

Silica-supported bidentate arsine palladium(0) complex: a highly active and stereoselective catalyst for arylation of conjugated alkenes

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Abstract

A silica-supported bidentate arsine palladium(0) complex has been prepared from 4-oxa-6,7-dichloroheptyltriethoxysilane via immobilization on fumed silica, followed by reacting with potassium diphenylarsenide and palladium chloride, and then the reduction with hydrazine hydrate. The complex has been characterized by X-ray photoelectron spectroscopy and it is a highly active and stereoselective catalyst for arylation of styrene and acrylic acid with aryl halides affording a variety of *trans*-stilbenes and substituted *trans*-cinnamic acids in high yields.

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1. Introduction

The palladium-catalyzed arylation of alkenes is an important discovery in organopalladium chemistry made by Heck et al. and has found wide application in organic synthesis [1,2]. In this reaction, homogeneous palladium complexes such as Pd(OAc)₂ are usually used as the catalysts and the amount of catalyst used is about 1 mol% of reactant. Although homogeneous palladium catalysts have proven to be efficient, their activity and stereoselectivity are moderate and use of homogeneous palladium catalysts is still uneconomic for large scale preparation. As Heck [3,4] has noted, practical application of the reaction under such conditions is not feasible due to its expensive cost. Easy recovery and reuse of the catalytic species make the reaction very attractive commercially.

Polymer-supported organotransition metal complexes catalysts offer several significant advantages in synthetic and industrial chemistry and are currently attracting great interest. Terasawa et al. [5] have studied Heck arylation of styrene with iodobenzene using polystyrene-

supported palladium(0) catalyst and obtained 78% stereoselectivity. Andersson et al. [6] have compared polystyrene-supported phosphine palladium complex with analogous homogeneous palladium complex, palladium salts, Pd/C in terms of catalyst activity and selectivity and found that polymer-supported phosphine palladium complex with P/Pd ratio of 1 is highly active, but noticeable deactivation of catalyst during repeated use was the main disadvantage. Zhang et al. [7] described a polymer-supported phenanthroline palladium(0)-catalyzed arylation of acrylamide, however when tributylamine was used as the base, the activity of the catalyst was remarkably lowered on recycling and moreover the preparation of the catalyst is rather complicated. Choudary et al. [8] also reported a clay anchored phosphine palladium complex catalyzed arylation of acrylates and cross coupling of phenylvinyl acetate with aryl iodides, but no procedure to recover the catalyst was detailed. Recently, we have found that the silica-supported sulfur palladium(0) complex is an efficient catalyst for Heck arylation of styrene and acrylic acid with aryl iodides [9]. However, none of the reported polymeric palladium catalysts [5–9] shows activity for the arylation of conjugated alkenes with aryl bromides. Study of new types of polymer-bound palladium catalysts which might be suitable for Heck

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arylation of conjugated alkenes has theoretical and practical significance. To our knowledge, little attention has so far been given to organoarsenium transition metal complexes [10,11] and no Heck arylation of conjugated alkenes with aryl halides catalyzed by a organoarsenium palladium complex has been reported. In this paper, we wish to report the synthesis of silica-supported bidentate arsine palladium(0) complex (abbreviation: 'Si'-2As-Pd(0)) and its catalytic properties in the arylation of conjugated alkenes with aryl halides.

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 Pd(0) complexes as practical catalysts because of their instability to air and moisture. A silica-supported bidentate arsine palladium(0) complex, the first polymeric organoarsenium palladium(0) complex, was conveniently prepared from 4-oxa-6,7-dichloroheptyltriethoxysilane 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 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. The X-ray photoelectron spectroscopy (XPS) has been used to characterize this polymeric palladium catalyst. Table 1 shows the XPS data for 'Si'-2As-Pd(0), 'Si'-2As-Pd(II), 'Si'-2As and PdCl₂. It can be seen that the

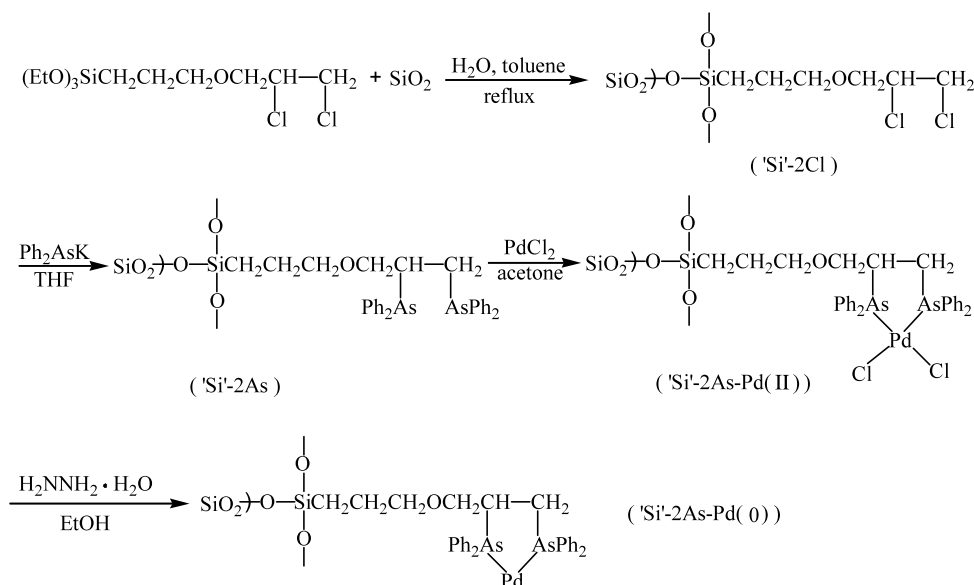
Table 1
XPS data for 'Si'-2As-Pd(0), 'Si'-2As-Pd(II), 'Si'-2As and PdCl₂ (in eV)

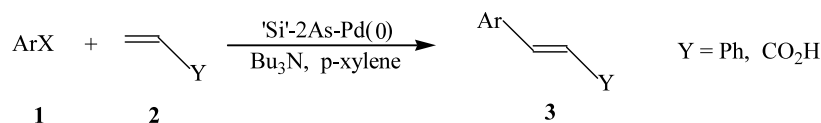
Sample	Pd _{3d5/2}	As _{3d}	Si _{2p}	O _{1s}	Cl _{2p}
'Si'-2As-Pd(0)	335.7	42.7	103.1	532.4	
'Si'-2As-Pd(II)	336.8	42.6	103.2	532.4	199.0
'Si'-2As		41.7	103.1	532.3	
PdCl ₂	338.3				199.2

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

binding energies of Si_{2p} and O_{1s} of 'Si'-2As-Pd(II) are similar to those of 'Si'-2As, and the binding energy of Cl_{2p} of 'Si'-2As-Pd(II) is similar to that of PdCl₂. However the difference of As_{3d} binding energies between 'Si'-2As-Pd(II) and 'Si'-2As is 0.9 eV. The difference of Pd_{3d5/2} binding energies between 'Si'-2As-Pd(II) and PdCl₂ is 1.5 eV. These results show that a coordination bond between As and Pd is formed. The binding energy (335.7 eV) of Pd_{3d5/2} of 'Si'-2As-Pd(0) is lower than the binding energy (336.8 eV) of Pd_{3d5/2} of 'Si'-2As-Pd(II). The Pd_{3d5/2} 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_{3d5/2} binding energy only. However, the binding energy of Cl_{2p} in the 'Si'-2As-Pd(0) can not be detected, the shift (lower) of Pd_{3d5/2} 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.

In order to test the catalytic activity of the novel polymer-supported palladium(0) catalyst ('Si'-2As-Pd(0)), the arylation reactions of styrene and acrylic acid with aryl halides were studied (Scheme 2). The





Scheme 2.

reactions were carried out under conditions similar to those used in the corresponding homogeneous reactions. The results are summarized in Table 2.

Synthesis of *trans*-stilbenes assumes importance because of their large molecular hyperpolarizable property suited for the construction of non-linear optics [12] and their uses as organic intermediates [13]. Synthesis of *trans*-stilbenes usually involves a tedious multistep synthetic procedure and the yields are poor to moderate. An arylation of alkenes attempted by Heck using palladium salts as catalyst afforded moderate yields on longer reaction time [4]. Andersson et al. [6] indicated that polymeric palladium catalysts tend to be more efficient in the Heck reaction. As seen from Table 2, the arylation reaction of styrene with aryl iodides proceeded smoothly at 100 °C using 'Si'-2As-Pd(0) as catalyst to give the desired *trans*-stilbenes in high yields. The *trans*-selectivity was always near quantitative and no *cis*-product was observed. In the presence of a catalytic amounts of 'Si'-2As-Pd(0) and triphenylphosphine, the arylation reaction of styrene with aryl bromides could also proceed smoothly at 140 °C to afford the desired *trans*-products in moderate to good yields. When palladium acetate was used as the catalyst in the

presence of PPh₃ in the arylation of styrene with bromobenzene, only 1.5% *trans*-stilbene was found [14]. Terasawa et al. [5] tried to react bromobenzene with styrene using a polymer-bound tetrakis(triphenylphosphine)palladium analogue as catalyst, only traces of *trans*-stilbene was found in that study. In present study, 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. Probably because the oxidative addition reaction of aryl bromides with this polymeric palladium(0) complex is slow, the electron-withdrawing substituents on benzene ring can facilitate the oxidative addition of C–Br bond with 'Si'-2As-Pd(0). This polymeric catalyst can be easily recovered by simple filtration. When 'Si'-2As-Pd(0) was used in four consecutive runs for the arylation reaction of styrene with iodobenzene, *trans*-stilbene was formed in 91, 90, 88 and 89% yield, respectively. This result suggests that the bidentate arsine ligand can efficiently prevent palladium leaching from the polymer support.

β-Arylacrylic acids are important chemical substances and organic intermediates and usually prepared by

Table 2
trans-Stilbenes **3a–g** and cinnamic acids **3h–n** prepared

Entry	ArX	Y	Temperature (°C)	Time (h)	Product	Yield ^a (%)
1	PhI	Ph	100	6	3a	91
2	PhBr	Ph	140	12	3a	52
3	4-ClC ₆ H ₄ I	Ph	100	6	3b	92
4	4-ClC ₆ H ₄ Br	Ph	140	12	3b	64
5	4-CH ₃ OC ₆ H ₄ I	Ph	100	6	3c	92
6	4-CH ₃ C ₆ H ₄ I	Ph	100	6	3d	88
7	4-CH ₃ C ₆ H ₄ Br	Ph	140	12	3d	43
8	4-O ₂ NC ₆ H ₄ I	Ph	100	6	3e	87
9	4-O ₂ NC ₆ H ₄ Br	Ph	140	12	3e	74
10	3-O ₂ NC ₆ H ₄ I	Ph	100	6	3f	90
11	4-CH ₃ OCOC ₆ H ₄ Br	Ph	140	12	3g	67
12	PhI	CO ₂ H	100	6	3h	92
13	4-ClC ₆ H ₄ I	CO ₂ H	100	6	3i	95
14	4-ClC ₆ H ₄ Br	CO ₂ H	140	12	3i	55
15	4-CH ₃ OC ₆ H ₄ I	CO ₂ H	100	6	3j	91
16	4-CH ₃ C ₆ H ₄ I	CO ₂ H	100	6	3k	90
17	4-O ₂ NC ₆ H ₄ I	CO ₂ H	100	6	3l	93
18	4-O ₂ NC ₆ H ₄ Br	CO ₂ H	140	12	3l	78
19	3-O ₂ NC ₆ H ₄ I	CO ₂ H	100	6	3m	87
20	4-CH ₃ OCOC ₆ H ₄ Br	CO ₂ H	140	12	3n	86

Reactions were carried out with 5 mmol of aryl halide, 5.5 mmol of styrene or acrylic acid, 0.03 mmol of palladium catalyst, 6 mmol of Bu₃N in 0.5 ml of *p*-xylene. When aryl bromide was used as the arylating agent, 0.05 mmol of PPh₃ was added.

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

Perkin reaction, however, the yields and stereoselectivity are poor to moderate [15]. In the presence of 'Si'-2As-Pd(0) and tributylamine, a variety of substituted *trans*-cinnamic acids were prepared from acrylic acid and aryl iodides in high yields and high stereoselectivity. When aryl bromides with electron-withdrawing substituents were used as the arylating agents in the present study, the arylation reaction of acrylic acid in the presence of PPh₃ also proceeded smoothly at 140 °C and the desired *trans*-products were obtained in moderate to good yields on longer time. In all reactions only 0.6 mol% catalyst based on the aryl halides was used. As for the arylation reaction of styrene with iodobenzene, the mole turnover numbers of 152 are much larger than those of 75 in the corresponding homogeneous reaction reported by Heck et al. [16]. 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.

3. Experimental

Melting points were taken with a Yanaco micro melting point apparatus and are 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 CDCl₃ or DMSO-*d*₆ as solvent. Microanalyses were obtained using a Perkin-Elmer 240 elemental analyzer.

4-Oxa-6,7-dichloroheptyltriethoxysilane was prepared by a literature method [17]. *p*-Xylene, Bu₃N and styrene were distilled before use, other reagents were used as received without further purification.

3.1. 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 °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 10.8 g of silica-supported poly-4-oxa-6,7-dichloroheptylsiloxane ('Si'-2Cl). The chlorine content was 1.97 mmol g⁻¹.

A mixture of AsPh₃ (3.62 g, 11.83 mmol) and potassium (0.93 g, 23.66 mmol) in THF (60 ml) was stirred under nitrogen at 60 °C for 16 h. After being cooled to room temperature, the mixture was treated with *t*-BuCl (1.10 g, 11.83 mmol) for 1 h to give a brown solution. The resulting 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*-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 4.97 g of silica-supported bidentate arsine ligand ('Si'-2As). The arsenium content was 1.52 mmol g⁻¹.

3.2. Preparation of silica-supported bidentate arsine palladium(0) complex ('Si'-2As-Pd(0))

To a solution of PdCl₂ (0.156 g) in acetone (40 ml) was added 'Si'-2As (2.01 g). The mixture was refluxed under nitrogen for 48 h. The brown solid product was filtered, 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 1.94 g of the black polymeric palladium(0) complex ('Si'-2As-Pd(0)). The arsenium content was 1.39 mmol g⁻¹ and the palladium content was 0.42 mmol g⁻¹.

3.3. Typical procedure for arylation of styrene with aryl halides

A mixture of styrene (0.57 g, 5.5 mmol), iodobenzene (1.02 g, 5 mmol), Bu₃N (1.11 g, 6 mmol), *p*-xylene (0.5 ml) and the 'Si'-2As-Pd(0) complex (75 mg, 0.03 mmol of Pd) was stirred under N₂ in an oil bath at 100 °C for 6 h. The mixture was cooled and dissolved in Et₂O (50 ml). The 'Si'-2As-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 × 10 ml), brine (4 × 10 ml) and dried (MgSO₄) and filtered. The solid product formed after concentration of the ethereal solution was recrystallized (EtOH) to give (*E*)-1,2-diphenylethene (**3a**) (0.818 g, 91%).

3.3.1. (*E*)-1,2-Diphenylethene (**3a**)

M.p. 123–124 °C, Ref. [18]. M.p. 124 °C. IR (KBr): ν (cm⁻¹) 3021, 1598, 1500, 760, 690. ¹H-NMR: δ 7.70–7.11 (m, 10H), 7.09 (s, 2H).

3.3.2. (*E*)-1-(4-Chlorophenyl)-2-phenylethene (**3b**)

M.p. 128–129 °C, Ref. [19]. M.p. 129 °C. IR (KBr): ν (cm⁻¹) 3058, 1592, 1496, 940, 815, 700. ¹H-NMR: δ 7.47–7.26 (m, 9H), 7.09 (s, 2H).

3.3.3. (*E*)-1-(4-Methoxyphenyl)-2-phenylethene (**3c**)

M.p. 135–136 °C, Ref. [20]. M.p. 136 °C. IR (KBr): ν (cm⁻¹) 3052, 1600, 1498, 1250, 1171, 820, 754. ¹H-

NMR: δ 7.58–7.20 (m, 7H), 7.02 (s, 2H), 6.87 (d, $J = 9.0$ Hz, 2H), 3.83 (s, 3H).

3.3.4. (*E*)-1-(4-Methylphenyl)-2-phenylethene (**3d**)

M.p. 119–120 °C, Ref. [21]. M.p. 120 °C. IR (KBr): ν (cm^{-1}) 3028, 1597, 1492, 941, 825, 715. $^1\text{H-NMR}$: δ 7.65–7.03 (m, 9H), 7.02 (s, 2H), 2.32 (s, 3H).

3.3.5. (*E*)-1-(4-Nitrophenyl)-2-phenylethene (**3e**)

M.p. 156–157 °C, Ref. [21]. M.p. 157 °C. IR (KBr): ν (cm^{-1}) 3046, 1591, 1526, 1500, 1340, 840, 760, 690. $^1\text{H-NMR}$: δ 8.44–8.12 (m, 2H), 7.80–7.20 (m, 7H), 7.18 (s, 2H).

3.3.6. (*E*)-1-(3-Nitrophenyl)-2-phenylethene (**3f**)

M.p. 105–106 °C. IR (KBr): ν (cm^{-1}) 3081, 3026, 1571, 1520, 1495, 1350, 968, 808, 756, 695. $^1\text{H-NMR}$: δ 8.38 (s, 1H), 8.10 (d, $J = 8.2$ Hz, 1H), 7.80 (d, $J = 8.0$ Hz, 1H), 7.56–7.26 (m, 6H), 7.22 (s, 1H), 7.16 (s, 1H). Anal. Found: C, 74.41; H, 4.73; N, 6.01. $\text{C}_{14}\text{H}_{11}\text{NO}_2$ Calc.: C, 74.67; H, 4.89; N, 6.22%.

3.3.7. (*E*)-1-(4-Methoxycarbonylphenyl)-2-phenylethene (**3g**)

M.p. 157–158 °C, Ref. [22]. M.p. 159–160 °C. IR (KBr): ν (cm^{-1}) 3025, 1715, 1600, 1180, 835, 770, 699. $^1\text{H-NMR}$: δ 8.03 (d, $J = 9.0$ Hz, 2H), 7.63–7.20 (m, 7H), 7.15 (s, 2H), 3.94 (s, 3H).

3.4. Typical procedure for arylation of acrylic acid with aryl halides

A mixture of acrylic acid (0.40 g, 5.5 mmol), iodobenzene (1.02 g, 5 mmol), Bu_3N (2.04 g, 11 mmol), *p*-xylene (0.5 ml) and the 'Si'-2As-Pd(0) complex (75 mg, 0.03 mmol of Pd) was stirred under N_2 in an oil bath at 100 °C for 6 h. After the reaction mixture was cooled, H_2O (20 ml) and NaHCO_3 (1.10 g) were added. After stirring for 10 min, the 'Si'-2As-Pd(0) complex was separated from the mixture by filtration. The aqueous phase was separated and acidified with 5 N HCl (1.8 ml). After cooling to 0 °C, the solid precipitate was filtered, washed with H_2O (5×20 ml) and air dried to give (*E*)-3-phenylacrylic acid (**3h**) (0.682 g, 92%).

3.4.1. (*E*)-3-Phenylacrylic acid (**3h**)

M.p. 130–131 °C, Ref. [23]. M.p. 132–133 °C. IR (KBr): ν (cm^{-1}) 2915, 1690, 1625, 1498, 1419, 760, 700. $^1\text{H-NMR}$: δ 7.83 (d, $J = 16.0$ Hz, 1H), 7.69–7.21 (m, 5H), 6.45 (d, $J = 16.0$ Hz, 1H).

3.4.2. (*E*)-3-(4-Chlorophenyl)acrylic acid (**3i**)

M.p. 248–249 °C, Ref. [24]. M.p. 249–250 °C. IR (KBr): ν (cm^{-1}) 2930, 1688, 1636, 1590, 1496, 954, 825.

$^1\text{H-NMR}$: δ 7.86–7.40 (m, 5H), 6.57 (d, $J = 16.0$ Hz, 1H).

3.4.3. (*E*)-3-(4-Methoxyphenyl)acrylic acid (**3j**)

M.p. 172–173 °C, Ref. [25]. M.p. 174 °C. IR (KBr): ν (cm^{-1}) 2920, 1681, 1632, 1600, 1499, 1250, 1170, 830. $^1\text{H-NMR}$: δ 7.66 (d, $J = 16.0$ Hz, 1H), 7.50 (d, $J = 9.0$ Hz, 2H), 6.90 (d, $J = 9.0$ Hz, 2H), 6.32 (d, $J = 16.0$ Hz, 1H), 3.86 (s, 3H).

3.4.4. (*E*)-3-(4-Methylphenyl)acrylic acid (**3k**)

M.p. 200–201 °C, Ref. [24]. M.p. 198–199 °C. IR (KBr): ν (cm^{-1}) 2924, 1687, 1630, 1598, 1496, 835. $^1\text{H-NMR}$: δ 7.81–7.40 (m, 3H), 7.24 (d, $J = 9.0$ Hz, 2H), 6.41 (d, $J = 16.0$ Hz, 1H), 2.33 (s, 3H).

3.4.5. (*E*)-3-(4-Nitrophenyl)acrylic acid (**3l**)

M.p. 286–287 °C, Ref. [24]. M.p. 288 °C. IR (KBr): ν (cm^{-1}) 2950, 1685, 1632, 1598, 1525, 1345, 845. $^1\text{H-NMR}$: δ 8.22 (d, $J = 9.0$ Hz, 2H), 7.96 (d, $J = 9.0$ Hz, 2H), 7.67 (d, $J = 16.0$ Hz, 1H), 6.75 (d, $J = 16.0$ Hz, 1H).

3.4.6. (*E*)-3-(3-Nitrophenyl)acrylic acid (**3m**)

M.p. 195–196 °C. IR (KBr): ν (cm^{-1}) 2963, 1699, 1635, 1577, 1524, 1359, 979, 715. $^1\text{H-NMR}$: δ 8.41 (s, 1H), 8.27 (d, $J = 8.0$ Hz, 1H), 7.89–7.55 (m, 3H), 6.58 (d, $J = 16.0$ Hz, 1H). Anal. Found: C, 55.69; H, 3.42; N, 7.02. $\text{C}_9\text{H}_7\text{NO}_4$ Calc.: C, 55.96; H, 3.63; N, 7.25%.

3.4.7. (*E*)-3-(4-Methoxycarbonylphenyl)acrylic acid (**3n**)

M.p. 240–241 °C, Ref. [9]. M.p. 241–242 °C. IR (KBr): ν (cm^{-1}) 2915, 1714, 1687, 1630, 1600, 1100, 852, 770. $^1\text{H-NMR}$: δ 8.04 (d, $J = 9.0$ Hz, 2H), 7.76–7.50 (m, 3H), 6.46 (d, $J = 16.0$ Hz, 1H), 3.90 (s, 3H).

4. Conclusions

We have described a new polymer-bound bidentate arsine palladium(0) complex whose preparation is simple and convenient. This complex has not only high activity and stereoselectivity for arylation of conjugated alkenes with aryl halides, but also offers practical advantages such as easy handling, separation from the product and reuse. The arylation of styrene and acrylic acid with aryl iodides or bromides catalyzed by 'Si'-2As-Pd(0) provides a better and practical procedure for the synthesis of unsymmetrical *trans*-stilbenes and substituted *trans*-cinnamic acids.

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References

- [1] (a) R.F. Heck, *Org. React.* 27 (1982) 345;
(b) R.A. Abramovitch, D.H.R. Barton, J.P. Finet, *Tetrahedron* 44 (1988) 3039.
- [2] (a) G.T. Crisp, *Chem. Soc. Rev.* 27 (1998) 427;
(b) I.P. Beletskaya, A.V. Cheprakov, *Chem. Rev.* 100 (2000) 3009.
- [3] R.F. Heck, *Pure Appl. Chem.* 50 (1978) 691.
- [4] R.F. Heck, *Acc. Chem. Res.* 12 (1979) 146.
- [5] M. Terasawa, K. Kaneda, T. Imanaka, S. Teranishi, *J. Organomet. Chem.* 162 (1978) 403.
- [6] C.M. Andersson, K. Karabelas, A. Hallberg, *J. Org. Chem.* 50 (1985) 3891.
- [7] Z.Y. Zhang, Y. Pan, H.W. Hu, T.Y. Kao, *Synthesis* (1991) 539.
- [8] B.M. Choudary, R.M. Sarma, K.K. Rao, *Tetrahedron* 48 (1992) 719.
- [9] M.Z. Cai, C.S. Song, X. Huang, *Synthesis* (1997) 521.
- [10] J. Tsuji, M. Hara, K. Ohno, *Ger. Offen.* 1, 942, 798; *C.A.*, 73, 15497y (1970).
- [11] (a) Y.Y. Chen, X.R. Lu, Z.Y. Wang, *Chin. J. Catal.* 11 (1990) 75;
(b) L. Ripa, A. Hallberg, *J. Org. Chem.* 62 (1997) 595.
- [12] A. Ulmann, C. Willand, W.K. Douglas, R. Rebello, D.J. Williams, L. Handley, *J. Am. Chem. Soc.* 112 (1990) 7083.
- [13] B.J. Bridson, P. Nair, *Tetrahedron* 37 (1981) 173.
- [14] Z.Y. Zhang, H.W. Hu, T.Y. Kao, *React. Polym. Ion Exch. Sorbents* 9 (1988) 249.
- [15] J.R. Johnson, *Org. React.* 1 (1942) 210.
- [16] R.F. Heck, J.P. Nolley, *J. Org. Chem.* 37 (1972) 2320.
- [17] X.R. Lu, Z.L. Zhong, Y.Y. Chen, *Chem. J. Chin. Univ.* 11 (1990) 561.
- [18] Z.Y. Zhang, H.W. Hu, T.Y. Kao, *React. Polym. Ion Exch. Sorbents* 12 (1990) 229.
- [19] A. Sekiguchi, W. Ando, *J. Org. Chem.* 44 (1979) 413.
- [20] A.R. George, R.G.W. Spickett, *J. Chem. Soc.* (1949) 2724.
- [21] F. Bergmann, D. Schapira, *J. Org. Chem.* 12 (1947) 57.
- [22] H.A. Dieck, R.F. Heck, *J. Am. Chem. Soc.* 96 (1974) 1133.
- [23] B.A. Patel, C.B. Ziegler, N.A. Cortese, J.E. Plevyak, T.C. Zebovitz, M. Terpko, R.F. Heck, *J. Org. Chem.* 42 (1977) 3903.
- [24] T.A. Wittstruck, E.N. Trachtenberg, *J. Am. Chem. Soc.* 89 (1967) 3803.
- [25] J.F.J. Dippy, J.E. Page, *J. Chem. Soc.* (1938) 357.