

Synthesis of silica-supported poly- ω -(methylseleno)undecylsiloxane palladium(0) complex and its catalytic properties for Heck arylation of alkenes

Mingzhong Cai^{a,*}, Gang Liu^b, Jun Zhou^a

^a Department of Chemistry, Jiangxi Normal University, Nanchang 330027,
PR China

^b Department of Chemistry, Jiangxi Science and Technology College, Nanchang 330013,
PR China

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Abstract

A silica-supported poly- ω -(methylseleno)undecylsiloxane palladium(0) complex has been prepared from ω -chloroundecyltriethoxysilane via immobilization on fumed silica, followed by reacting with sodium methylselenolate in ethanol and palladium chloride in acetone and then the reduction with hydrazine hydrate in ethanol. The complex is a highly active and stereoselective catalyst for arylation of conjugated alkenes with aryl halides. This polymeric palladium catalyst can be recovered and reused.

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Keywords: Supported palladium catalyst; Selenide palladium(0) complex; Heck arylation; Stereoselective synthesis

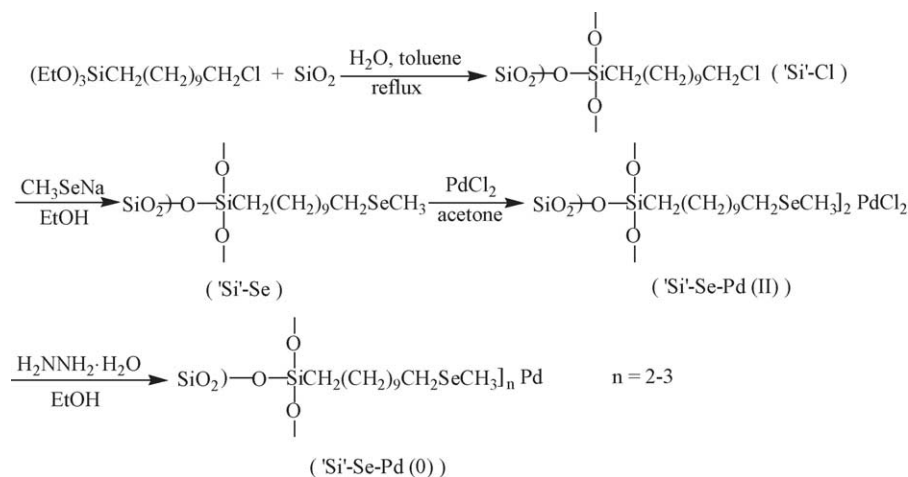
1. Introduction

The palladium-catalyzed arylation of alkenes, the Heck reaction, provides a very convenient method for forming carbon–carbon bonds at an unsubstituted vinylic position and has found wide application in organic synthesis [1,2]. It is a homogeneous reaction, generally using palladium compounds such as Pd(OAc)₂ as catalysts. The amount of catalyst used is about 1 mol% of reactant; however, use of homogeneous palladium catalysts is still uneconomic for large-scale preparations in the laboratory and for industrial production. As Heck [3,4] has noted, practical application of the reaction under such conditions is not feasible due to its high cost. Polymer-supported organotransition metal complexes having high activity and selectivity are currently attracting great interest because they 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 the most important.

Study of new types of polymer-supported palladium catalyst which might be suitable for the Heck arylation of alkenes has theoretical and practical significance. In the past, most of these studies have been related to polymer-supported phosphine palladium catalysts [5–7]. It is known that catalysts containing phosphine ligands are unstable [8]. Furthermore, the procedure for preparing the polymer-supported phosphine palladium complex is rather complicated; the non-crosslinked poly(chloromethylstyrene) is not commercially available, and the chloromethylation requires the use of carcinogenic chloromethyl methyl ether. Zhang et al. [9] described a polymer-supported phenanthroline palladium(0)-catalyzed arylation of acrylamide with aryl iodides, however when tributylamine was used as the base, the activity of the catalyst was remarkably lowered on recycling and moreover

* Corresponding author. Tel.: +86 791 8517500; fax: +86 791 8517500.
E-mail address: caimingz@tom.com (M. Cai).



Scheme 1.

the preparation of the catalyst is also rather complicated. Recently, we have found that the silica-supported sulfur palladium(0) complex [10] is an efficient catalyst for Heck arylation of styrene and acrylic acid with aryl iodides. However, none of the reported polymeric palladium catalysts [5–7,9,10] show activity for the arylation of conjugated alkenes with aryl bromides. To our knowledge, little attention has so far been given to organoselenium transition metal complexes which, to date, remain largely confined to the organoselenium platinum complexes [11,12]. In this paper, we report the synthesis of silica-supported poly- ω -(methylseleno)undecylsiloxane palladium(0) complex (abbreviation: 'Si'–Se–Pd(0)) and its catalytic properties in the Heck arylation of conjugated alkenes with aryl halides. This complex could be easily prepared from ω -chloroundecyltriethoxysilane via immobilization on fumed silica, followed by reacting with sodium methylselenolate in ethanol and palladium chloride in acetone, and then the reduction with hydrazine hydrate in ethanol (Scheme 1).

2. Experimental

All arylation 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 using a Perkin-Elmer 683 instrument. ^1H NMR spectra were recorded on a JEOL FX-90Q (90 MHz) or a Bruker AC-P300 (300 MHz) spectrometer with TMS as an internal standard in CDCl_3 or DMSO-d_6 as solvent. Microanalyses were obtained using a Perkin-Elmer 240 elemental analyzer. X-ray photoelectron spectroscopy (XPS) was obtained on a KRATOS XSAM 800 spectrometer. Dimethyl diselenide was prepared according to literature procedure [13]. *p*-Xylene, Bu_3N and DMF were distilled before use, other reagents were used as received without further purification.

2.1. Preparation of silica-supported poly- ω -(methylseleno)undecylsiloxane ('Si'–Se)

A mixture of fumed silica (6.0 g) and ω -chloroundecyltriethoxysilane (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 6.7 g of silica-supported poly- ω -chloroundecylsiloxane ('Si'–Cl). The chlorine content was 0.82 mmol/g.

To a well-stirred solution of dimethyl diselenide (1.04 g, 5.5 mmol) in 50 ml of ethanol was added NaBH_4 (0.43 g, 11 mmol) portionwise under Ar atmosphere at room temperature until the reaction mixture was decolorized. After being stirred for another 3 h, 'Si'–Cl (10.0 g, 8.2 mmol) was added and the mixture was refluxed for 24 h. The mixture was allowed to cool and filtered, washed with distilled water (5×20 ml), EtOH (3×20 ml) and then dried under vacuum to give 9.3 g of silica-supported poly- ω -(methylseleno)undecylsiloxane ('Si'–Se). The selenium content was 0.71 mmol/g.

2.2. Preparation of silica-supported poly- ω -(methylseleno)undecylsiloxane palladium(0) complex ('Si'–Se–Pd(0))

To a solution of PdCl_2 (0.156 g) in acetone (60 ml) was added 'Si'–Se (4.50 g). The mixture was refluxed under Ar for 72 h. The product was allowed to cool, then filtered. The resulting yellow solid was washed with distilled water (3×20 ml) and acetone (3×20 ml) to afford 'Si'–Se–Pd(II), which was then stirred with hydrazine hydrate (1.50 g) and EtOH (30 ml) at 30°C under Ar for 2 h. The resulting product was filtered, washed with EtOH (4×20 ml) and Et_2O (2×20 ml) and dried under vacuum to give 4.23 g of the

black polymeric palladium(0) complex ('Si'–Se–Pd(0)). The selenium and palladium content was 0.62 and 0.19 mmol/g, respectively.

2.3. Typical procedure for the arylation of butyl acrylate with aryl halides

A mixture of butyl acrylate (0.71 g, 5.5 mmol), iodobenzene (1.02 g, 5.0 mmol), Bu₃N (1.11 g, 6.0 mmol), *p*-xylene (1.0 ml) and the 'Si'–Se–Pd(0) complex (110 mg, 0.02 mmol of Pd) was stirred under Ar in an oil bath at 100 °C for 6 h. The mixture was cooled and dissolved in Et₂O (60 ml). The 'Si'–Se–Pd(0) complex was separated from the mixture by filtration, washed with distilled water (2 × 10 ml), EtOH (3 × 10 ml) and Et₂O (3 × 10 ml) and reused in the next run. The ethereal solution was washed with 5 N HCl (2 × 20 ml), brine (4 × 30 ml) and dried (MgSO₄) and filtered. The residue formed after concentration of the ethereal solution was purified by flash column chromatography on silica gel (light petroleum–ethyl acetate 19:1) to give (*E*)-butyl cinnamate (**3a**) (0.920 g, 90%).

2.4. Typical procedure for the arylation of acrylamide with aryl halides

A mixture of acrylamide (0.39 g, 5.5 mmol), iodobenzene (1.02 g, 5.0 mmol), Bu₃N (1.11 g, 6.0 mmol), DMF (1.0 ml) and the 'Si'–Se–Pd(0) complex (110 mg, 0.02 mmol of Pd) was stirred under Ar in an oil bath at 100 °C for 6 h. The reaction mixture was cooled and dissolved in DMF (3.0 ml) and water (1.0 ml). The 'Si'–Se–Pd(0) complex was separated from the mixture by filtration. The filtrate was poured into water (100 ml), the precipitated product was isolated by suction and washed with water (3 × 10 ml). The crude product was recrystallized from ethanol to afford (*E*)-cinnamamide (**3h**) (0.656 g, 89%).

3. Results and discussion

A silica-supported poly- ω -(methylseleno)undecylsiloxane palladium(0) complex was conveniently prepared from ω -chloroundecyltriethoxysilane via immobilization on fumed silica, followed by reacting with sodium methylselenolate in ethanol and palladium chloride in acetone, and then the reduction with hydrazine hydrate in ethanol (Scheme 1). The polymer-bound palladium(0) complexes catalysts are very stable to air and moisture as a result of the isolation of the reactive species by the polymer matrix. As a result, the present catalyst can be stored for a long period and is very convenient to use. This polymeric palladium catalyst was characterized by the X-ray photoelectron spectroscopy (XPS) and elemental analyses. The XPS data for 'Si'–Se–Pd(0), 'Si'–Se–Pd(II), 'Si'–Se and PdCl₂ are listed in Table 1. It can be seen that the binding energies of Si (2p) and O (1s) of 'Si'–Se–Pd(II) are similar to those of 'Si'–Se, and the bind-

Table 1
XPS data for 'Si'–Se–Pd(0), 'Si'–Se–Pd(II), 'Si'–Se and PdCl₂ (in eV)^a

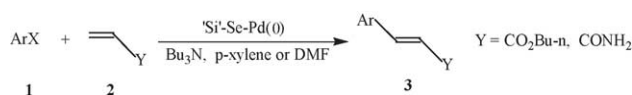
| Sample | Pd 3d _{5/2} | Se 3d | Si 2p | O 1s | Cl 2p |
|-------------------|----------------------|-------|-------|-------|-------|
| 'Si'–Se–Pd(0) | 336.4 | 55.8 | 103.1 | 532.4 | |
| 'Si'–Se–Pd(II) | 337.4 | 56.3 | 103.1 | 532.4 | 199.1 |
| 'Si'–Se | | 55.6 | 103.0 | 532.3 | |
| PdCl ₂ | 338.3 | | | | 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.

ing energy of Cl (2p) of 'Si'–Se–Pd(II) is similar to that of PdCl₂. However the difference of Se (3d) binding energies between 'Si'–Se–Pd(II) and 'Si'–Se is 0.7 eV. The difference of Pd 3d_{5/2} binding energies between 'Si'–Se–Pd(II) and PdCl₂ is 0.9 eV. These results show that a coordination bond between Se and Pd is formed. The binding energy (336.4 eV) of Pd 3d_{5/2} of 'Si'–Se–Pd(0) is lower than the binding energy (337.4 eV) of Pd 3d_{5/2} of 'Si'–Se–Pd(II). The Pd 3d_{5/2} binding energy depends strongly on the nature of the ligands. Consequently, it is impossible to identify the reduced complex as a zerovalent one on the basis of its Pd 3d_{5/2} binding energy only. However, the binding energy of Cl (2p) in the 'Si'–Se–Pd(0) cannot be detected, the shift (lower) of Pd 3d_{5/2} binding energy, together with the black color, suggests that the reduction of the starting palladium(II) complex to the lower valent state has taken place. The ratio of Se/Pd of the 'Si'–Se–Pd(0) was determined to be 3.3, this result supports that one Pd atom is bound to 2–3 polymer molecules as shown in Scheme 1.

In order to evaluate the catalytic activity of the new polymer-supported palladium(0) catalyst ('Si'–Se–Pd(0)), the arylation reactions of butyl acrylate and acrylamide with aryl halides were studied (Scheme 2). The reactions were carried out under conditions similar to those used in the corresponding homogeneous reactions. The results are summarized in Table 2.

Cinnamates are important synthetic intermediates and usually prepared by utilizing a Wittig type approach [14]. The palladium catalyzed arylation reaction of acrylates with aryl halides or arenosulphonyl chlorides has provided a direct route to stereoselective synthesis of *trans*-cinnamates [15], but the homogeneous palladium catalysts cannot be recovered and reused. As shown in Table 2, the arylation reaction of butyl acrylate with aryl iodides proceeded smoothly at 100 °C using 'Si'–Se–Pd(0) as catalyst to afford the desired *trans*-butyl cinnamates in high yields. The *trans*-selectivity was always near quantitative and no *cis*-product was observed. We found that when 1 mol% Pd(OAc)₂/2PPh₃ was used as the catalyst in the arylation



Scheme 2.

Table 2
trans-Butyl cinnamates (**3a–g**) and *trans*-cinnamamides (**3h–n**) prepared^a

| Entry | ArX | Y | Temperature (°C) | Time (h) | Product | Yield ^b (%) |
|-------|---|----------------------|------------------|----------|-----------|------------------------|
| 1 | PhI | CO ₂ Bu-n | 100 | 6 | 3a | 90 |
| 2 | PhBr | CO ₂ Bu-n | 140 | 12 | 3a | 61 |
| 3 | 4-ClC ₆ H ₄ I | CO ₂ Bu-n | 100 | 6 | 3b | 92 |
| 4 | 4-ClC ₆ H ₄ Br | CO ₂ Bu-n | 140 | 12 | 3b | 70 |
| 5 | 4-CH ₃ OC ₆ H ₄ I | CO ₂ Bu-n | 100 | 6 | 3c | 90 |
| 6 | 4-CH ₃ C ₆ H ₄ I | CO ₂ Bu-n | 100 | 6 | 3d | 87 |
| 7 | 4-CH ₃ C ₆ H ₄ Br | CO ₂ Bu-n | 140 | 12 | 3d | 57 |
| 8 | 4-O ₂ NC ₆ H ₄ I | CO ₂ Bu-n | 100 | 6 | 3e | 89 |
| 9 | 4-O ₂ NC ₆ H ₄ Br | CO ₂ Bu-n | 140 | 12 | 3e | 78 |
| 10 | 3-O ₂ NC ₆ H ₄ I | CO ₂ Bu-n | 100 | 6 | 3f | 92 |
| 11 | 4-CH ₃ OCOC ₆ H ₄ Br | CO ₂ Bu-n | 140 | 12 | 3g | 76 |
| 12 | PhI | CONH ₂ | 100 | 6 | 3h | 89 |
| 13 | 4-ClC ₆ H ₄ I | CONH ₂ | 100 | 6 | 3i | 92 |
| 14 | 4-ClC ₆ H ₄ Br | CONH ₂ | 140 | 12 | 3i | 73 |
| 15 | 4-CH ₃ OC ₆ H ₄ I | CONH ₂ | 100 | 6 | 3j | 93 |
| 16 | 4-CH ₃ C ₆ H ₄ I | CONH ₂ | 100 | 6 | 3k | 88 |
| 17 | 4-O ₂ NC ₆ H ₄ I | CONH ₂ | 100 | 6 | 3l | 91 |
| 18 | 4-O ₂ NC ₆ H ₄ Br | CONH ₂ | 140 | 12 | 3l | 83 |
| 19 | 3-O ₂ NC ₆ H ₄ I | CONH ₂ | 100 | 6 | 3m | 93 |
| 20 | 4-CH ₃ OCOC ₆ H ₄ Br | CONH ₂ | 140 | 12 | 3n | 80 |
| 21 | 4-CH ₃ C ₆ H ₄ Br | CONH ₂ | 140 | 12 | 3k | 62 |

^a Reactions were carried out with 5 mmol of aryl halide, 5.5 mmol of butyl acrylate or acrylamide, 0.02 mmol of palladium catalyst, 6 mmol of Bu₃N in 1.0 ml of *p*-xylene or DMF. When aryl bromide was used as the arylating agent, 0.05 mmol of PPh₃ was added.

^b Yield of isolated product **3** based on the aryl halide.

reaction of butyl acrylate with iodobenzene, the *trans*-butyl cinnamate was obtained in 76% yield under same conditions. In the presence of catalytic amounts of 'Si'-Se-Pd(0) and PPh₃, the arylation reaction of butyl acrylate with aryl bromides could also proceed smoothly at 140 °C to give the desired *trans*-products in moderate to good yields. Terasawa et al. [5] tried for a reaction between bromobenzene and methyl acrylate using a polymer-bound tetrakis(triphenylphosphine)palladium analogue as catalyst, only traces of *trans*-methyl cinnamate were found in that study. The similar observation was also made by Choudary et al. [7] that in the reaction of bromobenzene with methyl acrylate using a montmorilloniteethylsilyldiphenylphosphine palladium(II) chloride complex as the catalyst, no arylation product was formed. In our study, we found that the substituent effects in the aryl iodides appeared to be less significant than in the aryl bromides and the reactivity of aryl bromides with electron-withdrawing substituents was higher than that of aryl bromides with electron-donating substituents. This polymeric catalyst can be easily recovered by simple filtration. When 'Si'-Se-Pd(0) was used in four consecutive runs for the arylation reaction of butyl acrylate with iodobenzene, *trans*-butyl cinnamate was formed in 90, 88, 87 and 85% yield, respectively.

Cinnamamides are important chemical substances and organic intermediates [9,16]. In the presence of 'Si'-Se-Pd(0) and tributylamine, a variety of substituted *trans*-cinnamamides were synthesized from acrylamide and aryl iodides in high yields and high stereoselectivity. When aryl bromides were used as the arylating agents in the present study, the arylation reaction of acrylamide in the presence of a catalytic amount of PPh₃ could also take place

at 140 °C and the desired *trans*-products were obtained in moderate to good yields on longer time. In all reactions only 0.4 mol% polymeric catalyst based on the aryl halides was used. As for the arylation reaction of butyl acrylate with iodobenzene, the molar turnover numbers of 225 are much larger than those of 76 in the corresponding homogeneous reaction using Pd(OAc)₂/2PPh₃ as catalyst. Even after the catalyst had been exposed to air for 7 days, its activity did not remarkably decrease, this stability should result from polymer effects.

4. Conclusions

We have described a new polymer-bound organoselenium palladium(0) complex whose preparation is rather simple and convenient. This complex has not only high activity and stereoselectivity for arylation of conjugated alkenes with aryl halides, but offers practical advantages such as easy handling, separation from the product and reuse. The arylation of butyl acrylate and acrylamide with aryl iodides or bromides catalyzed by 'Si'-Se-Pd(0) provides a better and practical procedure for the synthesis of *trans*-butyl cinnamates and *trans*-cinnamamides.

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