Metallic Palladium in the Heck Reaction: Active Catalyst or Convenient Precursor?

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Novel experimental evidence is presented pointing out that "heterogeneous" palladium metal catalysts employed in Heck-type reactions mainly act as sources of soluble palladium(II) complexes, which are the true catalytically active species.

The Heck reaction has been the subject of thorough investigation for several years. This reaction is usually homogeneously catalyzed by palladium(II) complexes with ligands such as phosphanes, amines or heterocyclic carbenes.[1] However, Heck-type reactions can also be efficiently catalyzed by palladium metal dispersed onto a number of supports including carbon, silica, magnesium oxide or zeolites;[2−15] for example, palladium on carbon is reported to be currently employed in some small-scale industrial processes.[16,17] Palladium metal colloids appear to be active catalysts as well,[18−23] and there is speculation that metal colloids formed in situ are involved also in ligandless homogeneous Heck reactions with simple palladium salts.[22]

In spite of many claims that with all these catalysts the reaction takes place on the metal surface, more sound evidence that the catalysis is truly heterogeneous would be desirable. In fact, whereas some authors reported that the reaction stops after separating the catalyst,[8,12] this did not occur in other cases.[10,15] Indeed, a significant palladium leaching into the solution after just one catalytic cycle was often observed.[12,13]

In this communication, we wish to report that: (i) under Heck conditions heterogeneous palladium metal catalysts undergo significant metal leaching, caused primarily by the presence of aryl halides (bromides and even chlorides); (ii) the presence of a coordinating base such as sodium acetate promotes metal leaching with relatively less reactive aryl halides; (iii) the released soluble metal species are active catalysts for the Heck reaction.

We have tested a 1% w/w Pd/Al_2O_3 catalyst (from Alfa, serial 89112, lot 1969000), hereafter coded AO-Pd, and a 1% w/w Pd catalyst supported on a tailor-made ion-exchange resin (0.38 meq./g sulfonate groups, sodium form), hereafter coded PS-Pd (see Experimental Section). The catalysts were first employed in the Heck reaction of 4-bromo- and 4-chloroacetophenone (BA and CA, respectively) with *n*-butylacrylate (NBA) in *N*,*N*-dimethylacetamide (DMA) (Table 1). Both catalysts were active with BA, AO-Pd being slightly superior. In contrast, the yields with CA were low and did not increase even after 24 h. Remarkably, the catalysts invariably lost palladium: leaching from PS-Pd was virtually complete after the reaction with BA!

Table 1. Heck reactions[a] with supported Pd metal

Catalyst	Aryl halide	Yield (%)	Pd leached (%)
AO-Pd	BA	97	79
PS-Pd	BA	82	100
AO-Pd	CA	5	22
PS-Pd	CA	6	92

[a] Reaction conditions: 10 mmol aryl halide, 10 mmol NaOAc, 17 mmol NBA, 0.1 g catalyst (0.1% mol/mol), 25 mL DMA; inert atmosphere (N_2), 120 °C, 3 h. Selectivity for the Heck product was 100% in all cases.

In order to ascertain which agent caused the metal leaching, both catalysts were allowed to react separately with different components of the reaction mixture under the same conditions of the previous tests. The results are summarized in Table 2. No metal leaching occurred upon treatment with DMA alone or after addition of NaOAc and/or the acrylate. PS-Pd underwent extensive metal leaching when treated with a solution of BA in DMA. The combination of the aryl bromide with NaOAc caused an even higher leaching from PS-Pd and a noticeable leaching from AO-Pd. CA alone was ineffective; significant palladium dissolution took place only when it was combined with NaOAc. We did not observe palladium leaching with chlorobenzene, either alone or in combination with NaOAc (entries 8−9, Table 2).

After the leaching tests, we checked for the presence of active species in solution. The suspensions were filtered hot under an inert gas atmosphere, then NaOAc and NBA were added to the filtrate, which already contained the aryl halide. The resulting mixture was stirred for 3 h at 120 °C and then analyzed for the reaction products (Table 3). Yields were fully comparable to those reported in Table 1. This findings suggest that released palladium is actually also responsible for catalysis in the presence of the "heterogen-

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Table 2. Metal leaching from catalysts PS-Pd and AO-Pd in the presence of different components of the reaction mixture

Entry	Component(s)[a]	PS-Pd[b]	AO-Pd[b]
1	DMA	0	0
2	DMA + NaOAc	0	0
3	DMA + NaOAc + NBA	0	0
4	DMA + BA	85	nd
5	DMA + BA + NaOAc	88	11
6	DMA + CA	0	0
7	DMA + CA + NaOAc	92	10
8	DMA + CB	0	nd
9	DMA + CB + NaOAc	0	nd

[a] CB = chlorobenzene. – [b] Pd leaching (% w/w) after 18 h at 120 °C.

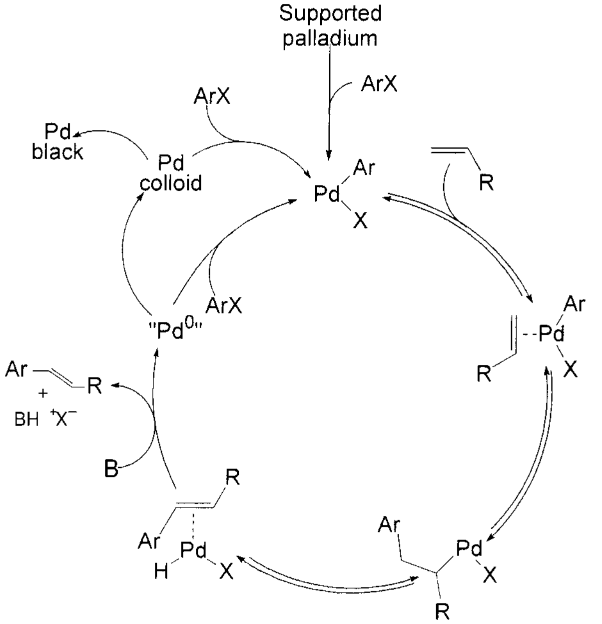
eous” catalyst. The Pd species released by CA (entry 7, Table 2) are almost as active as the species released by BA (entry 5, Table 3). The observed reactivity was quite comparable to that of $Pd(OAc)_2$ (last entry in Table 3). After the coupling, the solutions usually exhibited the typical orange color of palladium(II) species; tiny amounts of Pd black were observed only occasionally. It was even possible to perform a second reaction cycle by adding fresh reagents to the solution, although the residual catalytic activity was slightly lower. In one of the filtrates from AO-Pd (entry 4, Table 2) the second Heck coupling of BA occurred with 96% yield after 24 h.

Table 3. Homogeneous Heck reactions promoted by leached palladium species

Entry	Palladium source	Dissolved Pd (mmol)	Coupled aryl halide	Yield (%)[a]
1	PS-Pd (entry 5, Table 2)	0.088	BA[b]	100
2	PS-Pd (entry 4, Table 2)	0.085	BA[b]	100
3	AO-Pd (entry 5, Table 2)	0.011	BA[b]	83
4	AO-Pd (entry 7, Table 2)	0.020	CA[b]	8
5	PS-Pd (entry 7, Table 2)	0.092	CA[b] + BA[c]	95[d]
6	$Pd(OAc)_2$	0.050	BA	80

[a] Reaction conditions: 10 mmol aryl halide, 10 mmol NaOAc, 17 mmol NBA, 25 mL DMA; inert atmosphere (N_2), 120 °C, 3 h. – [b] Residue from leaching tests. – [c] Added to the filtrate. – [d] The yield is referred to BA.

As palladium leaching occurs only in the presence of an aryl halide, it should be the direct consequence of the oxidative addition of the halide to surface atoms of the metal particles. Hence, the palladium should be released in the +II oxidation state, and good coordinating agents towards palladium(II) should enhance the extent of metal leaching. The data of Table 2 show that NaOAc helps the solubilization of palladium in particular when the supposed oxidant is CA, which is less prone to oxidative addition than the analogous bromide. As acetate ions are much better ligands for palladium(II) than for palladium(0), this observation supports our hypothesis that the metal is released into solution in an oxidized form. Accordingly, we argue that the soluble palladium(II) species directly enter the catalytic cycle just after being generated from the supported metal (Scheme 1). Virtually the same cycle was originally proposed by Heck to account for the observed catalytic action of palladium black.[3]



Scheme 1. A possible catalytic cycle for the Heck reaction with Pd metal catalysts

It may be argued that the released palladium(II) species can in principle be reduced just after leaching to form soluble palladium colloids. This was proposed in order to explain “ligandless” catalysis of the Heck reaction by simple palladium(II) salts. Indeed, very recently Reetz has shown that the formation of Pd colloids parallels the onset of the Heck reaction catalyzed by bis(benzonitrile)dichloropalladium(II).[22] However, he also gave experimental evidence that Pd colloids are readily and quantitatively oxidized to palladium(II) species by a *stoichiometric* quantity of an activated aryl halide (iodobenzene). As we employed a 1000:1 excess of aryl halide to the metal, the presence of colloidal palladium under our conditions is very unlikely.

We did not measure the leaching rate in our experiments, but qualitative observations suggest that the accumulation of active palladium(II) species in the solution is a relatively slow process under the conditions employed in this work. This could explain why some authors did not observe significant catalytic activity in the filtrate after removal of the “heterogeneous” catalyst shortly after the onset of the reaction. Furthermore, this hypothesis can also explain the observations of other authors on the influence of the support[15] and of the structure of the Pd particles[21] on catalyst activity. Indeed, if the leaching process is slow, the overall reaction rate can become limited by the leaching process. Since leaching is truly a surface reaction, structure-activity relationships may be expected.

We believe that our results represent strong evidence that “heterogeneous” palladium metal catalysts employed for the Heck reaction are mainly sources of soluble palladium(II) complexes, which are the actual catalytic species (Scheme 1). We have investigated for the first time the mechanism of metal leaching and we have demonstrated that leaching is critically dependent on the presence of the aryl halide; the presence of a coordinating base may have a promoting effect. We have shown that metal leaching takes place not only with the more activated aryl halides such as iodobenzene, but also with bromo- and even chloroarenes, and that the leached species are active catalysts for the Heck reaction.

In conclusion, it seems that the only way to have a catalytic system for this reaction which could be properly defined "heterogeneous" is to devise a support able to coordinate and therefore to heterogenize the palladium(II) and palladium(0) species which occur in the different stages of the reaction cycle. In this area, Arai and co-workers recently reported that some inorganic supports are able to rebind leached Pd species after the end of the reaction.[13] We are currently engaged in the development of novel resin supports for this purpose.

Experimental Section

Preparation of Catalyst PS-Pd: Styrene (8.63 g) and technical grade divinylbenzene (0.65 g) (55% of crosslinking monomers) were dissolved in dimethyl sulfoxide (4 g). After addition of sulfoethyl methacrylate (0.76 g) the solution was exposed to γ-rays (^{60}Co) at 0.5 Gy s^{-1} and at a distance of 21 cm for 72 h at room temp. The obtained resin rod was crushed, extensively washed with methanol, acetone and diethyl ether, vacuum dried and sieved to a particle size of <0.18 mm. Palladium was incorporated by treating 2 g of the resin overnight with a solution of $Pd(OAc)_2$ (43.7 mg) in 40 mL THF, followed by reduction with 10 equivalents $NaBH_4$ in ethanol/THF (4:1). Pd was quantitatively incorporated into the resin as metal nanoparticles with an average size of 3−4 nm (TEM).

General Procedure for the Catalytic Tests: Aryl halide (10 mmol), NaOAc (0.84 g, 10 mmol), catalyst (0.1 g, 0.01 mmol Pd) and *N*,*N*-dimethylacrylamide (25 mL) were mixed at room temperature in a three-necked, round-bottomed flask equipped with a reflux condenser. The resulting mixture was degassed and put under an inert atmosphere (N_2). *n*-Butylacrylate (17 mmol) was added and the flask was put into an oil bath at 120 °C and stirred for 3 h. Yields were determined by GC.

General Procedure for the Leaching Tests: The catalyst (0.1 g) was suspended in *N*,*N*-dimethylacrylamide (25 mL) in a three-necked, round-bottomed flask equipped with a reflux condenser. One or more of the other reaction components was then added (Table 2); the quantity of each component was the same as in the catalytic experiments described above. The resulting mixture was degassed, put under an inert atmosphere (N_2) in an oil bath at 120 °C and stirred for 18 h. The resulting mixture was filtered hot under an inert atmosphere; the missing reaction components were immediately added to the liquid phase, after which the reaction mixture was put again in the oil bath at 120 °C and stirred for the desired reaction time. Yields were determined by GC. The filtered solids were extensively washed with water and acetone and dried under vacuum. The Pd content in the residual solid catalyst was determined, after mineralization, by ICP-AES spectroscopy.

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