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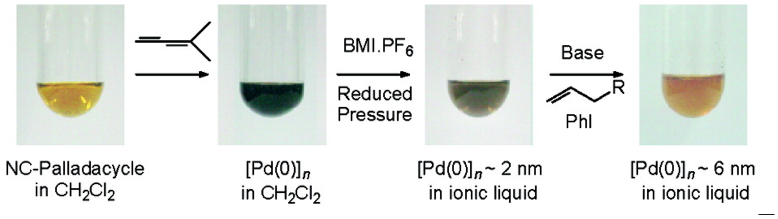
J. Am. Chem. Soc., **2005**, 127 (10), 3298-3299• DOI: 10.1021/ja0430043 • Publication Date (Web): 18 February 2005



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

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The Role of Pd Nanoparticles in Ionic Liquid in the Heck Reaction

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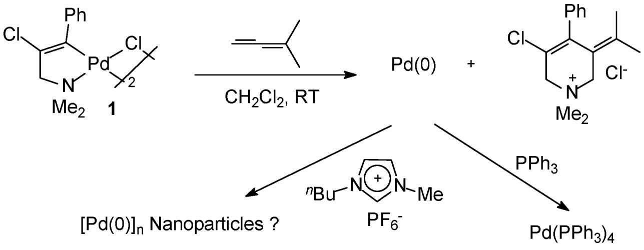
The arylation/vinylation of alkenes promoted by palladium-based catalyst precursors is one of the most investigated transition-metal-catalyzed C−C coupling reactions.[1] The arsenal of procedures involving Pd catalyst precursors, such as those associated with phosphines, carbenes, N-, S-, P-, and Se-containing palladacycles, and even ligand-free approaches, developed over the past few years is impressive.[2,3] In fact, the Heck reaction involving aryl iodides and bromides is promoted by almost any Pd(II) or Pd(0) catalyst precursor, usually at elevated temperatures.[4] In this respect, there are now several indications pointing to, at least in the case of phosphine-free palladium catalyst precursors, the involvement of soluble Pd nanoparticles as a reservoir of catalytically active species.[5] Not surprisingly, there is a profusion of reports on the use of colloidal Pd solutions as catalyst precursors in Heck coupling reactions,[6] but the question of whether the reaction is promoted by the nanoparticles themselves or whether they serve as a reservoir of soluble Pd catalytically active species still remains open.[6,7] Analysis of the metal content in the organic phase at different substrate conversions can provide indications of Pd leaching during the reaction. Transmission electron microscopy (TEM) analysis before and after catalysis can provide information about the modifications in size and shape of the nanoparticles during catalysis.[8] However, it is not possible to perform TEM experiments in situ since the sample must be treated (elimination of the solvents, for example, which may be involved in the stabilization of the nanoparticles) prior to analysis.

Imidazolium ionic liquids provide an excellent medium for the formation and stabilization of transition-metal nanoparticles,[9] and since these ionic fluids have no measurable vapor pressure, the size and shape of the metal nanoparticles can be investigated in situ by TEM.[10] Therefore, the system formed by Pd nanoparticles dispersed in imidazolium ionic liquids might be an ideal candidate for the in situ investigations of the size and shape modifications of Pd nanoparticles during the Heck coupling reaction.[11] We wish to disclose herein our results concerning the in situ TEM analysis of Pd nanoparticles dispersed in 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ($BMI{\cdot}PF_6$) ionic liquid, before and after the arylation of *n*-butyl acrylate, and the Pd leaching from the ionic liquid phase to the organic phase at different substrate conversions.

The first challenge was to prepare stable and ligand-free Pd nanoparticles dispersed in the $BMI{\cdot}PF_6$ ionic liquid.[12] It has been recently reported that the reaction of N-containing palladacycles with allenes affords cationic N-heterocycles and Pd(0) (Scheme 1).[13] The soluble Pd(0) species thus formed are relatively stable and were removed from the organic solution as $Pd(PPh_3)_4$ after treatment with PPh_3. Therefore, this reaction can constitute a source of Pd(0) species, which in the presence of stabilizing agents such as imidazolium ionic liquids, generates stable Pd(0) nanoparticles.

The reaction of palladacycle **1**[14] with a large excess of dimethylallene in dichloromethane at room temperature affords almost immediately a black solution. After being stirred for 15 min at room temperature, the black solution was dissolved in $BMI{\cdot}PF_6$, and the volatiles were removed under reduced pressure. A small amount of this ionic liquid "solution" was transferred to a carbon-coated copper grid and analyzed by TEM (Figure 1, left).

Scheme 1



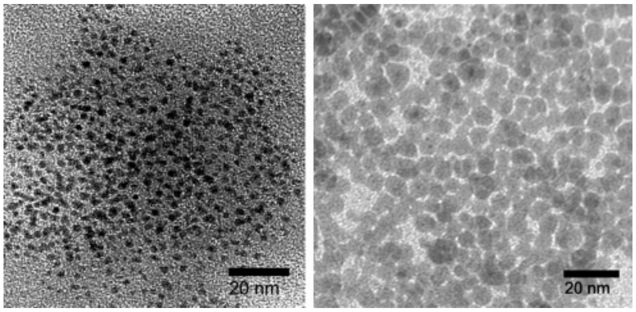


Figure 1. Part of the TEM micrographs showing the Pd nanoparticles dispersed in $BMI{\cdot}PF_6$ ionic liquid before (left) and after (right) catalysis, observed at 200 kV.

The particles display an irregular shape with a monomodal particle size distribution (1.7 ± 0.3 nm). Energy Dispersion Spectrometry confirms the presence of Pd on the sample (Figure S1 in the Supporting Information). Another part of the ionic liquid sample was centrifuged, affording a black powder that was washed with dichloromethane, dried under reduced pressure, and analyzed by X-ray diffraction analysis (XRD). The diffraction line (111) of Pd(0) can be clearly observed in the diffraction pattern (Figure S2 in the Supporting Information).

The catalytic properties of the Pd nanoparticles dispersed in $BMI{\cdot}PF_6$ were tested in the coupling of aryl halides with *n*-butylacrylate at different temperatures (Table 1). First, we tested different bases (NaOAc, $NEt(^iPr)_2$, DABCO, and Na_2CO_3) in the reaction of iodobenzene with *n*-butylacrylate at 80 °C ([PhI]/[Pd] = 1000). A mixture of the aryl halide (1.0 mmol) and *n*-butyl acrylate (1.2 mmol) with the Pd nanoparticles dispersed in 0.5 mL of ionic liquid gave a light-yellow solution in the presence of $NEt(^iPr)_2$ and suspensions in the presence of the other bases. After 14 h, the organic products form an upper phase layer that was extracted with diethyl ether and analyzed by GC (using methyl benzoate as internal standard) and GC−MS.

10.1021/ja0430043 CCC: $30.25 © 2005 American Chemical Society

Table 1. Heck Coupling between *n*-Butylacrylate (1.2 mmol) and Aryl Halides (1.0 mmol) by Pd Nanoparticles Dispersed in BMI·PF_6 (0.5 mL) for 14 h using $NEt(^iPr)_2$ (1.2 mmol)

entry	ArX	[ArX]/[Pd]	*T* (°C)	conversion[a] (%)	yield (%)
1	PhI	1000	30	0	0
2	PhI	1000	80	98	75
3	PhI[b]	1000	80	92	87
4	PhI	1000	100	100	86
5	4-$MeCOC_6H_4Br$	1000	130	98	77
6	4-$MeOC_6H_4Br$	200	130	30	30

[a] Based on PhI consumption. [b] Using 0.2 mL of the ionic liquid.

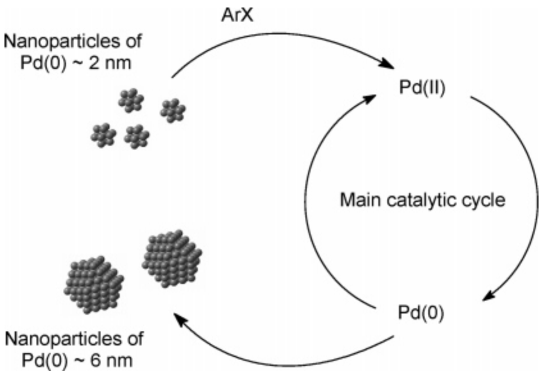


Figure 2. Possible pathways involved in the Heck reaction promoted by Pd nanoparticles dispersed in imidazolium ionic liquids.

Almost complete iodobenzene conversion was observed in the reaction experiment performed with $NEt(^iPr)_2$, whereas only <30% conversion was attained with the other bases. A small portion of the ionic liquid phase after the coupling reaction described in Table 1, entry 2, was placed in a carbon-coated copper grid and analyzed by TEM (Figure 1, right).

The Pd nanoparticles dispersed in the ionic liquid after the reaction display an irregular shape with a monomodal size distribution of 6.1 (±0.7) nm.

The palladium content in the organic phase during the arylation reaction was checked by ICP-AS and shows significant metal leaching from the ionic phase to the organic phase at low substrate conversions (34 and 12% at 3 and 11% iodobenzene conversion, respectively) and drops to 5−8% leaching at higher conversions (>60%). A similar trend was recently observed in Heck reactions promoted by a heterogeneous catalyst precursor where it was proposed that Pd dissolution and reprecipitation are inherent parts of the catalytic cycle.[15]

The TEM and ICP-AS results are strong indications that Pd nanoparticles dispersed in the ionic liquid act as a reservoir of catalytically active Pd species (Figure 2). The recovered organic phase extracted with diethyl ether after 4 h (containing around 25% Pd) is inactive for the coupling of PhI and *n*-butylacrylate in the presence of $NEt(^iPr)_2$ at 80 °C after 20 h. Moreover, attempts to identify Pd nanoparticles in the organic phase by TEM analysis have been unsuccessful so far. Thus, it is highly probable that the reaction proceeds through the oxidative addition of PhI on the nanoparticles surface, and the oxidized Pd species thus formed are detached from the surface and are entering in the main catalytic cycle. The Pd(0) formed in the main catalytic cycle, after β-hydride and reductive elimination steps, can either continue in the catalytic cycle or fall back to the nanoparticles reservoir. Moreover, these results are in line with the de Vries propositions for the ligand-free Pd catalysts in Heck coupling reactions.[3]

In summary, we have demonstrated that imidazolium ionic liquids are the media of choice for the in situ investigations of the changes in shape and in size of colloidal Pd catalysts. Further in situ investigations employing EXAFS in the Heck reaction promoted by Pd nanoparticles dispersed in imidazolium ionic liquids are under investigation in our laboratory.

Acknowledgment. Thanks are due to FAPERGS, CNPq, and CTPETRO for financial support, and CAPES for scholarships.

Supporting Information Available: Experimental procedure, XRD, and EDS spectra of the Pd nanoparticles. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA0430043