SHORT PAPER

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Heck arylation of conjugated alkenes catalysed by a silica-supported poly-γ-methylselenopropylsiloxane palladium(0) complex, the first polymeric organoselenium palladium complex[†]

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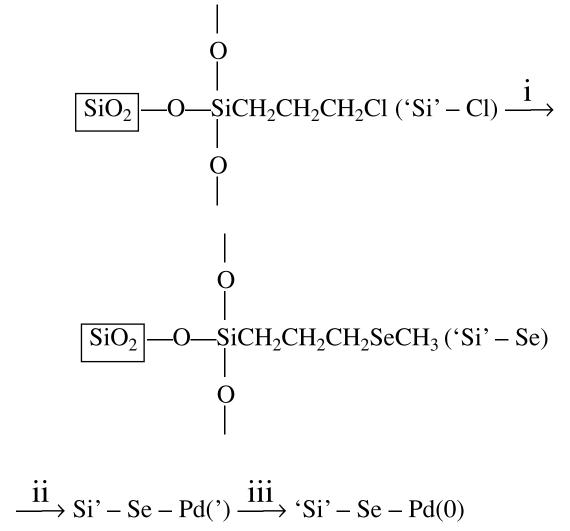
A silica-supported poly-γ-methylselenopropylsiloxane palladium(0) complex was prepared from poly-γ-chloropropylsiloxane by treatment with sodium methyl-selenolate, followed by reaction with palladium chloride and then reduction with hydrazine hydrate. The first polymeric organoselenium palladium complex is a highly active and stereoselective catalyst for the arylation of conjugated alkenes.

Keywords: Heck anylation, conjugated alkenes, polymeric organoselenium palladium complex

The palladium-catalysed arylation of olefins, the Heck reaction, has found wide application in organic synthesis[1,2]. It is a homogeneous reaction, generally using palladium compounds such as $Pd(OAc)_2$ as catalyst. 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 the expense. Polymer-bound organotransition metal complexes having high activity and selectivity 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 most important.

Study of new types of polymer-bound palladium catalyst which might be suitable for the Heck arylation of olefins 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-bound 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. Recently, we prepared a silica-supported sulfur palladium(0) complex and tested its catalytic activity for the Heck arylation of styrene and acrylic acid[9]. The first polymeric sulfur palladium(0) complex showed high activity and stereoselectivity in the arylation of styrene and acrylic acid with aryl iodides. However little attention has so far been given to organoselenium transition metal complexes which, to date, remains largly confined to the organoselenium platinum complexes[10,11]. To our knowledge, no Heck arylation of olefins catalysed by a organoselenium palladium complex has been reported. We now wish to report the preparation of silica-supported poly–γ–methylselenopropylsiloxane palladium(0) complex ('Si'– Se – Pd(0)) and its catalytic properties in the Heck arylation of conjugated alkenes. This complex is the first polymeric organoselenium palladium complex and could be easily prepared from polyñ(ñchloropropylsiloxane ('Si' – Cl) by treatment with sodium methylselenolate in ethanol, followed by reacting with palladium chloride in acetone and then the reduction with hydrazine hydrate in ethanol (Scheme 1).



Scheme 1
Reagents and conditions: i, CH_3SeNa, EtOH;
ii, $PdCl_2$, CH_3COCH_3; iii, $H_2NNH_2 \cdot H_2O$, EtOH

The X-ray photoelectron spectroscopy (XPS) has been used to characterise this polymeric palladium catalyst. Table 1 shows the XPS data for 'Si' – Se – Pd(0), 'Si' – Se – Pd(II), 'Si' – Se and $PdCl_2$. 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 binding energy of Cl(2p) of 'Si' – Se – Pd(II) is similar to that of $PdCl_2$. However the difference of Se(3d) binding energies between 'Si' – Se – Pd(II) and 'Si' – Se is 0.5 eV. The difference of $Pd(3d_{5/2})$ binding energies between 'Si' – Se – Pd(II) and $PdCl_2$ is 0.7eV. These results show that a coordination bond is formed between the selenium and palladium atom in the 'Si' – Se – Pd(II). The binding energy (336.6eV) of $Pd(3d_{5/2})$ of 'Si' – Se – Pd(0) is lower than the binding energy (337.6eV) 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) can not be detected, the shift (lower) of $Pd(3d_{5/2})$ binding energy, together with the black

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

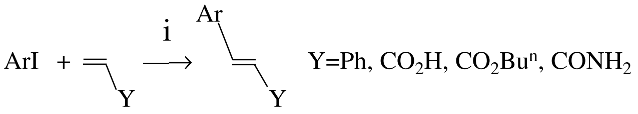
Table 1 XPS data for 'Si' – Se – Pd(0), 'Si' – Se – Pd(II), 'Si' – Se and $PdCl_2$ (in eV)[a]

Sample	$Pd_{3d_{5/2}}$	Se_{3d}	Si_{2p}	O_{1s}	Cl_{2p}
'Si' – Se – Pd(0)	336.6	55.6	103.3	532.6	
'Si' – Se – Pd(II)	337.6	56.2	103.4	532.8	199.0
'Si' – Se		55.7	103.2	532.7	
$PdCl_2$	338.3				199.2

[a]The binding energies are referenced to C_{1S}(284.8eV), and the energy differences were determined with an accuracy of ±0.2eV.

colour suggest that the reduction of the starting palladium(II) complex to the lower valent state has taken place.

In the presence of this polymeric palladium(0) complex and tributylamine, the arylation reaction of conjugated alkenes with aryl iodides proceeded smoothly. The syntheses of *trans*-stilbenes, *trans*-cinnamic acids, *trans*-butyl cinnamates and *trans*-cinnamamides could be readily achieved in high yields. The *trans*-selectivity was always near quantitative and no *cis*-product was observed (Scheme 2). The results are summarised in Table 2.



Scheme 2
Reagents and conditions: i, 'Si' – Se – Pd(0) (0.5 mol%), Bu^n_3N, 100°C

The initial experiment was carried out with styrene and iodobenzene using 'Si' – Se – Pd(0) as catalyst. The arylation reaction at 100°C required 6h to go to completion and stilbene was obtained in 91% yield. This polymeric palladium (0) catalyst not only has higher catalytic activity than $Pd(OAc)_2$ in arylation of styrene with iodobenzene, but also can be easily recovered by simple filtration. The activity of the recovered catalyst was tested for arylation of styrene with iodobenzene for two recycles and it was found that the yield of stilbene decreased by only 3 and 2% after each recycle, respectively. The arylation reactions of other conjugated alkenes with iodobenzene were carried out using 'Si' – Se – Pd(0) as catalyst under conditions similar to those used in the corresponding homogeneous reactions. It was found that the 'Si' – Se – Pd(0) was also suitable for the arylation of acrylic acid, butyl acrylate and acrylamide with iodobenzene and showed high activity and stereoselectivity.

As seen from the Table 2, the arylation reaction can tolerate a variety of functional groups on the aryl iodides; both strongly electron donating and with-drawing substituents can be present. In all reactions only 0.5mol% palladium catalyst based on the aryl iodides was used. As for the arylation of styrene with iodobenzene, the mole turnover numbers of 182 are much larger than those of 75 in the corresponding homogeneous reaction reported by Heck *et al.*[12] The arylation was not possible on conjugated alkenes using bromobenzene as arylating agent in the present studies. A similar observation has been made by Terasawa[5] and Choudary.[7] This polymeric palladium(0) complex is stable to air; 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.

In conclusion, we have described a new silica-supported poly–γ–methylselenop-ropylsiloxane palladium(0) complex whose preparation is simple and convenient. This complex has not only high activity and stereoselectivity for arylation reaction of conjugated alkenes, but offers practical advantages such as easy handling, separation from the product and reuse.

Experimental

Synthesis of 'Si' – Se: To a well stirred solution of dimethyl diselenide (1.04g, 5.5mmol) in 50mL of ethanol was added sodium borohydride (0.43g, 11mmol) portionwise under a nitrogen atmosphere at room temperature until the reaction mixture was decolorized. After being stirred for another 3h, 'Si' – Cl(4.65g) was added and the mixture was refluxed for 24h. The mixture was allowed to cool and filtered, washed with distilled water (5×20ml), ethanol (3×20ml) and then dried under vacuum to give 4.61g of silica-supported poly – γ – methylselenopropylsiloxane ('Si' – Se), the selenium content was 12.61wt%.

Synthesis of 'Si' – Se – Pd(II) and 'Si' – Se – Pd(0): To a solution of $PdCl_2$(0.20g) in acetone (40ml) was added 'Si' – Se(2.50g). The mixture was refluxed under nitrogen for 48h. The product was allowed to cool, then filtered. The resulting yellow powder was washed with distilled water (3×10ml) and acetone (3×10ml), then dried in vacuo to afford 2.51g of 'Si' – Se – Pd(II). The selenium and palladium content were 10.82wt% and 4.25wt%, respectively.

To a suspension of 'Si' – Se – Pd(II) (2.0g) in ethanol (20ml) was added hydrazine hydrate (1.0g) at 30°C. The mixture was stirred under nitrogen for 2h. The resulting product was filtered, washed with ethanol (4×20ml) and diethyl ether (3×20ml) and dried under vacuum to give 1.90g of the black polymeric palladium(0) complex. The selenium and palladium content were 10.91wt% and 4.28wt%, respectively.

Typical procedure for the arylation of styrene with aryl iodides: A mixture of styrene (0.57g, 5.5mmol), iodobenzene (1.02g, 5mmol),. Bu^n_3N (1.11g, 6mmol), *p*-xylene (0.5ml) and the 'Si' – Se – Pd(0) complex (62mg, 0.025mmol of Pd) was stirred under nitrogen at

Table 2 Heck arylation of conjugated alkenes with aryl iodides[a]

Entry	Ar	Y	Conditions	Product(yield, %)[b]
1	C_6H_5	Ph	A	*(E)*-$C_6H_5CH{=}CHC_6H_5$ (91)
2	4-ClC_6H_4	Ph	A	*(E)*-4-$ClC_6H_4CH{=}CHC_6H_5$ (93)
3	4-$CH_3C_6H_4$	Ph	A	*(E)*-4-$CH_3C6_6H_4CH{=}CHC_6H_5$ (87)
4	4-$CH_3OCOC_6H_4$	Ph	A	*(E)*-4-$CH_3OCOC_6H_4CH{=}CHC6_6H_5$ (90)
5	C_6H_5	CO_2H	B	*(E)*-$C_6H_5CH{=}CHCO_2H$ (94)
6	4-$CH_3OC_6H_4$	CO_2H	B	*(E)*-4-$CH_3OC_6H_4CH{=}CHCO_2H$ (96)
7	4-$CH_3OCOC_6H_4$	CO_2H	B	*(E)*-4-$CH_3OCOC_6H_4CH{=}CHCO_2H$ (93)
8	C_6H_5	CO_2Bu^n	C	*(E)*-4-$C_6H_5CH{=}CHCO_2Bu^n$ (91)
9	4-$CH_3C_6H_4$	CO_2Bu^n	C	*(E)*-4-$CH_3C_6H_4CH{=}CHCO_2Bu^n$ (88)
10	4-$O_2NC_6H_4$	CO_2Bu^n	C	*(E)*-4-$O_2NC_6H_4CH{=}CHCO_2Bu^n$ (90)
11	C_6H_5	$CONH_2$	D	*(E)*-4-$C_6H_5CH{=}CHCONH_2$ (88)
12	4-$CH_3OC_6H_4$	$CONH_2$	D	*(E)*-4-$CH_3OC_6H_4CH{=}CHCONH_2$ (85)
13	4-$O_2NC_6H_4$	$CONH_2$	D	*(E)*-4-$O_2NC_6H_4CH{=}CHCONH_2$ (89)

[a]Reactions were carried out at 100°C for 6h with 5mmol of aryl iodide, 5.5mmol of conjugated alkene, 0.025mmol of palladium catalyst. Reaction conditions A: Bu^n_3N (6mmol), *p*-xylene (0.5ml); B: Bu^n_3N (11mmol), *p*-xylene (0.5ml); C: Bu^n_3N(6mmol), *p*-xylene (1ml); D: Bu^n_3N(6mmol), DMF (1ml).

[b]Yields are of isolated, pure products and based on the aryl iodides.

100°C for 6h. The mixture was cooled and dissolved in diethyl ether (50ml). The 'Si' – Se – Pd(0) complex was separated from the mixture by filtration, washed with distilled water (2×10ml), ethanol (3×10ml) and diethyl ether (3×10ml) and reused in the next run. The ethereal solution was washed with 5N HCl(2×10ml), brine (4×10ml) and dried ($MgSO_4$) and filtered. The solid product formed after concentration of the ethereal solution was recrystallised from ethanol to afford (E) – stilbene (0.82g, 91%); M.p. 124°C (lit.[13] 124°C); ν_{max}(KBr)/cm^{-1} 3020, 1600, 1495, 760, 690; δ_H(90MHz, $CDCl_3$, Me_4Si) 7.09(s, 2H), 7.11~7.71(m, 10H).

(E)–4–Chlorostilbene. M.p. 126~127°C (lit.[14] 129°C); ν_{max}(KBr)/cm^{-1} 3060, 1595, 1500, 940, 814, 700; δ_H (90MHz, $CDCl_3$, Me_4Si) 7.08(s, 2H), 7.26~7.47(m, 9H).

(E)–4–Methylstilbene. M.p. 118~119°C (lit.[15] 120°C); ν_{max}(KBr)/cm^{-1} 3035, 1600, 1495, 940, 825, 710; δ_H (90MHz, $CDCl_3$, Me_4Si) 2.31(s, 3H), 7.02(s, 2H), 7.03~7.65 (m, 9H).

(E)–4–Methoxycarbonylstilbene. M.p. 156~157°C (lit.[16] 159~160°C); ν_{max}(KBr)/cm^{-1} 3030, 1715, 1600, 1180, 840, 770, 700; δ_H (90MHz, $CDCl_3$, Me_4Si) 3.93(s, 3H), 7.15(s, 2H), 7.21~7.64(m, 7H), 8.04(d, *J*9.0, 2H).

Typical procedure for the arylation of acrylic acid with aryl iodides: A mixture of acrylic acid (0.40g, 5.5mmol), iodobenzene (1.02g, 5mmol),. Bu^n_3N (2.04g, 11mmol), *p*-xylene (0.5ml) and the 'Si' – Se – Pd(0) complex (62mg, 0.025mmol of Pd) was stirred under nitrogen at 100°C for 6h. After the reaction mixture was cooled, water (20ml) and $NaHCO_3$ (1.10g) were added. After stirring for 10 min, the 'Si' – Se – Pd(0) complex was separated from the mixture by filtration. The aqueous phase was separated and acidified with 5N HCl (2.0ml). After cooling to 0°C, the solid precipitate was filtered, washed with water (3×20ml) and air dried to give *(E)*–cinnamic acid(0.69g, 94%); M.p. 131~132°C (lit.[17] 132~133°C); ν_{max}(KBr)/cm^{-1} 2915, 1690, 1625, 1500, 1419, 760, 700; δH(90MHz, DMSO–d_6, Me_4Si) 6.45(d, *J*16.0, 1H), 7.20~7.69(m, 5H), 7.84(d, *J*16.0, 1H).

(E)–4–Methoxycinnamic acid. M.p. 172~173°C (lit.[18] 174°C); ν_{max}(KBr)/cm^{-1} 2920, 1685, 1630, 1600, 1495, 1250, 1170, 830; δ_H (90MHz, DMSO–d_6, Me_4Si) 3.86(s, 3H), 6.31(d, *J*16.0, 1H), 6.91(d, *J*9.0, 2H), 7.49(d, *J*9.0, 2H), 7.64(d, *J*16.0, 1H).

(E)–4–Methoxycarbonylcinnamic acid. M.p. 241~242°C (lit.[19] 241~242°C); ν_{max} (KBr)/cm^{-1} 2910, 1710, 1685, 1630, 1596, 1100, 850, 770; δ_H (90MHz, DMSO–d_6, Me_4Si) 3.90(s, 3H),6.46(d, *J*16.0, 1H), 7.50~7.75(m, 3H), 8.05(d, *J*9.0, 2H).

Typical procedure for the arylation of butyl acrylate with aryl iodides: A mixture of butyl acrylate (0.71g, 5.5mmol), iodobenzene (1.02g, 5mmol), Bu^n_3N (1.11g, 6mmol), *p*-xylene (1ml) and the 'Si' – Se – Pd(0) complex (62mg, 0.025mmol of Pd) was stirred under nitrogen at 100°C for 6h. The mixture was cooled and dissolved in diethyl ether(50ml). The 'Si' – Se – Pd(0) complex was separated from the mixture by filtration. The ethereal solution was washed with 5N HCl (2×10ml), brine (4×20ml) and dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (light petroleum-ethyl acetate 19:1) to give *(E)*- butyl cinnamate[19] (0.93g, 91%); ν_{max}(film)/ cm^{-1} 3060, 2925, 2870, 1710, 1630, 1170, 825; δ_H (90MHz, $CDCl_3$, Me_4Si) 0.96(t, *J*7.5, 3H), 1.17~1.98(m, 4H), 4.20(t, *J*6.0, 2H), 6.40(d, *J*15.0, 1H), 7.04~7.80(m, 6H).

(E)-Butyl 4–methylcinnamate[19]. ν_{max} (film)/cm^{-1} 3030, 2930, 2860, 1715, 1640, 1175, 830; δ_H (90MHz, $CDCl_3$, Me_4Si) 0.96(t, *J*7.5, 3H), 1.14~1.95(m, 4H), 2.34(s, 3H), 4.22(t, *J*6.0, 2H), 6.36(d, *J*15.0, 1H), 7.05~7.78(m, 5H).

(E)-Butyl 4–nitrocinnamate. M.p. 67~68°C (lit.[19] 68~70°C); ν_{max} (KBr)/cm^{-1} 3070, 2920, 2860, 1710, 1640, 1510, 1340, 1170, 840; δ_H (90MHz, $CDCl_3$, Me_4Si) 0.96(t, *J*7.5, 3H), 1.18~2.05(m, 4H), 4.24(t, *J*6.0, 2H), 6.59(d, *J*15.0, 1H), 7.54~7.90 (m, 3H), 8.10~8.42(m, 2H).

Typical procedure for the arylation of acrylamide with aryl iodides: A mixture of acrylamide (0.39g, 5.5mmol), iodobenzene (1.02g, 5mmol), Bu^n_3N (1.11g, 6mmol), DMF (1ml) and the 'Si' – Se – Pd(0) complex (62mg, 0.025mmol of Pd) was stirred under nitrogen at 100°C for 6h. The reaction mixture was cooled and dissolved in DMF(2ml) and water (1ml). The 'Si' – Se – Pd(0) complex was separated from the mixture by filtration. The filtrate was poured into water (100ml), the precipitated product was isolated by suction and washed with water (3×10ml). The crude product was recrystallised from ethanol to afford (E)- cinnamamide (0.65g, 88%); M.p. 143~144! (lit.[20] 144°C); ν_{max}(KBr)/cm^{-1} 3370, 3165, 1665, 1600, 969, 760, 700; δ_H (90MHz, DMSO-d_6, Me_4Si) 6.70(d, *J*16.0, 1H), 7.33~7.69(m, 6H).

(E)-4-Methoxycinnamamide. M.p. 195~196°C (lit.[20] 195°C); ν_{max} (KBr)/cm^{-1} 3345, 3185, 1665, 1254, 1170, 985, 830; δ_H (90MHz, DMSO-d_6, Me_4Si) 3.86(s, 3H), 6.53(d, *J*16.0, 1H), 6.96(d, *J*9.0, 2H), 7.45(d, *J*9.0, 2H), 7.74(d, *J*16.0, 1H).

(E)-4-Nitrocinnamamide. M.p. 216°C (lit.[21] 217°C); ν_{max} (KBr)/cm^{-1} 3370, 3175, 1665, 1520, 1340, 980, 830; δ_H (90MHz, DMSO-d_6, Me_4Si) 6.75(d, *J*16.0, 1H), 7.40~7.79(m, 3H), 8.05~8.30(m, 2H).

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Notes and references

The poly-γ-chloropropylsiloxane('Si' – Cl) was prepared by a literature method[22], the chlorine content was 7.18wt%. *J* values are given in Hz.

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