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# A Practical Recycle of a Ligand-Free Palladium Catalyst for Heck Reactions

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Dedicated to Prof. Roger Sheldon on the occasion of his 60th birthday.

**Abstract:** Ligand-free palladium can be recovered almost quantitatively from Heck reaction mixtures by filtration after its deposition on a carrier such as silica or celite. Subsequently, it is re-activated to its original activity by adding a small amount of iodine or bromine prior to the next reaction cycle. The catalyst

results in excellent yields and selectivities, even for the less reactive aryl bromides. A catalytic cycle based on anionic palladium intermediates is proposed.

**Keywords:** catalyst recovery; Heck reaction; iodine; ligand-free; palladium; re-activation

## Introduction

The number of highly (enantio)selective homogeneous catalysed transformations is growing rapidly,<sup>[1]</sup> and the advantages of homogeneous catalysis in applications are broadly recognised.<sup>[2]</sup> Initially, asymmetric hydrogenation appeared to be the most important reaction class,<sup>[3]</sup> but in recent years aromatic substitution reactions and CO chemistry are rapidly gaining in importance. However, to date only a small percentage of fine chemicals are produced using homogeneous catalysis. This modest role is due to a whole range of critical factors from which the following ones are probably most decisive:

- i) The activity and stability of the catalyst.
- ii) The availability and cost of the catalyst and matching starting materials.
- iii) The short development time for a production process (a few months to 1 year) limiting the possibility to change complex synthetic routes.

Carbon-carbon bond forming reactions, such as the Heck reaction are used to some extent in fine chemical production.<sup>[4]</sup> The wide functional group tolerance of these palladium-catalysed reactions allows their application at a late stage of total synthesis and eliminates the need for protecting groups.

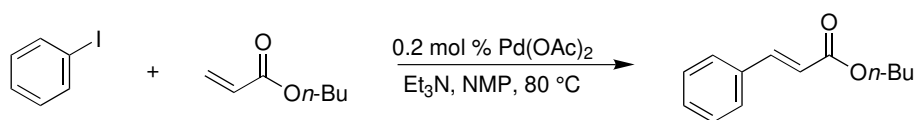
Heck chemistry is traditionally associated with the palladium-phosphine-catalysed reaction of aryl bromides or iodides with olefins presenting one of the simplest ways to obtain various substituted olefins.<sup>[4,5]</sup>

Recently, a lot of effort has been put into the development of new, active and stable palladium catalysts such as palladacycles and other underligated single-phosphine systems.<sup>[5]</sup> However, the use of phosphorus ligands in fine chemical processes is less desirable. They are usually unrecoverable and frequently hamper the isolation and purification of the desired product as well as the performance of consecutive catalytic steps of the total synthesis.

On the other hand, phosphine-free systems have shown excellent activities in Heck reactions.<sup>[6]</sup> Successful ligand-free approaches have also been described when phase-transfer agents,<sup>[7]</sup> aqueous systems,<sup>[8]</sup> palladium nanoparticles<sup>[9]</sup> or less usual leaving groups such as diazonium salts,<sup>[10]</sup> acid chlorides<sup>[11]</sup> or anhydrides<sup>[12]</sup> are used.

Next to the activity of the catalyst, recovery and recycling of the expensive palladium is a major development issue. Several approaches based on biphasic liquid-liquid and polymer-supported systems have been reported but reactivity is often lower. Furthermore, due to the instability of the palladium complexes, leaching is a common problem.<sup>[13]</sup>

Palladium-on-carbon-catalysed Heck reactions have been described and utilised in applied syntheses,<sup>[13,14]</sup> but the true catalytically active species is arguably a leached soluble palladium complex.<sup>[15]</sup> Recently, several palladium catalysts supported on various metal oxides, molecular sieves and zeolites have been separated from Heck reaction mixtures and re-used without any loss of activity.<sup>[16]</sup>

**Scheme 1.**

Here we would like to present a practical method to recycle, *and* re-activate a ligand-free palladium catalyst for Heck reactions using the merits of both homogeneous and heterogeneous catalysis i.e., high activity and easy recovery, respectively.

## Results and Discussion

By now the general acceptance is that none of the steps in the Heck catalytic cycle requires the presence of a strongly bound (phosphine) ligand in the coordination shell of palladium.<sup>[5a]</sup> The most serious drawback of homogeneous ligand-free palladium catalysis is that deactivation of the instable palladium species occurs, mainly caused by the formation of inactive palladium(0) sediments. Tuning of the reaction conditions could in principle lead to highly active ligand-free palladium caught in the catalytic cycle, converting all aryl compound present prior to its precipitation to palladium black.

In order to find those conditions for the ligand-free Heck reaction of iodobenzene and *n*-butyl acrylate we investigated at 80 °C several combinations of solvents (NMP, DMF, DMA, DMSO, and acetonitrile), bases ( $\text{K}_2\text{CO}_3$  and  $\text{Et}_3\text{N}$ ) and palladium precursors [ $\text{PdCl}_2$  and  $\text{Pd(OAc)}_2$ ]. The reaction procedure using NMP,  $\text{Et}_3\text{N}$ , and  $\text{Pd(OAc)}_2$  proceeded remarkably faster and more selectively (conversion and selectivity to the *trans*-cinnamate are both > 99%, Scheme 1) than those that utilised other combinations.<sup>[17]</sup>

In addition, all combinations invariably led to precipitation of palladium, whether full conversion of iodobenzene was reached or not.

To get a more economical procedure we focused our investigation on the recovery and re-use of the precipitated catalyst. Recovery of the precipitated palladium(0) after the reaction performed as described in Scheme 1, followed by re-use in the same reaction showed that the activity had greatly diminished. As this might well be due to the reduced surface area of the catalyst the effect of deposition on carrier materials, like silica, or celite was studied. The use of these materials resulted in almost quantitative precipitation of the palladium (only ppb concentrations of palladium in the filtrate, ICP-MS) and facilitated the separation from the reaction mixture. No palladium precipitation on the glass tube wall was observed. However, the activity of these grey materials in the test reaction of Scheme 1 was still more than 10 times less on average than the original



**Figure 1.** TEM picture of palladium (black circles) deposited on silica from Heck reaction.

$\text{Pd(OAc)}_2$ . Analysis with TEM (transmission electron microscopy) revealed that the deposited palladium on the carrier materials is in the form of fairly large crystalline clusters with a size of 40–100 nm (Figure 1).

At this stage we envisioned that the only manner in which the palladium could be restored to its original activity would be to oxidise it back to its monomeric form.

Therefore, several different oxidising agents and salts (as a solution in NMP) were added to the precipitated palladium on celite prior to the reagents and base necessary for the test reaction. This screening of suitable re-activators was performed in a fully automated synthesiser by using a reactor block equipped with a filter (8 vessels). In this manner we examined several different re-activators in 3 successive runs of the test reaction.

In the first run all vessels were filled with the same reagents including Pd(OAc)<sub>2</sub> and celite, obviously giving the same results: >98% conversion, >98% selectivity to the *trans* product after 60 minutes (see Table 1, entries 1–8). The vessels were cooled, and the reaction mixtures were separated from the precipitated palladium on celite by filtration. The residues were washed with methyl *t*-butyl ether (MTBE) and filtered to exclude any residual homogeneous palladium. The resulting grey materials were treated with the different additives dissolved in NMP before the next Heck reaction was performed (Run 2, see Table 1, entries 1–8). Remarkably, I<sub>2</sub> and Br<sub>2</sub> were able to dissolve the precipitated palladium and led to full restoration of the original activity of Pd(OAc)<sub>2</sub> while other additives, such as HOAc, LiI, and HI did not result in a catalytic activity to the same extent.<sup>[18]</sup> When no re-activator or stronger oxidants (HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, NaIO<sub>4</sub>) were used, hardly any Heck product was formed in the successive runs.

Therefore addition of only 2 mol equivalents of I<sub>2</sub> (or Br<sub>2</sub>) dissolved in NMP to the recovered palladium precipitated on celite (or silica), followed by stirring at RT for a few minutes to dissolve the palladium prior to the following Heck reaction run, has led to the development of a very practical recycle of palladium, reducing the costs of the catalyst significantly. By using this mode 8 successive runs of the test reaction were performed manually in normal glass equipment without significant losses in activity.<sup>[19]</sup>

The re-activation with I<sub>2</sub> of the precipitated palladium was also successful in the Heck reaction of iodobenzene with styrene giving the same performance as in run 1. Yields and selectivities found with this catalyst are comparable with those found for other catalytic systems (entry 9). Ligand-free Heck reactions on the less reactive aryl bromides are hardly known.<sup>[5a,15b,16a,16c]</sup> Thus, we were delighted to see that by carefully adjusting the conditions, the coupling of 3-bromopyridine and *n*-butyl acrylate proceeded smoothly without any added ligand.<sup>[20]</sup> Moreover, the I<sub>2</sub> re-activation mode is also applicable (entry 10). Activities and selectivities of this recyclable palladium catalyst are, for both the iodobenzene and 3-bromopyridine, comparable with the recently reported supported ligand-free systems.<sup>[16]</sup>

### Mechanistic Considerations

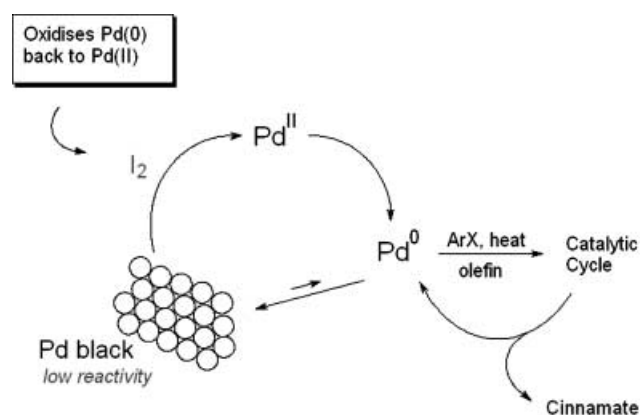
When the solution obtained after stirring with I<sub>2</sub> was separated from the silica (or celite), the solution showed high rates in the Heck reaction, but the silica was not active. Stirring of the precipitated palladium on silica with only NMP and testing the solution in the Heck reaction showed almost no activity. In an independent experiment we showed that commercial palladium black could also be dissolved using I<sub>2</sub> in NMP, and that

this solution was active in the Heck reaction. The combination of silica and iodine in the absence of palladium but otherwise equal conditions did not show any activity in the Heck reaction.

All these experiments are confirming the assumption that the precipitated palladium is oxidised back to Pd(II) by I<sub>2</sub> (or Br<sub>2</sub>),<sup>[21]</sup> which is then reduced again in the next Heck reaction to form the highly active palladium(0) species, see Figure 2.

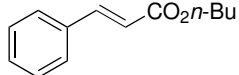
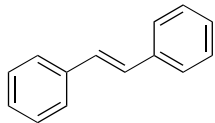
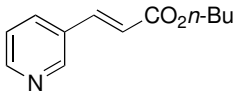
On the molecular level very little is known about the catalytic cycle of these ligand-free Heck reactions. Extensive research has been performed on the use of anionic palladium phosphine catalysts in the Heck reaction.<sup>[22]</sup> We thus attempted to gain more information about the ligand-free systems by the use of negative ion electron spray MS. The Heck reaction of Scheme 1 was followed over time and the anionic palladium complexes were recorded. Most striking observations are the presence of a unique palladium(0) species, [(H<sub>2</sub>O)PdOAc]<sup>-</sup>, at low conversion and the palladium(II) species, [ArPdI<sub>2</sub>]<sup>-</sup> and [PdI<sub>3</sub>]<sup>-</sup>, at higher conversion (>5%).<sup>[23]</sup> Therefore we propose the mechanism depicted in Figure 3 based on the assumption that [PdI<sub>3</sub>]<sup>-</sup>, or its dimer [Pd<sub>2</sub>I<sub>6</sub>]<sup>2-</sup>, is in equilibrium with the highly active PdI<sup>-</sup> (or a dimer/cluster thereof). More details of this study will be published elsewhere as it is outside the scope of this paper.

In summary, we reported in this work a highly practical, cost-effective and robust solution for performing Heck reactions, combining the advances of heterogeneous and homogeneous catalysis. The precipitated palladium sediments can easily be recovered by filtration, and re-activated (“homogenised”) by addition of I<sub>2</sub> or Br<sub>2</sub>. The re-activated palladium catalyst is homogeneous in character, most likely as a mononuclear anionic species, although the presence of nanoparticles cannot be excluded.<sup>[9]</sup> Scale-up studies using this ligand-free mode of Heck reactions are under investigations in our laboratories.



**Figure 2.** A practical catalyst recycle for ligand-free Heck reactions.

**Table 1.** Re-activation and re-use of the palladium catalyst (0.5 mol %) in ligand-free Heck reactions.<sup>[a]</sup>

Entry	ArX	Olefin	Temp. [°C]	Base	Product	Re-activator <sup>[b]</sup>	Time [h]	Run 1		Time [h]	Run 2		Time [h]	Run 3	
								Conv. <sup>[c]</sup> [%]	Yield <sup>[c]</sup> [%]		Conv. <sup>[c]</sup> [%]	Yield <sup>[c]</sup> [%]		Conv. <sup>[c]</sup> [%]	Yield <sup>[c]</sup> [%]
1	Iodo benzene	<i>n</i> -butyl acrylate	80	Et <sub>3</sub> N		I <sub>2</sub>	1	98	98	1	100	99	1	99	99
2	"	"	"	"	"	Br <sub>2</sub>	1	99	99	1	99	99	1	100	98
3	"	"	"	"	"	NaIO <sub>4</sub>	1	99	98	1	10	10	1	8	2
4	"	"	"	"	"	H <sub>2</sub> O <sub>2</sub>	1	100	99	1	19	2	1	11	2
5	"	"	"	"	"	LiI	1	98	98	1	65	70	1	63	57
6	"	"	"	"	"	HOAc	1	99	99	1	38	41	1	23	17
7	"	"	"	"	"	HI	1	100	99	1	80	81	1	60	56
8	"	"	"	"	"	–	1	99	99	1	15	9	1	5	1
9 <sup>[d]</sup>	Iodo benzene	styrene	120	Et <sub>3</sub> N		I <sub>2</sub>	3	98	94	3	97	92			
10 <sup>[e]</sup>	3-bromo pyridine	<i>n</i> -butyl acrylate	130	NaOAc		I <sub>2</sub>	4	95	85	4	92	83			

<sup>[a]</sup> All experiments were performed under a nitrogen atmosphere in the ASW 2000 of Chemspeed<sup>TM</sup>, a fully automated synthesiser, unless stated otherwise. Sequence of the procedure: Heck reaction run 1 (amount of reagents and additives: 2.0 mmol of aryl compound, 2.8 mmol of olefin, 0.01 mmol of Pd(OAc)<sub>2</sub>, 2.5 mmol of base, 25 mg of celite, and 3 mL of NMP), cooling to RT, filtration, washing of the solids with MTBE (3 mL), filtration, addition of the oxidant/additive (0.02 mmol in 1 mL of NMP) to the solid grey material (palladium deposited on celite), Heck reaction run 2 (2.0 mmol aryl compound, 2.8 mmol of olefin, 2.5 mmol of base, 2 mL of NMP), followed by another cycle starting with cooling to RT.

<sup>[b]</sup> Added just before Heck reaction run 2, and just before run 3. Two mol equivalents of re-activator with respect to the amount of palladium.

<sup>[c]</sup> Determined by GC using dihexyl ether as internal standard.

<sup>[d]</sup> Performed manually in a 10-mL round-bottom flask. Amount of reagents and additives: 5.0 mmol of iodobenzene, 5.5 mmol of styrene, 0.0125 mmol of Pd(OAc)<sub>2</sub> (0.25 mol %), 5.5 mmol of Et<sub>3</sub>N, 35 mg of celite, and 5 mL of NMP. No MTBE wash between the 2 runs.

<sup>[e]</sup> Performed manually in a 50-mL Schlenk vessel. Amount of reagents and additives: 16.8 mmol of 3-bromopyridine, 30 mmol of *n*-butyl acrylate, 0.057 mmol of Pd(OAc)<sub>2</sub> (0.3 mol %), 25.6 mmol of NaOAc, 400 mg of celite, and 30 mL of NMP.



through celite. The inorganic material was washed with toluene (100 mL) and the solvents were evaporated; yield: >90%.  $^1\text{H}$  and  $^{13}\text{C}$  NMR are in full accordance with the literature.

### Electron Spray MS

Negative ion electrospray (ESI) of reaction samples diluted to a 5% solution in acetonitrile were recorded using a PE SCIEX API150 single quadrupole mass spectrometer (Applied Biosystems/MDS SCIEX, Toronto, Ontario, Canada). The samples were introduced by direct infusion of the sample solution at  $5\ \mu\text{L}\ \text{min}^{-1}$  with a syringe pump (Harvard Apparatus, Saint Laurent, Quebec, Canada). The spray capillary voltage was maintained at  $-4\ \text{kV}$ , while the defragmentation potential was set at  $10\ \text{V}$ . The quadrupole resolution was set to high resolution. Mass spectra were collected in full scan mode, scanning from  $100\text{--}700\ \text{amu}$  in 40 seconds.

### Acknowledgements

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