

Carbonylation of aryl halides catalyzed by a silica-supported sulfur and phosphine mixed bidentate palladium complex

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Abstract

A silica-supported sulfur and phosphine mixed bidentate palladium complex has been prepared from 4-thia-6-chlorohexyltrimethoxysilane via immobilization on fumed silica, followed by reacting with potassium diphenylphosphide in tetrahydrofuran (THF) and then the reaction with palladium chloride in acetone. This polymeric palladium complex is an efficient catalyst for Heck carbonylation of aryl halides with aniline or *n*-butyl alcohol under atmospheric pressure of carbon monoxide and can be recovered and reused without loss of activity.

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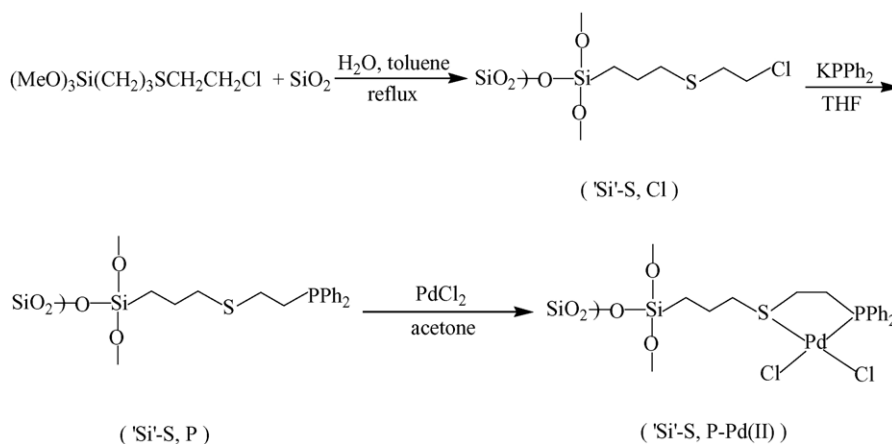
1. Introduction

The development of environmental friendly catalysts for organic transformation is becoming an area of growing importance [1]. The palladium complex catalyzed carbonylation of aryl halides with carbon monoxide is a very versatile reaction and has been widely used in organic synthesis because it has the advantage of proceeding smoothly under low pressure of carbon monoxide. For example, the synthesis of carboxylic acids [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 palladium complexes, such as Pd(OAc)₂, Pd(PPh₃)₂Cl₂ are usually used as the catalysts and they are expensive, air-sensitive and cannot be recovered from the products. Easy recovery and reuse of the catalytic species make them very attractive commercially.

Immobilized palladium catalysts have been expected to solve these problems and polymer-supported palladium catalysts have successfully been used for a variety of organic

reactions [8]. However, polymer-supported palladium catalysts catalyzed carbonylation of aryl halides has received less attention. Reddy et al. [9] 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 [10], selenide–palladium complex [11] and arsine–palladium complex [12] 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 and have excellent reusability has theoretical and practical significance. To our knowledge, no Heck carbonylation of aryl halides catalyzed by a polymer-supported mixed bidentate palladium complex has been reported. In this paper, we wish to report the synthesis of silica-supported sulfur and phosphine mixed bidentate palladium complex (abbreviation: ‘Si’–S, P–Pd(II)) and its catalytic properties in the Heck carbonylation of aryl halides. This complex is the first polymer-bound sulfur and phosphine mixed bidentate palladium complex and could be easily prepared from 4-thia-6-chlorohexyltrimethoxysilane via immobilization on fumed silica, followed by reacting with potassium diphenylphos-

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Scheme 1.

phide in tetrahydrofuran (THF) and then the reaction with palladium chloride in acetone (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. ^1H NMR spectra were recorded on a JEOL FX-90 Q (90 MHz) spectrometer with TMS as an internal standard in 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-Thia-6-chlorohexyltrimethoxysilane was prepared by a literature method [13]. Tetrahydrofuran was distilled over sodium benzophenone ketyl immediately before use. 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 sulfur and phosphine mixed bidentate ligand ('Si'-S, P)

A mixture of fumed silica (8.0 g) and 4-thia-6-chlorohexyltrimethoxysilane (3.75 g) in toluene (160 ml) was stirred under Ar at 120°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 (4×50 ml) and dried at 200°C in vacuo for 5 h. The resulting white powder was washed with acetone (3×50 ml), followed by drying under vacuum to give 8.8 g of silica-supported poly-4-thia-6-chlorohexylsiloxane. The sulfur and chlorine content was 0.97 and 0.98 mmol/g, respectively.

A mixture of PPh_3 (1.442 g, 5.5 mmol) and potassium (0.429 g, 11.0 mmol) in THF (60 ml) was stirred under Ar

at 60°C for 16 h. After being cooled to room temperature, the mixture was treated with *t*-BuCl (0.509 g, 5.5 mmol) for 1 h to give a brown solution. Into the resulting solution was added 'Si'-S, Cl (4.50 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*-BuCl (2 ml) for 2 h. The mixture was filtered and washed with 95% ethanol (4×40 ml), distilled water (5×40 ml), acetone (3×40 ml) and then dried under vacuum to give 4.48 g of silica-supported sulfur and phosphine mixed bidentate ligand. The sulfur and phosphine content was 0.88 and 0.79 mmol/g, respectively.

2.2. Preparation of silica-supported sulfur and phosphine mixed bidentate palladium complex

To a solution of PdCl_2 (0.220 g) in acetone (40 ml) was added 'Si'-S, P (2.60 g). The mixture was refluxed under Ar for 72 h. The product was allowed to cool, then filtered. The resulting yellow powder was washed with distilled water (3×30 ml) and acetone (3×20 ml), then dried in vacuo to give 2.74 g of 'Si'-S, P-Pd(II). The sulfur, phosphine and palladium content was 0.74, 0.68 and 0.40 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'-S, P-Pd(II) (200 mg, 0.08 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 palladium catalyst 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

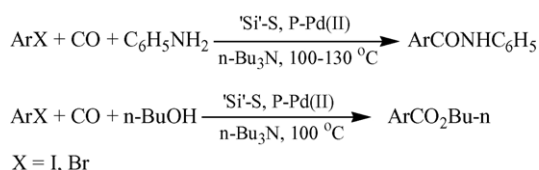
salts and excess amines. The extracts were washed with distilled water (3 × 50 ml). The ether layer was decolorized with decolorizing carbon, dried over anhydrous magnesium sulfate and filtered. The solid product formed after concentration of the solution was filtered and air-dried to provide 0.812 g (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'-S, P-Pd(II) (200 mg, 0.08 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 palladium catalyst 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 0.778 g (87% yield) of *n*-butyl benzoate.

3. Results and discussion

A silica-supported poly-4-thia-6-diphenylphosphinohe- xylsiloxane palladium complex, the first polymeric mixed bidentate palladium complex, was conveniently prepared from 4-thia-6-chlorohexyltrimethoxysilane via immobilization on fumed silica, followed by reacting with potassium diphenylphosphide in THF and then by reacting with palladium chloride in acetone (Scheme 1). The X-ray photoelectron spectroscopy has been used to characterize this polymeric palladium catalyst. The XPS data of 'Si'-S, P-Pd(II), 'Si'-S, P and PdCl₂ are listed in Table 1. It can be seen that the binding energies of Si(2p) and O(1s) of 'Si'-S, P-Pd(II) are similar to those of 'Si'-S, P and the binding energy of Cl(2p) of 'Si'-S, P-Pd(II) is similar to that of PdCl₂. However, the difference of S(2p) binding energies between 'Si'-S,



Scheme 2.

P-Pd(II) and 'Si'-S, P is 0.7 eV, the difference of P(2p) binding energies between 'Si'-S, P-Pd(II) and 'Si'-S, P is 0.5 eV, which indicate that the S and P in the 'Si'-S, P-Pd(II) are the electron donors. The difference of Pd (3d5/2) binding energies between 'Si'-S, P-Pd(II) and PdCl₂ is 1.1 eV, which indicates that the Pd in the 'Si'-S, P-Pd(II) is the electron acceptor. These results show that both the coordination bond between S and Pd and the coordination bond between P and Pd are formed.

In order to evaluate the catalytic activity of the novel polymer-bound mixed bidentate palladium catalyst ('Si'-S, P-Pd(II)), 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. As expected, 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. The amidation of aryl bromides were carried out at 130 °C and needed longer time. The reactivity of bromobenzenes having electron-withdrawing substituents was higher than that of bromobenzenes having electron-donating substituents. But, the amidation of 4-nitrobromobenzene was an exception. As preceded in the work of Heck and co-worker [4a], the *N*-phenylamidation of 4-nitrobromobenzene was complicated since the reduction of the nitro group catalyzed by palladium also occurred to form an *N*-phenylurea group from the nitro group, CO and aniline. The amidation of 1-bromonaphthalene with bulky group was also carried out in moderate yield. The reactivity of aryl chlorides was poor and the amidation reaction did not occur under same conditions. 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 PPh₃. Table 2 contains one example of particular interest: the butoxycarbonylation of both methyl 4-iodobenzoate and methyl 4-bromobenzoate afford *n*-butyl methyl terephthalate only with none of the symmetrical esters being formed. Benzyl bromide also reacted with CO and *n*-butyl alcohol without PPh₃, but the yield was low. In the presence of a catalytic amount of PPh₃, the butoxycarbonylation of 1-bromonaphthalene gave an ester after 72 h in low yield. The reactivity of aryl chlorides was poor and the

Table 1
XPS data for 'Si'-S, P-Pd(II), 'Si'-S, P and PdCl₂ (in eV)^a

Sample	Pd (3d5/2)	S (2p)	P (2p)	Si (2p)	O (1s)	Cl (2p)
'Si'-S, P-Pd(II)	337.2	164.6	133.6	103.3	532.6	199.7
'Si'-S, P		163.9	133.1	103.4	532.5	
PdCl ₂	338.3					199.8

^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.

Table 2
Amidation and butoxycarbonylation of aryl halides catalyzed by 'Si'-S, P-Pd(II)^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	86
4	4-ClC ₆ H ₄ Br	C ₆ H ₅ NH ₂	130	15	4-ClC ₆ H ₄ CONHC ₆ H ₅	75
5	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	74
6	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	66
7	4-O ₂ NC ₆ H ₄ Br	C ₆ H ₅ NH ₂	130	9	4-O ₂ NC ₆ H ₄ CONHC ₆ H ₅	39
8	1-C ₁₀ H ₇ Br	C ₆ H ₅ NH ₂	130	36	1-C ₁₀ H ₇ CONHC ₆ H ₅	45
9	C ₆ H ₅ I	<i>n</i> -BuOH	100	20	C ₆ H ₅ CO ₂ Bu- <i>n</i>	87
10	4-ClC ₆ H ₄ I	<i>n</i> -BuOH	100	20	4-ClC ₆ H ₄ CO ₂ Bu- <i>n</i>	90
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>	88
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>	90
13	4-CH ₃ OCOC ₆ H ₄ I	<i>n</i> -BuOH	100	20	4-CH ₃ OCOC ₆ H ₄ CO ₂ Bu- <i>n</i>	91
14	4-CH ₃ OCOC ₆ H ₄ Br ^c	<i>n</i> -BuOH	100	36	4-CH ₃ OCOC ₆ H ₄ CO ₂ Bu- <i>n</i>	66
15	4-ClC ₆ H ₄ Br ^c	<i>n</i> -BuOH	100	36	4-ClC ₆ H ₄ CO ₂ Bu- <i>n</i>	62
16	4-O ₂ NC ₆ H ₄ Br ^c	<i>n</i> -BuOH	100	36	4-O ₂ NC ₆ H ₄ CO ₂ Bu- <i>n</i>	58
17	C ₆ H ₅ CH ₂ Br	<i>n</i> -BuOH	100	36	C ₆ H ₅ CH ₂ CO ₂ Bu- <i>n</i>	36
18	1-C ₁₀ H ₇ Br ^c	<i>n</i> -BuOH	100	72	1-C ₁₀ H ₇ CO ₂ Bu- <i>n</i>	41

^a Reactions were carried out with 1 atm of CO, 5 mmol of aryl halide, 0.08 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.

butoxycarbonylation reaction did not occur under same conditions.

In order to compare the activity with the homogeneous palladium complex, we carried out the amidation and butoxycarbonylation reaction of iodobenzene catalyzed by Pd(PPh₃)₂Cl₂ (1.6 mol%) under the same reaction conditions as Table 2, *N*-phenylbenzamide and *n*-butyl benzoate were obtained in 83 and 86% yield, respectively. These results indicate that the catalytic activity of 'Si'-S, P-Pd(II) is comparable to that of the homogeneous catalyst (Pd(PPh₃)₂Cl₂). This polymeric palladium catalyst can be easily separated from products by a simple filtration and can be reused many times. When 'Si'-S, P-Pd(II) was used in five consecutive runs for the amidation reaction of iodobenzene or for the butoxycarbonylation reaction of iodobenzene, *N*-phenylbenzamide was formed in 82, 81, 82, 80 and 81% yield and *n*-butyl benzoate in 87, 86, 86, 85 and 86% yield, respectively. Although both 'Si'-S-Pd [10] and 'Si'-S, P-Pd(II) gave the same results in butoxycarbonylation of aryl halides, the 'Si'-S, P-Pd(II) had better reusability than the 'Si'-S-Pd since the sulfur and phosphine mixed bidentate palladium complex was more stable than the monodentate sulfur-palladium complex. The formation of palladium black was not observed during the carbonylation of aryl halides. The palladium content of the catalyst was determined to be 0.39 mmol/g after five consecutive runs in amidation of iodobenzene, and it was found that only 2.5% of palladium had been lost from the polymer support. In order to determine if the carbonylation reaction of aryl halides catalyzed by the 'Si'-S, P-Pd(II) 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 cannot catalyze the butoxycarbonylation reaction of the left iodobenzene. This result suggests that the sulfur and phosphine mixed bidentate ligand can efficiently prevent the palladium on polymer support from being leached and the amidation and the butoxycarbonylation of aryl halides catalyzed by the 'Si'-S, P-Pd(II) are heterogeneous reactions.

4. Conclusions

We have described the first polymer-bound sulfur and phosphine mixed bidentate palladium complex catalyst 'Si'-S, P-Pd(II), which could be conveniently prepared by using common chemicals fumed silica, 4-thia-6-chlorohexyltrimethoxysilane, potassium diphenylphosphide and palladium chloride. This polymeric palladium catalyst not only has high activity in 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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