 0.9 eV. The difference of Pd 3d_{5/2} binding energies between 'Si'-As-Pd and PdCl₂ is 1.6 eV. These results show that a coordination bond between As and Pd is formed.

In order to evaluate the catalytic activity of the novel polymer bound palladium catalyst ('Si'-As-Pd), the amidation and butoxycarbonylation of aryl halides were studied. The results are summarized in Table 2. The reactions were carried out under conditions similar to those used in the corresponding homogeneous reactions [3,4]. It was found that this polymeric palladium catalyst exhibited 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. As seen from Table 2, aryl iodides were more reactive than the bromides and the substituent electronic 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 and the reactivity of the

Table 2

Amidation and butoxycarbonylation of aryl halides catalyzed by 'Si'-As-Pd^a

Entry	Aryl halide	Amine/alcohol	Temperature (°C)	Time (h)	Product (% yield) ^b
1	C ₆ H ₅ I	C ₆ H ₅ NH ₂	100	8	C ₆ H ₅ CONHC ₆ H ₅ (82)
2	4-ClC ₆ H ₄ I	C ₆ H ₅ NH ₂	100	8	4-ClC ₆ H ₄ CONHC ₆ H ₅ (87)
3	4-CH ₃ OC ₆ H ₄ I	C ₆ H ₅ NH ₂	100	10	4-CH ₃ OC ₆ H ₄ CONHC ₆ H ₅ (84)
4	4-CH ₃ C ₆ H ₄ I	C ₆ H ₅ NH ₂	100	10	4-CH ₃ C ₆ H ₄ CONHC ₆ H ₅ (81)
5	4-ClC ₆ H ₄ Br	C ₆ H ₅ NH ₂	130	15	4-ClC ₆ H ₄ CONHC ₆ H ₅ (75)
6	4-CH ₃ OCOC ₆ H ₄ Br	C ₆ H ₅ NH ₂	130	15	4-CH ₃ OCOC ₆ H ₄ CONHC ₆ H ₅ (77)
7	C ₆ H ₅ Br	C ₆ H ₅ NH ₂	130	15	C ₆ H ₅ CONHC ₆ H ₅ (68)
8	4-CH ₃ OC ₆ H ₄ Br	C ₆ H ₅ NH ₂	130	20	4-CH ₃ OC ₆ H ₄ CONHC ₆ H ₅ (64)
9	C ₆ H ₅ I	<i>n</i> -BuOH	100	20	C ₆ H ₅ CO ₂ Bu- <i>n</i> (84)
10	4-ClC ₆ H ₄ I	<i>n</i> -BuOH	100	20	4-ClC ₆ H ₄ CO ₂ Bu- <i>n</i> (89)
11	4-CH ₃ OC ₆ H ₄ I	<i>n</i> -BuOH	100	23	4-CH ₃ OC ₆ H ₄ CO ₂ Bu- <i>n</i> (92)
12	4-O ₂ NC ₆ H ₄ I	<i>n</i> -BuOH	100	20	4-O ₂ NC ₆ H ₄ CO ₂ Bu- <i>n</i> (88)
13	4-CH ₃ OCOC ₆ H ₄ Br ^c	<i>n</i> -BuOH	100	30	4-CH ₃ OCOC ₆ H ₄ CO ₂ Bu- <i>n</i> (58)
14	4-ClC ₆ H ₄ Br ^c	<i>n</i> -BuOH	100	30	4-ClC ₆ H ₄ CO ₂ Bu- <i>n</i> (62)
15	4-O ₂ NC ₆ H ₄ Br ^c	<i>n</i> -BuOH	100	30	4-O ₂ NC ₆ H ₄ CO ₂ Bu- <i>n</i> (67)

^a Reactions were carried out with 1 atm of CO, 5 mmol of aryl halide, 0.078 mmol of palladium catalyst, 7 mmol of *n*-Bu₃N and 8 mmol of aniline or 4 ml of *n*-butyl alcohol.

^b Yields are of isolated, pure products.

^c PPh₃ (0.1 mmol) was added.

aryl bromides with electron-withdrawing substituents was higher than that of the aryl bromides with electron-donating substituents. 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 PPh_3 . When this polymeric palladium catalyst was used in three consecutive runs for the amidation reaction of iodobenzene or for the butoxycarbonylation of iodobenzene, *N*-phenylbenzamide was formed in 82, 80 and 75% yield and butyl benzoate in 84, 81 and 79% 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 0.36 mmol/g after three consecutive runs in amidation of iodobenzene and it was found that only 8% of palladium had been lost from the polymer support. This result suggests that As is a strong ligand for Pd and the amidation and the butoxycarbonylation of aryl halides catalyzed by the 'Si'–As–Pd are heterogeneous reactions.

4. Conclusions

We have described the first polymer-bound organoarsenium 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 halides, but offers some practical advantages such as easy handling, separation from the products and reuse.

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