

Heck Vinylation of Aryl Iodides by a Silica Sol–Gel Entrapped Pd(II) Catalyst and Its Combination with a Photocyclization Process

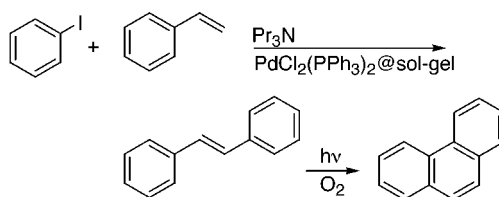
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ABSTRACT



Silica sol–gel encaged PdCl₂(PPh₃)₂ is a recyclable catalyst for the Heck vinylation of aryl iodides. It is possible to couple the Heck reaction with photocyclization in a one-pot process.

Since the Heck coupling of aryl halides with olefins became one of the most powerful tools in organic synthesis for building C–C bonds, it also became the subject of very intensive research.¹ Much effort has been directed to the development of efficient methods for the recovery and the recycling of costly palladium and solvents. Notable are the studies on the Heck coupling on solid supports,² vinylation under phase-transfer conditions,³ reactions in polymeric⁴ or ionic liquids,⁵ coupling by palladium–nickel clusters,⁶ reac-

tions in the presence of palladium entrapped within supramolecular host–guest molecules,⁷ and processes promoted by palladium-supported on carbon,^{3d,8} on organic polymers,⁹ on inorganic oxides and zeolites,¹⁰ on clays,¹¹ or on molecular sieves.¹² Silica was used in different forms as support. Heck catalysts have been prepared by simple adsorption of

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Table 1. Heck Coupling Catalyzed by Sol–Gel Entrapped $\text{PdCl}_2(\text{PPh}_3)_2^a$

entry	haloarene	unsaturated substrate	time (h)	T (°C)	products (yield, %) ^{b,c}
1	PhI	$\text{PhCH}=\text{CH}_2$	12	110	$\text{PhCH}=\text{CHPh}$ (<i>E</i> , 84; <i>Z</i> , 5)
2	PhI	$4\text{-ClC}_6\text{H}_4\text{CH}=\text{CH}_2$	12	110	$4\text{-C}_6\text{H}_4\text{CH}=\text{CHPh}$ (<i>E</i> , 41)
3	PhI	$\text{MeOCOCH}=\text{CH}_2$	12	110	$\text{PhCH}=\text{CHCO}_2\text{Me}$ (<i>E</i> , 86)
4	PhI	$\text{NCCH}=\text{CH}_2$	8	90	$\text{PhCH}=\text{CHCN}$ (<i>E</i> , 39; <i>Z</i> , 30) ^d
5	PhI	$\text{PhC}\equiv\text{CH}$	12	90	$\text{PhC}\equiv\text{CPh}$ (48) ^{d,e}
6	$4\text{-O}_2\text{NC}_6\text{H}_4\text{Br}$	$\text{PhCH}=\text{CH}_2$	16	110	$4\text{-O}_2\text{NC}_6\text{H}_4\text{CH}=\text{CHPh}$ (<i>E</i> , 28)

^a Reaction conditions: 4 mmol of haloarene, 4 mmol of unsaturated substrate, 5 mmol of Pr_3N , catalyst containing 0.0427 mmol of $\text{PdCl}_2(\text{PPh}_3)_2$ in 15 mL of toluene. ^b In entries 1–4 and 6, the missing percentages reflect the unreacted starting materials. ^c The NMR, IR, and MS of the products were found to be identical with those of authentic samples either obtained from commercial sources or prepared according to literature procedures.¹⁷ ^d Contaminated with some polymeric material. ^e Yield in the third run.

palladium complexes on silicas of various porosity and surface areas, as well as on supported liquid-phase catalysts.¹³ One approach to prepare supported leach-proof catalysts for the Heck reaction is based on the application of chemically bound palladium compounds to functionalized porous silica.¹⁴ Indeed, some of these variations in the Heck reaction proved to give high yields and to permit recycling of the catalysts. However, the preparation of most of these heterogenized catalysts is associated with tedious procedures.

In this study, we have employed for the first time a sol–gel physically entrapped version of the $\text{PdCl}_2(\text{PPh}_3)_2$ catalyst for the Heck coupling process. This heterogeneous catalyst is characterized by its extremely simple preparation.¹⁵ It is a perfectly leach proof, highly porous material (typical N_2 –BET surface areas of $490\text{ m}^2\text{ g}^{-1}$, and average pore diameters of 27 \AA have been recorded) and completely air stable for many months.

When, for example, a solution of 417 mg (4 mmol) of freshly distilled styrene, 816 mg (4 mmol) of iodobenzene, and 1.14 mL (5 mmol) of tripropylamine in 15 mL of toluene was refluxed for 12 h in the presence of a sol–gel encapsulated catalyst containing 30 mg (0.0427 mmol) of $\text{PdCl}_2(\text{PPh}_3)_2$, the resulting solution consisted, after removal of the catalyst, of 84 and 5% *trans*- and *cis*-stilbene, respectively, as well as 10% unreacted starting materials. Column chromatography of several experiments afforded 77–82% of the products. The filtered catalyst was treated with 15 mL of boiling CH_2Cl_2 for 10 min followed by 20 min of sonication with the same solvent, dried briefly at 1 mm, and reused. Four runs of 12 h indicated that the immobilized catalyst does not lose any catalytic activity upon recycling.

Some further Heck coupling experiments by the sol–gel-entrapped $\text{PdCl}_2(\text{PPh}_3)_2$ have been conducted. The results are

summarized in Table 1. Whereas iodobenzene couples smoothly with styrenes and acrylic acid derivatives, bromobenzene reacts very slowly ($\sim 2\%$ after 20 h). It can, however, be activated by introduction of an electron-attracting group into the aromatic ring (see, e.g., entry 6). The arylation products of acrylonitrile and of phenylacetylene in boiling toluene were accompanied with some polymerization products. The polymerization could however be decreased significantly by lowering the reaction temperature to $90\text{ }^\circ\text{C}$. Upon recycling of the immobilized catalyst, the yields were hardly affected in all cases tested except in the arylation of phenylacetylene. Under the conditions given in Table 1, the yields of isolated tolan in the first three runs of 12 h were 25, 30, and 48%, respectively. Such an increase in rate has already been observed in our previous studies and is attributed to slow modification and activation of the entrapped palladium compound in the presence of alkynes.¹⁶

We have already shown that the entrapment of catalysts within sol–gel matrixes not only permits facile recycling of the dopant but also protects it from “hostile” and opposing chemicals. This enabled us to conduct multistep one-pot reactions with entrapped catalysts in the presence of (separately) entrapped catalyst poisons¹⁸ and with acidic catalysts in the presence of bases,¹⁹ to perform simultaneously oxidation and catalytic hydrogenation,²⁰ and to carry out esterifications by sol–gel entrapped lipase in the presence of an enzyme destroying metallic catalyst.²¹ Now we have investigated the possibility to couple the Heck vinylation by entrapped $\text{PdCl}_2(\text{PPh}_3)_2$ with a photochemical process in the same reaction flask.

Photocyclization of stilbenes is well-known,²² and the combination of a Heck vinylation with photolysis in two separate steps has been employed in the syntheses of various

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(15) Typically, 5 mL (33.9 mmol) of tetramethoxysilane (TMOS) was hydrolyzed by stirring for 1 h at $25\text{ }^\circ\text{C}$ with 4 mL (222 mmol, $r = 6.7$) of triply distilled water (TDW). A solution of 30 mg (4.27×10^{-2} mmol) of $\text{PdCl}_2(\text{PPh}_3)_2$ in 11 mL of THF was added. Addition of $50\text{ }\mu\text{L}$ of an 0.1 M solution of tetrabutylammonium fluoride induced gelation of the reaction mixture within 5–8 min. After being aged for 16 h, the solid catalyst was treated for 1 h with boiling toluene, dried for 10 h at 1 mm, sonicated, and refluxed for 30 min with 15 mL of CH_2Cl_2 and redried for 3 h at 1 mm to give 2.3 g of the entrapped catalyst.

(16) Cf. the gradual activation of another sol–gel entrapped catalyst during hydrogenation reactions: Blum, J.; Gelman, F.; Abu-Reziq, R.; Miloslavski, I.; Schumann, H.; Avnir, D. *Polyhedron* **2000**, *19*, 509.

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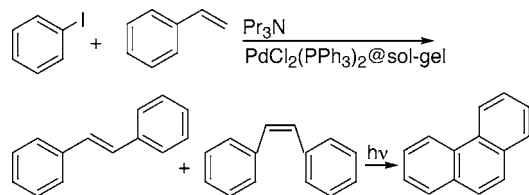
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polycyclics.²³ With the aid of sol–gel entrapped $\text{PdCl}_2(\text{PPh}_3)_2$, we were able to carry out in one-pot the two-step reactions shown in Scheme 1. When a mixture of 4 mmol

Scheme 1. One-Pot Heck Coupling and Photocyclization.
Formation of Phenanthrene

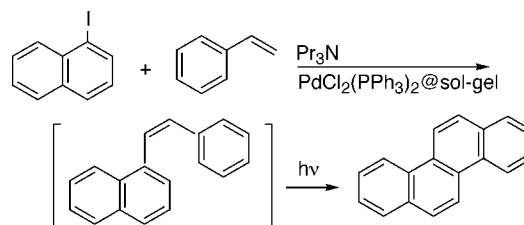


of iodobenzene, 4 mmol of styrene, 5 mmol of Pr_3N , 2.4 g of silica sol–gel containing 4.27×10^{-2} mmol of $\text{PdCl}_2(\text{PPh}_3)_2$, and 15 mL of toluene was placed in a quartz well, refluxed with stirring under an ambient atmosphere for 12 h, and then irradiated with a 150 W Hanovia medium-pressure mercury lamp, after 3 h the catalyst-free solution afforded pure phenanthrene in 85% yield. Under these conditions, addition of I_2 to the reaction mixture was unnecessary. The recovered immobilized catalyst was washed and sonicated with CH_2Cl_2 and reused in three further runs giving practically the same yields of phenanthrene as in the first run. Since the UV light decomposes the aryl halide forming a phenyl cation,²⁴ the irradiation process was started only after most of the iodobenzene was consumed in the Heck reaction. When the irradiation was initiated after 2.5, 4, 7, or 10 h, the yields of phenanthrene were 40, 56, 65, and 71%, respectively. It should be noted that the sequence of reactions shown in Scheme 1 takes place also in the presence of nonentrapped $\text{PdCl}_2(\text{PPh}_3)_2$. There are, however, two important differences: (i) the homogeneous palladium catalyst cannot be reused and (ii) the activity of the free $\text{PdCl}_2(\text{PPh}_3)_2$ as a Heck coupling catalyst decreases during irradiation of iodobenzene, while that of the entrapped

complex is not affected. When the entrapped and the nonentrapped complex (both samples contained exactly the same amount of palladium) were heated in boiling toluene under identical conditions with iodobenzene, styrene, and tripropylamine for 12 h and to each of the reaction mixtures was then added another portion of iodobenzene, the yield of stilbenes after a total of 24 h was 87% in the reaction with the heterogenized catalyst and only up to 77% in an experiment with the soluble palladium complex. Since the differences in yields were not very large, we repeated these experiments four times to ensure the validity of the results. We assume that an irradiation product of the iodobenzene acts as an inhibitor for the free $\text{PdCl}_2(\text{PPh}_3)_2$ but does not affect the encaged complex.

A sequence of reactions similar to that shown in Scheme 1 was carried out using 1-iodonaphthalene instead of iodobenzene. After allowing the Heck coupling to take place for 12 h, the reaction mixture was irradiated for 4 h yielding 74% of pure chrysene (Scheme 2). As in the formation of phenanthrene, the heterogenized catalyst could be reused without loss of catalytic activity.

Scheme 2. One-Pot Heck Coupling and Photocyclization.
Formation of Chrysene



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Supporting Information Available: Experimental details and physical data of the isolated products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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