

Carbonyl allylation of aldehydes catalyzed by a silica-supported poly- γ -diphenylarsinopropylsiloxane palladium(0) complex

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Abstract

A silica-supported poly- γ -diphenylarsinopropylsiloxane palladium(0) complex has been prepared from γ -chloropropyltriethoxysilane via immobilization on fumed silica, followed by reacting with potassium diphenylarsenide and palladium chloride, and then the reduction with hydrazine hydrate. The palladium(0) complex has been found to catalyze the allylation of aldehydes via the formation of π -allylpalladium complexes, using allylic chlorides as allylating agent and SnCl₂ as reducing agent. This polymeric palladium complex can be recovered and reused.

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Keywords: Supported palladium catalyst; Arsine palladium(0) complex; Carbonyl allylation; π -Allylpalladium complex; Aldehyde

1. Introduction

Nucleophilic substitution of π -allylpalladium complexes has provided a new method for carbon–carbon bond formation and has been applied into the synthesis of wide range of natural products and other complex organic molecules [1–4]. If the π -allylpalladium complexes were used not only as electrophiles but also as nucleophiles, the chemistry of π -allylpalladium complexes could be further developed in organic synthesis. The utilization of π -allylpalladium complexes as nucleophiles has been exemplified by the transformation of allylic esters [5–7] or allylic alcohols [8] or allylic chlorides [9] to allylic metal compounds with palladium(0) catalyst and low-valent metals, which have been applied to carbonyl allylation. Some other carbonyl allylation reactions of aldehydes with different mechanisms could afford the same adduct [10]. Masuyama et al. [11,12] reported that stannous chloride is more effective as a reducing agent than other low-valent metals in palladium-catalyzed carbonyl allylation by allylic esters. However, in most cases, homogeneous palladium com-

plexes such as Pd(PPh₃)₄, Pd(PPh₃)₂Cl₂ and Pd(PhCN)₂Cl₂ are usually used for formation of π -allylpalladium complexes. The amount of palladium 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 transition metal complexes having high activity and selectivity are currently attracting great interest because they combine the advantages of homogeneous and heterogeneous catalyzed processes. Polymer-supported palladium catalysts have successfully been used for a variety of organic reactions [13–16]. However, polymer-supported palladium catalysts for carbonyl allylation has received less attention. Recently, we have found that the silica-supported poly- γ -cyanopropylsiloxane palladium complex (abbreviated as ‘Si’–CN–Pd) is an efficient catalyst for carbonyl allylation of aldehydes and ketones with allyl chloride and allyl acetate, but the activity of the catalyst decreased gradually with repeated use [17]. Study of new types of polymer-bound palladium catalysts which might be suitable for carbonyl allylation of aldehydes or ketones has theoretical and practical significance. However, little attention has so far been given to arsenic transition

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metal complexes [18,19]. To our knowledge, no allylation of aldehydes and ketones catalyzed by an arsenic palladium complex has been reported. In this paper we wish to report the synthesis of silica-supported poly- γ -diphenylarsinopropylsiloxane palladium(0) complex (abbreviated as 'Si'-As-Pd(0)) and its catalytic properties in the carbonyl allylation of aldehydes and ketones with allylic chlorides.

2. Results and discussion

It is well known that zero-valent palladium complexes show unique reactivity in various organic reactions. However, it is very difficult to use the homogeneous Pd(0) complexes as practical catalysts because of their instability to air and moisture. A silica-supported poly- γ -diphenylarsinopropylsiloxane palladium(0) complex was conveniently prepared from γ -chloropropyltriethoxysilane via immobilization on fumed silica, followed by reacting with potassium diphenylarsenide in THF and palladium chloride in acetone, and then the reduction with hydrazine hydrate in ethanol (Scheme 1).

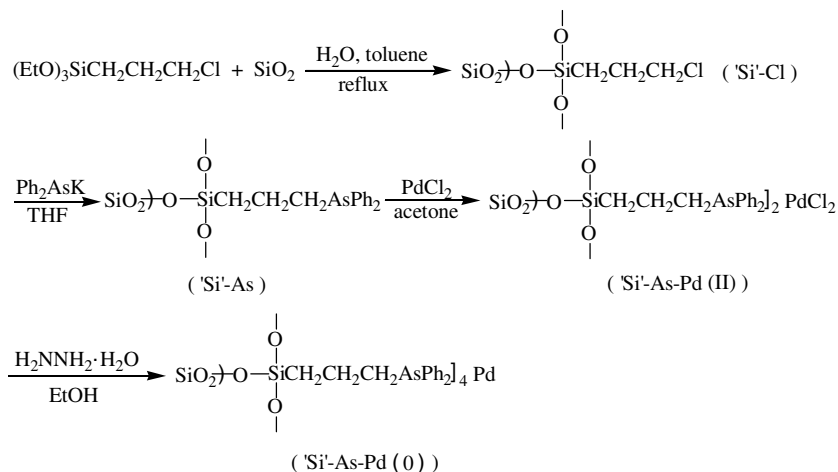
The X-ray photoelectron spectroscopy (XPS) has been used to characterize this polymeric palladium catalyst. Table 1 shows the XPS data for 'Si'-As-Pd(0), 'Si'-As-Pd(II), 'Si'-As and PdCl₂. It can be seen that the binding energies of Si(2p) and O(1s) of 'Si'-As-Pd(II) are similar to those of 'Si'-As, and the binding energy of Cl(2p) of 'Si'-As-Pd(II) is similar to that of PdCl₂. However the difference of As(3d) binding energies between 'Si'-As-Pd(II) and 'Si'-As is 0.9 eV. The difference of Pd_{3d_{5/2}} binding energies between 'Si'-As-Pd(II) and PdCl₂ is 1.6 eV. These results show that a coordination bond between As and Pd is formed. The binding energy (335.7 eV) of Pd_{3d_{5/2}} of 'Si'-As-Pd(0) is lower than the binding energy (336.7 eV) of Pd_{3d_{5/2}} of 'Si'-As-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 zero-valent one on the basis of its Pd_{3d_{5/2}} binding energy only. However, the binding energy of Cl(2p) in the 'Si'-As-Pd(0) cannot be detected, the shift (lower) of Pd_{3d_{5/2}} binding energy, together with the black color suggest that the reduction of the starting palladium(II) complex to the lower valent state has taken place. The 'Si'-As-Pd(0) has the formula (SiO₂)₂₄(SiCH₂CH₂CH₂As(C₆H₅)₂)₄Pd according to the elemental analyses, which suggests that the probable local structure of the 'Si'-As-Pd(0) is below (Scheme 2).

In order to test the catalytic activity of the new polymer-bound palladium(0) catalyst ('Si'-As-Pd(0)), the carbonyl allylation of aldehydes with allylic chlorides was studied (Scheme 3). The reactions were carried out under conditions similar to those used in the corresponding homogeneous reactions. The results are summarized in Table 2.

The allylation of benzaldehyde with allyl chloride was carried out at 25 °C in the presence of SnCl₂ using DMF as solvent. When 2.0 mol% palladium catalyst ('Si'-As-Pd(0)) was used, the allylation of benzaldehyde could be accomplished within 48 h and 1-phenylbut-3-en-1-ol was obtained in 85% yield. When 2.0 mol% PdCl₂(PhCN)₂ was used, 1-phenylbut-3-en-1-ol was obtained in 80% yield under same conditions. This polymeric palladium catalyst not only has higher catalytic activity in the allylation of benzaldehyde than PdCl₂(PhCN)₂, but also can be recovered by simple filtration. The activity of the recovered catalyst was tested for two recycles and it was found that the yield of 1-phenylbut-3-en-1-ol decreased by only 2% and 3% after each recycle, respectively.

The reaction is suitable for a variety of functional groups on the aromatic aldehydes; both strongly electron donating and withdrawing substituents can be present. The allylation of various aromatic aldehydes with allyl chloride has been achieved with good to high

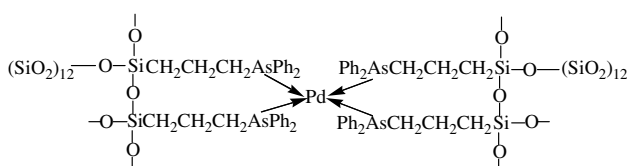


Scheme 1.

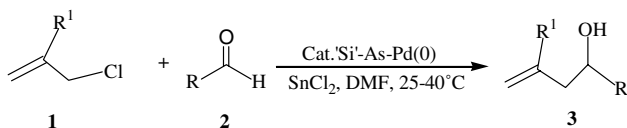
Table 1
XPS data for 'Si'-As-Pd(0), 'Si'-As-Pd(II), 'Si'-As and PdCl₂ (in eV)^a

Sample	Pd _{3d5/2}	As _{3d}	Si _{2p}	O _{1s}	Cl _{2p}
'Si'-As-Pd(0)	335.7	42.6	103.1	532.3	
'Si'-As-Pd(II)	336.7	42.5	103.1	532.4	199.1
'Si'-As		41.6	103.0	532.3	
PdCl ₂	338.3				199.2

^aThe binding energies are referenced to C_{1s} (284.6 eV), and the energy differences were determined with an accuracy of ±0.2 eV.



Scheme 2.



Scheme 3.

Table 2
Carbonyl allylation of aldehydes catalyzed by 'Si'-As-Pd(0)

Entry	R	R ¹	Temperature (°C)	Product	Yield (%) ^a
1	Ph	H	25	3a	85
2	Ph	CH ₃	40	3b	81
3	4-ClC ₆ H ₄	H	25	3c	87
4	4-ClC ₆ H ₄	CH ₃	40	3d	89
5	4-O ₂ NC ₆ H ₄	H	25	3e	57
6	4-O ₂ NC ₆ H ₄	CH ₃	40	3f	60
7	4-CH ₃ OC ₆ H ₄	H	25	3g	82
8	3,4-CH ₂ O ₂ C ₆ H ₃	H	25	3h	86
9	3,4-CH ₂ O ₂ C ₆ H ₃	CH ₃	40	3i	84
10	2-HOC ₆ H ₄	H	25	3j	85
11	2-HOC ₆ H ₄	CH ₃	40	3k	82
12	<i>n</i> -C ₃ H ₇	H	25	3l	81
13	<i>n</i> -C ₃ H ₇	CH ₃	40	3m	78
14	<i>n</i> -C ₆ H ₁₃	H	25	3n	80
15	<i>n</i> -C ₆ H ₁₃	CH ₃	40	3o	76

Reactions were carried out with 1 mmol of aldehyde, 2 mmol of allylic chloride, 1.5 mmol of SnCl₂, 0.02 mmol of palladium catalyst in 3 ml of DMF for 48 h.

^aYield of isolated product **3** based on the aldehyde.

yields. The allylation of aliphatic aldehydes with allylic chloride also proceeded smoothly in the presence of 'Si'-As-Pd(0) at 25 °C and the corresponding homoallylic alcohols were obtained in good yields. The allylation of aldehydes with methallyl chloride was very slow at 25 °C and only trace amounts of products was formed after 48 h. However, the allylation reactions proceeded very smoothly at 40 °C and the corresponding homoallylic alcohols were obtained in good to high yields after 48 h.

The allylation of ketones with allylic chlorides did not occur at all under same reaction conditions. Thus, chemoselective addition to an aldehyde can be realized in the presence of a ketone by using 'Si'-As-Pd(0) as catalyst.

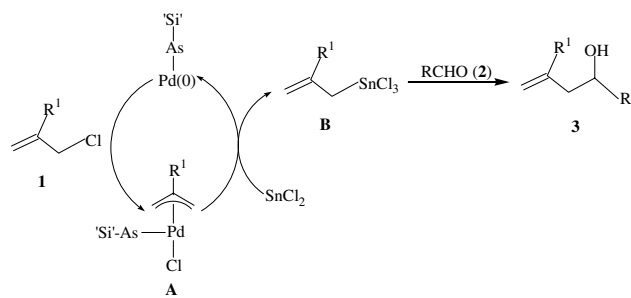
A plausible mechanism is shown in Scheme 4. Oxidative addition of allylic chlorides **1** to the 'Si'-As-Pd(0) gives the polymer-bound η₃-allyl(chloro)palladium complexes **A**, and the reduction of **A** with SnCl₂ produces the allylic trichlorotins **B** and regenerates the 'Si'-As-Pd(0). Nucleophilic addition of the allylic trichlorotins **B** to aldehydes **2** affords homoallylic alcohols **3**.

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 CDCl₃ as solvent. Microanalyses were obtained using a Perkin-Elmer 240 elemental analyzer. DMF was 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 carbon, hydrogen and chlorine content was 6.45, 13.10 and 2.08 mmol/g, respectively. The 'Si'-Cl has the formula (SiO₂)₂₄(SiCH₂CH₂CH₂Cl)₄ according to the elemental analyses.

A mixture of Ph₃As (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



Scheme 4. Proposed mechanism for the carbonyl allylation of aldehydes catalysed by 'Si'-As-Pd(0).

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 carbon, hydrogen and arsenic content was 23.86, 25.75 and 1.58 mmol/g, respectively. The 'Si'-As has the formula (SiO₂)₂₂(SiCH₂CH₂CH₂As(C₆H₅)₂)₄ according to the elemental analyses.

2.2. Preparation of silica-supported poly- γ -diphenylarsinopropylsiloxane palladium(0) complex ('Si'-As-Pd(0))

To a solution of PdCl₂ (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 brown solid was washed with distilled water (3 × 30 ml) and acetone (3 × 20 ml), then stirred with hydrazine hydrate (1.5 g) and EtOH (20 ml) at 30 °C under nitrogen for 2 h. The resulting product was filtered, washed with EtOH (4 × 30 ml) and Et₂O (2 × 30 ml) and dried under vacuum to give 1.96 g of the black polymeric palladium(0) complex ('Si'-As-Pd(0)). The carbon, hydrogen, arsenic and palladium content was 21.42 mmol/g, 23.24 mmol/g, 1.40 mmol/g and 0.39 mmol/g, respectively. The 'Si'-As-Pd(0) has the formula (SiO₂)₂₄(SiCH₂CH₂CH₂As(C₆H₅)₂)₄Pd according to the elemental analyses.

2.3. General procedure for the allylation of aldehydes with allylic chlorides

To a mixture of SnCl₂ (1.5 mmol), aldehyde (1 mmol), and allylic chloride (2 mmol) in DMF (3 ml) was added 'Si'-As-Pd(0) (50 mg, 0.02 mmol Pd) at the temperature indicated in Table 2 under a nitrogen atmosphere. After being stirred for 48 h, the mixture was filtered and the catalyst was washed with DMF (2 × 10 ml), diethyl ether (2 × 10 ml) and reused in the next run. The filtrate was diluted with 120 ml of a mixed solvent (diethyl ether:dichloromethane = 2:1) and washed successively with aqueous 10% HCl solution (2 × 10 ml), aqueous NaHCO₃ solution (10 ml), and water (3 × 10 ml). The extracts were dried over anhydrous MgSO₄. After removal of the solvent under reduced pressure, the residue was purified by preparative TLC on silica gel (light petroleum:ethyl acetate = 7:1) to afford a colorless oil.

2.3.1. 1-Phenylbut-3-en-1-ol (3a)

IR (film): ν (cm⁻¹) 3390, 3075, 3030, 2907, 1641, 1603, 1493, 1020, 750, 690. ¹H NMR: δ 7.36–6.95 (m,

5H), 5.88–5.50 (m, 1H), 5.14–4.89 (m, 2H), 4.66 (t, $J = 6.8$ Hz, 1H), 2.51–2.26 (m, 2H), 2.17 (br, 1H). Anal. Found: C, 80.89; H, 7.90. C₁₀H₁₂O Calc. C, 81.08; H, 8.11%.

2.3.2. 1-Phenyl-3-methylbut-3-en-1-ol (3b)

IR (film): ν (cm⁻¹) 3399, 3073, 3030, 2936, 1647, 1603, 1493, 1453, 1375, 1054, 891, 756, 699. ¹H NMR: δ 7.40–7.24 (m, 5H), 4.94–4.86 (m, 2H), 4.82 (t, $J = 6.8$ Hz, 1H), 2.43 (d, $J = 6.8$ Hz, 2H), 2.15 (br, 1H), 1.81 (s, 3H). Anal. Found: C, 81.22; H, 8.48. C₁₁H₁₄O Calc. C, 81.48; H, 8.64%.

2.3.3. 1-(4-Chlorophenyl)but-3-en-1-ol (3c)

IR (film): ν (cm⁻¹) 3387, 3078, 3028, 2907, 1641, 1597, 1492, 1411, 1051, 919, 830. ¹H NMR: δ 7.28 (s, 4H), 5.90–5.56 (m, 1H), 5.17–4.95 (m, 2H), 4.71 (t, $J = 6.8$ Hz, 1H), 2.53–2.28 (m, 2H), 2.16 (br, 1H). Anal. Found: C, 65.51; H, 5.83. C₁₀H₁₁OCl Calc. C, 65.75; H, 6.03%.

2.3.4. 1-(4-Chlorophenyl)-3-methylbut-3-en-1-ol (3d)

IR (film): ν (cm⁻¹) 3400, 3076, 3028, 2971, 2936, 1647, 1598, 1491, 1444, 1376, 1064, 1014, 894, 830. ¹H NMR: δ 7.28 (s, 4H), 4.94–4.85 (m, 2H), 4.79 (t, $J = 6.8$ Hz, 1H), 2.38 (d, $J = 7.2$ Hz, 2H), 2.16 (br, 1H), 1.80 (s, 3H). Anal. Found: C, 67.25; H, 6.56. C₁₁H₁₃OCl Calc. C, 67.18; H, 6.62%.

2.3.5. 1-(4-Nitrophenyl)but-3-en-1-ol (3e)

IR (film): ν (cm⁻¹) 3398, 3074, 3025, 2958, 1650, 1602, 1525, 1493, 1346, 845. ¹H NMR: δ 8.21 (d, $J = 8.8$ Hz, 2H), 7.53 (d, $J = 8.8$ Hz, 2H), 5.82–5.74 (m, 1H), 5.22–5.16 (m, 2H), 4.87 (t, $J = 5.6$ Hz, 1H), 2.59–2.44 (m, 2H), 2.23 (br, 1H). Anal. Found: C, 61.89; H, 5.52; N, 7.08. C₁₀H₁₁NO₃ Calc. C, 62.18; H, 5.70; N, 7.25%.

2.3.6. 1-(4-Nitrophenyl)-3-methylbut-3-en-1-ol (3f)

IR (film): ν (cm⁻¹) 3400, 3075, 3027, 2972, 1648, 1601, 1524, 1492, 1345, 846. ¹H NMR: δ 8.22 (d, $J = 8.5$ Hz, 2H), 7.57 (d, $J = 8.5$ Hz, 2H), 5.00–4.88 (m, 3H), 2.44–2.31 (m, 3H), 1.83 (s, 3H). Anal. Found: C, 63.51; H, 6.02; N, 6.53. C₁₁H₁₃NO₃ Calc. C, 63.77; H, 6.28; N, 6.76%.

2.3.7. 1-(4-Methoxyphenyl)but-3-en-1-ol (3g)

IR (film): ν (cm⁻¹) 3386, 3072, 3019, 2930, 2850, 1640, 1600, 1500, 1450, 1380, 1240, 1175, 1030, 830. ¹H NMR: δ 7.15 (d, $J = 8.8$ Hz, 2H), 6.79 (d, $J = 8.8$ Hz, 2H), 5.89–5.49 (m, 1H), 5.13–4.82 (m, 2H), 4.69 (t, $J = 6.8$ Hz, 1H), 3.78 (s, 3H), 2.50–2.24 (m, 2H), 2.09 (br, 1H). Anal. Found: C, 74.27; H, 7.78. C₁₁H₁₄O₂ Calc. C, 74.16; H, 7.87%.

2.3.8. 1-(3,4-Methylenedioxyphenyl)but-3-en-1-ol (3h)

IR (film): ν (cm⁻¹) 3360, 3070, 3024, 2880, 1640, 1600, 1490, 1440, 1240, 1030, 990, 870. ¹H NMR: δ 6.88 (d,

$J = 1.6$ Hz, 1H), 6.81–6.74 (m, 2H), 5.95 (s, 2H), 5.86–5.71 (m, 1H), 5.18–5.12 (m, 2H), 4.65 (t, $J = 6.8$ Hz, 1H), 2.50–2.46 (m, 2H), 1.99 (br, 1H). Anal. Found: C, 68.51; H, 6.30. $C_{11}H_{12}O_3$ Calc. C, 68.75; H, 6.25%.

2.3.9. *1-(3,4-Methylenedioxyphenyl)-3-methylbut-3-en-1-ol (3i)*

IR (film): ν (cm^{-1}) 3365, 3060, 2881, 1630, 1601, 1489, 1440, 1375, 1243, 1040, 990, 870. 1H NMR: δ 6.89 (d, $J = 1.6$ Hz, 1H), 6.84–6.75 (m, 2H), 5.95 (s, 2H), 4.93–4.84 (m, 2H), 4.82 (t, $J = 6.8$ Hz, 1H), 2.45–2.37 (m, 2H), 2.07 (br, 1H), 1.79 (s, 3H). Anal. Found: C, 69.71; H, 6.62. $C_{12}H_{14}O_3$ Calc. C, 69.90; H, 6.80%.

2.3.10. *1-(2-Hydroxyphenyl)but-3-en-1-ol (3j)*

IR (film): ν (cm^{-1}) 3400, 3060, 3028, 1635, 1598, 1490, 1440, 1200, 1030, 695. 1H NMR: δ 8.00 (s, 1H), 7.21–6.82 (m, 4H), 5.92–5.79 (m, 1H), 5.25–5.20 (m, 2H), 4.88 (m, 1H), 2.76 (br, 1H), 2.65–2.49 (m, 2H). Anal. Found: C, 73.25; H, 7.18. $C_{10}H_{12}O_2$ Calc. C, 73.17; H, 7.32%.

2.3.11. *1-(2-Hydroxyphenyl)-3-methylbut-3-en-1-ol (3k)*

IR (film): ν (cm^{-1}) 3396, 3070, 3026, 1638, 1601, 1495, 1443, 1200, 1030, 696. 1H NMR: δ 8.09 (s, 1H), 7.20–6.81 (m, 4H), 5.05–4.91 (m, 3H), 2.74 (br, 1H), 2.66–2.43 (m, 2H), 1.84 (s, 3H). Anal. Found: C, 73.89; H, 7.74. $C_{11}H_{14}O_2$ Calc. C, 74.16; H, 7.87%.

2.3.12. *1-Propylbut-3-en-1-ol (3l)*

IR (film): ν (cm^{-1}) 3350, 2930, 2854, 1641, 1450, 1375, 1056, 1028. 1H NMR: δ 5.89–5.78 (m, 1H), 5.18–5.03 (m, 2H), 3.80–3.52 (m, 1H), 2.36–2.10 (m, 2H), 1.63–1.20 (m, 5H), 0.89 (t, $J = 6.8$ Hz, 3H). Anal. Found: C, 73.49; H, 12.07. $C_7H_{14}O$ Calc. C, 73.68; H, 12.28%.

2.3.13. *1-Propyl-3-methylbut-3-en-1-ol (3m)*

IR (film): ν (cm^{-1}) 3355, 2928, 2857, 1630, 1446, 1375, 1054, 1028. 1H NMR: δ 4.89–4.80 (m, 2H), 3.78–3.69 (m, 1H), 2.25–2.06 (m, 2H), 1.78 (s, 3H), 1.62–1.35 (m, 5H), 0.90 (t, $J = 6.8$ Hz, 3H). Anal. Found: C, 74.84; H, 12.37. $C_8H_{16}O$ Calc. C, 75.00; H, 12.50%.

2.3.14. *1-Hexylbut-3-en-1-ol (3n)*

IR (film): ν (cm^{-1}) 3360, 2932, 2858, 1640, 1446, 1375, 1052, 1030. 1H NMR: δ 5.87–5.79 (m, 1H), 5.19–5.02 (m, 2H), 3.68–3.51 (m, 1H), 2.39–2.06 (m, 2H), 1.62–1.19 (m, 11H), 0.90 (t, $J = 6.8$ Hz, 3H). Anal. Found: C, 76.81; H, 12.63. $C_{10}H_{20}O$ Calc. C, 76.92; H, 12.82%.

2.3.15. *1-Hexyl-3-methylbut-3-en-1-ol (3o)*

IR (film): ν (cm^{-1}) 3358, 2930, 2857, 1641, 1442, 1375, 1054, 1025. 1H NMR: δ 4.88 (s, 1H), 4.80 (s, 1H), 3.76–3.66 (m, 1H), 2.26–2.05 (m, 2H), 1.76 (s, 3H), 1.71 (s, 1H), 1.53–1.23 (m, 10H), 0.89 (t, $J = 6.8$ Hz, 3H). Anal. Found: C, 77.48; H, 12.72. $C_{11}H_{22}O$ Calc. C, 77.65; H, 12.94%.

3. Conclusions

We have described a new polymer-bound arsine palladium(0) complex whose preparation is simple and convenient. This complex has not only high activity and chemoselectivity for allylation of aldehydes with allylic chlorides, but also offers practical advantages such as easy handling, separation from the products and reuse.

Acknowledgements

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References

- [1] R.F. Heck, Palladium Reagents in Organic Synthesis, Academic Press, London, 1985, p. 117.
- [2] B.M. Trost, L. Weber, P.E. Strege, T.J. Fullerton, T.J. Dietsche, J. Am. Chem. Soc. 100 (1978) 3407.
- [3] G.P. Chiusoli, Pure Appl. Chem. 52 (1980) 635.
- [4] J. Tsuji, in: F.R. Hartley, S. Patai (Eds.), The Chemistry of the Metal–Carbon Bond, vol. 3, Wiley, New York, 1985, p. 163.
- [5] B.M. Trost, J.W. Herndon, J. Am. Chem. Soc. 106 (1984) 6835.
- [6] Y. Masuyama, N. Kinugawa, Y. Kurusu, J. Org. Chem. 52 (1987) 3702.
- [7] P. Zhang, W. Zhang, T. Zhang, Z. Wang, W. Zhou, J. Chem. Soc., Chem. Commun. (1991) 491.
- [8] (a) J.P. Takahara, Y. Masuyama, Y. Kurusu, J. Am. Chem. Soc. 114 (1992) 2577; (b) Y. Masuyama, J.P. Takahara, Y. Kurusu, J. Am. Chem. Soc. 110 (1988) 4473; (c) L. Carde, A. Llebaria, A. Delgado, Tetrahedron Lett. 42 (2001) 3299; (d) T.S. Jang, G. Keum, S.B. Kang, B.Y. Chung, Y. Kim, Synthesis (2003) 775.
- [9] (a) T. Okano, J. Kiji, T. Doi, Chem. Lett. (1998) 5; (b) T. Hirashita, T. Kamei, M. Satake, T. Horie, H. Shimizu, S. Araki, Org. Biomol. Chem. 1 (2003) 3799; (c) S. Thoonen, B.J. Deelman, G. Koten, Tetrahedron 59 (2003) 10261.
- [10] (a) H. Nakamura, N. Asao, Y. Yamamoto, J. Chem. Soc., Chem. Commun. (1995) 1273; (b) H. Nakamura, M. Bao, Y. Yamamoto, Angew. Chem. Int. Ed. Engl. 40 (2001) 3208; (c) O.A. Wallner, K.J. Szabo, J. Org. Chem. 68 (2003) 2934.
- [11] Y. Masuyama, R. Hayashi, K. Otake, Y. Kurusu, J. Chem. Soc., Chem. Commun. (1988) 44.
- [12] Y. Masuyama, K. Otake, Y. Kurusu, Tetrahedron Lett. 29 (1988) 3563.
- [13] M. Terasawa, K. Kaneda, T. Imanaka, S. Teranishi, J. Organomet. Chem. 162 (1978) 403.
- [14] B.M. Trost, R.W. Warner, J. Am. Chem. Soc. 105 (1983) 5940.
- [15] S.I. Khan, M.W. Grinstaff, J. Org. Chem. 64 (1999) 1077.
- [16] S.K. Kang, T.G. Baik, S.Y. Song, Synlett (1999) 327.
- [17] M.Z. Cai, C.S. Song, X. Huang, Synth. Commun. 27 (1997) 3087.
- [18] J. Tsuji, M. Hara, K. Ohno, Ger. Offen. 1, 942, 798; C.A., 73, 15497y (1970).
- [19] Y.Y. Chen, X.R. Lu, Z.Y. Wang, Chin. J. Catal. 11 (1990) 75.