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Palladium Nanoparticles Stabilized by an Ionic Polymer and Ionic Liquid: A Versatile System for C−C Cross-Coupling Reactions

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Highly stable palladium nanoparticles (Pd NPs), protected by an imidazolium-based ionic polymer (IP) in a functionalized ionic liquid (IL), have been prepared and characterized by transmission electron microscopy (TEM). These Pd NPs are excellent precatalysts for Suzuki, Heck, and Stille coupling reactions and can be stored without undergoing degradation for at least 2 years. The NP−IP−IL system may therefore be considered as an alternative to the traditional palladium on carbon (Pd/C) precatalyst employed in many C−C coupling reactions, also allowing reactions to be conducted under "solvent-free" conditions.

Introduction

Palladium nanoparticles and complexes are the most useful catalyst precursors in organic process such as C−C or C−N coupling reactions.[1] In C−C coupling reactions, the active catalyst corresponds to mononuclear Pd(0) species, which undergo oxidative addition with the substrate to form Pd(II) intermediates, although the identity of the true catalyst often remains elusive.[2–4] According to such a mechanism, palladium metal, supported on finely divided inorganic salts such as carbonates, zeolites or on carbon structures, represent good precatalysts. Therefore, many solid palladium catalysts have been prepared and evaluated in coupling reactions.[1] While these solid catalysts are highly convenient to use, high catalyst loadings are generally required, typically between 5 and 10 mol %.[5] These materials are also incompatible with certain solvents and with certain substrates. Finally, commercially available palladium catalyst reservoirs such as palladium on carbon (Pd/C), palladium on calcium carbonate (Pd/$CaCO_3$), palladium strontium carbonate (Pd/$SrCO_3$), and palladium titanium oxide (Pd/TiO_2) are prepared using concentrated acids and generate a lot of waste which is not ideal from an environmental perspective.

One approach to overcome these disadvantages associated with palladium immobilized on solid supports is to prepare nanosized palladium particles suspended in organic solvents or aqueous solutions, enhancing catalytic activity due to increased surface area and rotational degrees of freedom.[6] A plethora of palladium nanoparticles (Pd NPs) with different topologies have been prepared and their catalytic activities have been investigated. In general, the larger the surface area (i.e., the samaller the size of the NP), the greater the catalytic activity.[7] Thus, smaller NPs are preferable, although they tend to be less stable and are prone to aggregation ultimately leading to less effective catalysts.[8] In order to obtain the optimum balance between stability and reactivity, polymers such as polyvinylpyrrilidone (PVP), polyvinyl alcohol (PVA), and copolymers have been used as stabilizers for Pd NPs. However, the solubility properties of the polymers and copolymers can cause problems, such that immobilization of polymer stabilized Pd NPs is not always ideal. Ionic polymers (IPs) present a different set of solubility parameters

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compared[9–11] to conventional polymers and can be structurally tuned to influence metal–polymer or metal−counterion interactions.[12] A number of imidazolium-based polymers have been reported,[10,11,13–15] including poly(3-(4-vinylbenzyl)-1-methylimidazolium chloride, an excellent stabilizer for metal NPs.[16]

Ionic liquids (ILs) have been widely studied as alternative solvents for C−C coupling reactions, and it is now well established that ILs are able to stabilize metal NPs.[17] The Tf_2N^- anion appears to provide an optimum balance between stability and catalytic activity in C−C coupling reaction employing NPs as catalyst reservoirs.[18] The nature of the IL cation markedly influences the stability of NPs, and active catalytic species generated from them, with weakly coordinating functional groups attached to the cation–offering some advantages in C−C coupling reactions.[19,20]

In this paper, we describe an all-in-one system comprising Pd NP catalyst resevoirs, protected with an ionic imidazolium-based polymer, immobilized in a functionalized IL. The system is highly stable toward aggregation for prolonged periods, may be used directly for C−C coupling reactions at relatively low catalyst loadings, and can be viewed as an alternative to Pd/C and other heterogeneous Pd-based catalysts.

Results and Discussion

Poly(3-(4-vinylbenzyl)-1-methylimidazolium bis(trifluoromethylsulfonyl)imide) **1** (Figure 1) is obtained from the parent polymer chloride by anion exchange with lithium bis(trifluoromethylsulfonyl)imide ($LiTf_2N$). The ionic polymer (IP) **1** is insoluble in water, but soluble in commonly used ionic liquids, especially those composed of the bis(trifluoromethylsulfonyl)imide [Tf_2N] anion, and also polar organic solvents such as acetonitrile and acetone.

Mixing an acetonitrile solution of IP **1** with the nitrile functionalized IL **2** (Figure 1),[21] followed by removal of the acetonitrile under vacuum, affords a viscous solution, termed IP−IL, although at ≤1% (w/w) IP **1** the viscosity of the IP−IL solution is relatively low (see Experimental Details). Due to the presence of the weakly coordinating nitrile group attached to the IL cation $PdCl_2$ readily dissolves in the IP−IL solution. Reduction of the dissolved $PdCl_2$ in IP−IL with $NaBH_4$, followed by washing with water and drying under vacuum, affords a black solution containing NPs, i.e. NP−IP−IL. Under the conditions employed (see Experimental Details for full details), transmission electron microscopy (TEM) analysis reveals that the Pd NPs have an average size of 5.0 ± 0.2 nm (Figure 1). The NPs are remarkably stable, having been stored in our laboratory without any special precautions to exclude air or moisture for ca. 2 years, without undergoing aggregation or precipitation. The NP−IP−IL solution is inert to moisture and consequently is easy to use by extracting the required amount with a syringe.

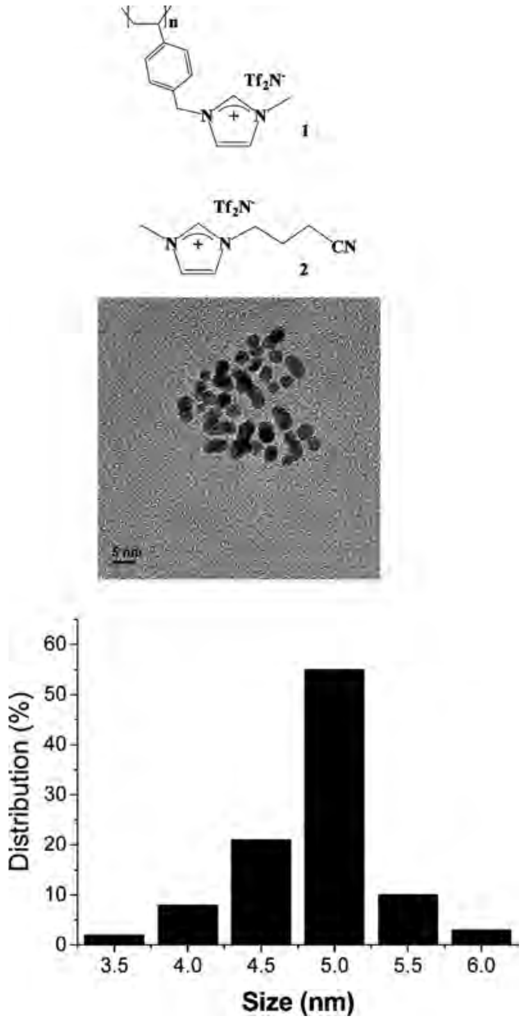

Figure 1. Ionic polymer **1**, ionic liquid **2**, TEM image of the Pd NPs in NP−IP−IL (scale bar = 5.0 nm), and histogram showing the particle size distribution.

In order to demonstrate the utility of the NP−IP−IL solution it was evaluated in a selection of C−C cross-coupling reactions including Suzuki, Heck, and Stille reactions. The Suzuki reaction[22] is one of the most investigated reactions in ionic

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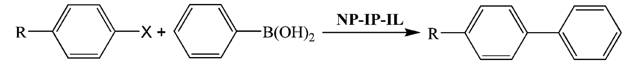
Table 1. Suzuki Coupling Reactions Using NP−IP−IL as Catalyst and Solvent[a]



entry	aryl halide	time (h)	yield (%)
1	R = H, X = Br	6	55
2	R = H, X = I	6	90
3[b]	R = CN, X = Br	6	98
4[b]	R = CN, X = I	2.5	>99
5[b]	R = NO_2, X = Br	6	99
6[b]	R = NO_2, X = I	2.5	>99
7	R = OMe, X = Br	6	6
8	R = OMe, X = I	6	82
9[c]	R = COOH, X = Br	10	57
10[c]	R = COOH, X = I	10	>99
11[d]	R = H, X = I	6	46
12[e]	R = H, X = I	6	83

[a] Conditions: a mixture of aryl halide (0.5 mmol), phenylboronic acid (0.55 mmol), and Na_2CO_3 (1.05 mmol in 0.5 mL H_2O), concentration of palladium (1.0 mol %) based on aryl halide in NP−IP−IL (1.0 mL) with concentration of polymer (0.5 w/w %) based on IP−IL at 100 °C, analyzed by GC using biphenyl as external standard. [b] Concentration of palladium (0.5 mol %) based on aryl halide. [c] Concentration of Pd NPs (0.5 mol %) based on aryl halide without any IL or polymer, Na_2CO_3 (1.05 mmol in 2.5 mL H_2O), at 35 °C, analyzed using ^{1}H NMR using a literature method.[27] [d] Conditions as described in footnote *a*, but using palladium nanoparticles prepared in IL **2** by reduction with $NaBH_4$ in the absence of the IP **1**. [e] Conditions as described in footnote *a*, $PdCl_2$ as catalyst in IP−IL without prior reduction with $NaBH_4$.

liquids. Welton and co-workers showed that $Pd(PPh_3)_4$ in 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]) gives high yields in short reaction times.[23] Subsequently, they found that mixed phosphine-imidazolylidene palladium complexes formed in situ, which probably corresponds to the active catalyst.[24] Shreeve and co-workers demonstrated that a hemilabile pyrazolyl-functionalized *N*-heterocyclic carbene palladium(II) complex has high catalytic activity in Suzuki cross-coupling reactions in [bmim][PF_6]. The excellent catalytic activity of the complex was attributed to the presence of the strong Pd(II)–carbene bond and the weak Pd(II)–nitrogen bond;[25] the weak coordination of the pyrazolyl nitrogen facilitating the formation of Pd(0) and subsequent oxidative addition of substrates during catalysis. We have shown that nitrile functionalized ILs not only stabilize Pd NPs, but also Pd(II) species released into solution following oxidative addition.[20] Thus, the catalytic activity of the NP−IP−IL solution was evaluated in a series of Suzuki coupling reactions. Using 1.0 mol % NP−IP−IL solution excellent yields of various biphenyl products were obtained (see Table 1). The activity is superior to that using the NP−IL solution in the absence of IP **1** (90 versus 46% conversion, respectively, in the coupling of iodobenzene under equivalent conditions, cf. Table 1, entries 2 and 11). In addition, if the palladium salt precursor dissolved in IP−IL is not reduced to NPs the yield is slightly lower (Table 1, entry 12), presumably due to the precursor being in a less active form. The NP−IP−IL system also compares very favorably with reactions conducted in [bmim][Tf_2N] containing 2 mol % of a palladium carbene precatalyst.[26]

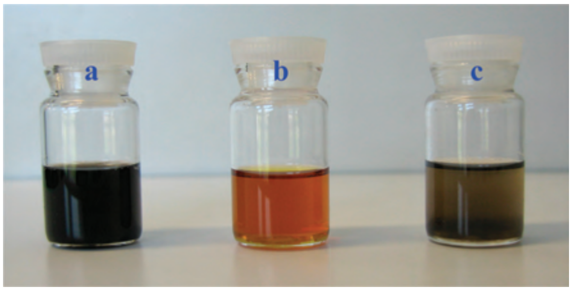


Figure 2. NP−IP−IL (a) before reaction, (b) after reaction with 1-iodo-4-nitrobenzene, and (c) after reaction with 1-bromo-4-nitrobenzene.

The activity of the NP−IP−IL solution was also investigated in water using benzoic acid derivatives in combination with phenylboronic acid since both reactants are water soluble. In water the palladium loading can be reduced and reactions proceed at ambient temperatures (Table 1, entries 9 and 10).

It has previously been noted that the color of IL solutions containing NPs may change during catalysis.[28,29] The original black color of the NP−IP−IL system (Figure 2a) becomes orange following reaction of aryl iodide substrates at 100 °C (Figure 2b). With aryl bromides decomposition is observed (Figure 2c). The change in color to orange indicates that the initial Pd NPs are converted to Pd(II). Oxidation of Pd NPs during C−C coupling has been reported previously;[8,31] however, the isolation and characterization of the Pd(II) species is not a trivial task.

UV–vis spectrophotometry indicated that Pd(II) species had indeed formed (see below), but we were unable to establish the nature of the Pd(II) species directly in the IL. Thus, Pd NPs were extracted from the NP−IP−IL solution and evaluated as precatalysts in the coupling reaction between 1-iodo-4-nitrobenzene and phenylboronic acid in DMF using triethylamine base. Upon completion of the reaction a deep orange colored solution had formed. Removal of the solvent followed by washing with diethyl ether gave a deep-red solid. The ESI-MS spectrum of this material in acetonitrile displays peaks at *m*/*z* 386 and 487 in negative ion mode, representative of $[Pd(CN)I_2]^-$ [30] and

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(26) Suzuki reactions with yields >90% can be obtained at 100 °C within 2.5 h, although a high concentration of a palladium (2 mol %) has to be used. See Liu, S.; Fukuyama, T.; Sato, M.; Ryu, I. *Synlett* **2004**, *10*, 1814.

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(30) It is known that the C−C bond in acetonitrile can be cleaved to form CN^- species in the ESI-MS experiment using acetonitrile as solvent. As an example, if PdI_2 is dissolved in acetonitrile, the main peak in the ESI-MS (negative ion mode) is observed at *m*/*z* 386 which corresponds to $[Pd(CN)I_2]^-$. The C−C bond in acetonitrile can be also cleaved by palladium carbene complex. See Liu, Q.-X.; Xu, F.-B.; Li, Q.-S.; Song, H.-B.; Zhang, Z.-Z. *Organometallics* **2004**, *23*, 610.

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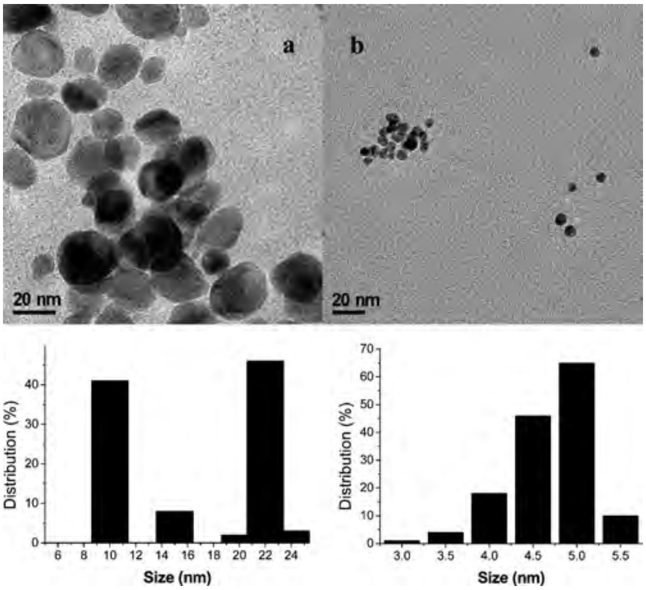
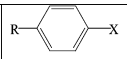


Figure 3. (top) TEM images of the Pd NPs present in (a) NP−IP−IL−**2** and (b) in NP−IP−IL−**2** following catalysis and (bottom) histograms showing the particle size distribution in parts a and b.

Table 2. Suzuki Coupling between Aryl Halide and Phenylboronic Acid Using NP−IP−IL−**2**[a]

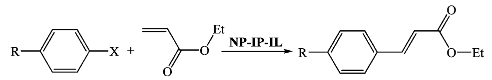
Entry		Time (h)	Yield (%)
1	R = CN, X = Br	6	27%
2	R = CN, X = I	2.5	97%
3	R = NO_2, X = Br	6	33%
4	R = NO_2, X = I	2.5	97%

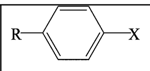
[a] Conditions: a mixture of aryl halide (0.5 mmol), phenylboronic acid (0.55 mmol), and Na_2CO_3 (1.05 mmol in 0.5 ml H_2O), concentration of palladium (1.0 mol %), based on aryl halide in NP−IP−IL−**2** (1.0 ml) was heated 100 °C for the appropriate time. The product was extracted with diethyl ether and analyzed by GC using biphenyl as the external standard.

$[PdI_3]^-$. The origin of these Pd(II) fragments might be from $[(Et_3NH)]_2[Pd_2I_6]$, previously shown to form in Heck reactions operating under similar conditions.[31]

Larger Pd NPs ranging in diameter from 10 to 22 nm (Figure 3) were prepared using a seeding growth method,[32,33] affording a solution termed NP−IP−IL−**2**. The NP−IP−IL−**2** solution was used in coupling reactions between activated aryl iodides and phenylboronic acid, with comparable yields to those using NP−IP−IL (Table 2). However, in reactions of aryl bromides the yields are significant lower under the same conditions. Examination of the NP−IP−IL−**2** phase after reaction (from entry 4, Table 2) by TEM reveals that the Pd NPs has decreased in size to ca. 5.0 nm. The decrease in size the Pd NPs is due to the rapid formation of the homogeneous (mononuclear) catalyst from the NP reservoir, with mononuclear Pd(II) species persisting after catalysis is complete.

Table 3. Heck Reaction C−C Coupling Reactions Using NP−IP−IL[a]



Entry		Time (h)	Yield (%)
1	R = H, X = I	4	81
2	R = H, X = I	1.5	49
3	R = CN, X = I	2	>99
4	R = NO_2, X =I	2	>99

[a] Conditions: a mixture of aryl halide (1.0 mmol), ethyl acrylate (1.5 mmol, 1.5 equiv), tributylamine (1.5 mmol, 1.5 equiv), and Pd (0.5 mol %) based on aryl halide in NP−IP−IL (1.0 ml) with a concentration of polymer (0.5 w/w %) based on the IL at 80 °C. After the appropriate reaction time, the product was extracted by diethyl ether and analyzed by GC using biphenyl as external standard.

Heck reactions have also been extensively studied in ionic liquids. For example, Xiao and co-workers reported Heck reactions in [bmim]Br and observed the in situ formation of *N*-heterocyclic carbene complexes[34] Hagiwara and co-workers reported Heck reactions catalyzed by Pd/C in $[bmim][PF_6]$.[35] With high catalyst loadings high yields could be obtained with aryl iodides in short reaction times, although aryl bromide substrates gave comparatively low yields. Dupont and co-workers reported an in-depth study of the role of Pd nanoparticles in the Heck reaction performed in $[bmim][PF_6]$. It was found that Pd NPs with a diameter of ca. 1.7 nm aggregate to form larger nanoparticles (ca. 7.0 nm).[36] We have shown that nitrile-functionalized ILs are excellent solvents for Heck-type reactions based on Pd NPs and can lead to increased yields at reduced reaction times compared to reactions in DMF.[37] Similarly, the Heck reaction between aryl iodides and ethyl acrylate proceeds in NP−IP−IL (Table 3). With activated aryliodides quantitative yields can be reached within 2 h. As we observed in Suzuki reactions, after reaction the solution is orange and Pd(II) is present in solution (see below).

Stille cross-coupling reactions[38] were also carried out using the NP−IP−IL solution as catalyst and solvent. It has already been shown that the Stille reaction can be performed in $[bmim][BF_4]$ with high palladium loadings in the presence of $AsPh_3$ base. Chiappe and co-workers reported ligandless Stille reactions between iodobenzene and tributylvinylstanne in different ILs.[39] We have also shown that nitrile functionalized ILs are excellent media for Stille reactions with Pd NPs being observed in some instances depending on the IL used.[18,20]

The NP−IP−IL system is effective for Stille coupling of all aryl iodide and activated aryl bromide substrates (Table 4). Notably, the NP−IP−IL system gives higher yields than the corresponding reaction using the pyridinium based ionic

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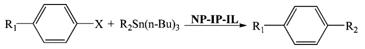
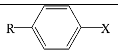
Table 4. Stille Reaction C−C Coupling Reactions Using NP−IP−IL[a]



Entry		R$_2$Sn(n-Bu)$_3$	Time (h)	Yield (%)
1	R$_1$ = H, X = I	R$_2$ = phenyl	4	74
2	R$_1$ = NO$_2$, X =I	R$_2$ = phenyl	2	100
3[b]	R$_1$ = NO$_2$, X =I	R$_2$ = phenyl	4	45
4	R$_1$ = H, X = I	R$_2$ = vinyl	4	96
5	R$_1$ = H, X = Br	R$_2$ = vinyl	4	10
6	R$_1$ = NO$_2$, X = I	R$_2$ = vinyl	2	100
7	R$_1$ = CN, X = I	R$_2$ = vinyl	2	100
8	R$_1$ = NO$_2$, X = Br	R$_2$ = vinyl	4	100
9	R$_1$ = CN, X = Br	R$_2$ = vinyl	4	35
10	R = NO$_2$, X = Cl	R$_2$ = vinyl	4	0

[a] Conditions: a mixture of aryl halide (1.0 mmol), organostannane (1.2 mmol, 1.2 equiv), and Pd (0.5 mol %) based on aryl halide in NP−IP−IL (1.0 ml) with polymer (0.5 w/w %) based on IL at 80 °C. The product was extracted with diethyl ether and analyzed by GC using biphenyl as external standard. [b] Temperature = 45 °C.

liquid *N*-butyronitrile pyridinium bis(trifluoromethylsulfonyl)imde, [C$_3$CNpy][Tf$_2$N], bearing the same nitrile functionality with PdCl$_2$ as catalyst precusor at 80 °C for 12 h.[19] In the NP−IP−IL system containing 0.5 mol % of palladium, biphenyl was obtained in 74% yield after 4 h at 80 °C (Table 4, entry 1), while in IL [C$_3$CNpy][Tf$_2$N] with a palladium loading of 5 mol % a yield of 63% was obtained under the same conditions.[19] Furthermore, for activated aryl iodides near quantitative yields can be reached under equivalent conditions.

On the basis of our experiments, we assume that the C−C coupling reactions using NP−IP−IL follows the classic mechanism.[3,4] In all cases, the first step involves oxidative addition of the aryl halide to the zerovalent palladium on the NP surface, leading to the formation of Pd(II) species that are solubilized and stabilized in the IL. The UV–vis spectrum of the original NP−IP−IL solution contains a major peak at 215 nm corresponding to the absorptions of the arene ring in the polymer, the absorption of the Pd NPs is usually in this region but is very week and therefore cannot be distinguished (Figure 4). After the Suzuki and Heck reactions a peak around 250 nm is observed indicating the presence of Pd(II) species. After the Stille reaction Pd(II) species are hardly detectable although after six recycles a very weak absorbance indicative of Pd(II) is present.

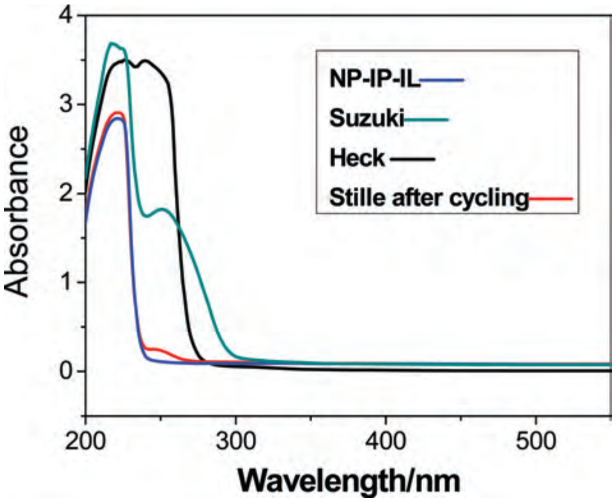


Figure 4. UV–vis spectra of NP−IP−IL before and after reaction in Suzuki, Heck, and Stille reactions (after six cycles in the case of the Stille reaction).

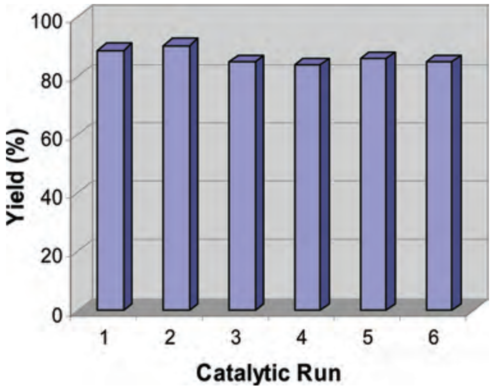


Figure 5. Recycling of the NP−IP−IL for Stille reaction between tributylvinylstannane and iodobenzene. Conditions are the same as those given in Table 4 with a reaction time of 4 h.

Recycling experiments using NP−IP−IL were investigated with the Stille reactions since these were shown to reform NPs following catalysis. The NP−IP−IL system could be recycled five times with essentially no loss in activity (Figure 5). Inductively coupled plasma spectroscopy (ICP) was used to analyze the organic fractions after catalysis for palladium content and it was found the palladium concentrations was below the detectable limit of 1 ppm. Recycling was also possible for Suzuki reactions although a slight decrease in yield was observed after each cycle (ca. 1%).

In conclusion, we have prepared an "all-in-one" system containing Pd NPs and IL as catalyst and solvent, respectively, that incorporates an IP which provides both long-term stability during storage and increased reactivity during catalysis. While ILs have been shown to be good solvents for direct stabilization of NPs,[17] it is clear from this work that stabilizer additives further enhance the properties and performance of NPs in ILs.

The NP−IP−IL system catalyzes the coupling of aryliodides efficiently, and to some extent arylbromide, but is inactive for aryl chloride substrates. Compared to Pd/C systems that typically require Pd loadings of 2–5 mol %,[18–20,23,26] lower loadings of 0.5–1.0 mol % can be employed using the NP−IL−IL system. Thus, the NP−IP−IL represents an economic approach to active palladium catalysts which have been previously obtained using more complicated synthetic methods, and overall, the NP−IP−IL system can be considered as an altanative for traditional precatalyst such as Pd/C due to its robust nature, water stability, and good activity.

Experimental Details

General Remarks. All chemicals were purchased from Aldrich and used without further purification. The ionic polymer, poly(1-methyl-3-(4-vinylbenzyl)imidazolium chloride), was prepared according to a literature method.[40] NMR spectra were measured on a Bruker DMX 400, using Me_4Si as an external standard at 20 °C. Electrospray ionization mass (ESI-MS) spectra for synthesized compounds were recorded on a Thermo Finnigan LCQ Deca XP Plus quadrupole ion-trap instrument using a literature protocol.[41] UV–vis spectra were recorded in quartz cells using a Jasco V-550 spectrophotometer at 25 °C. IR spectra were recorded on a Perkin-Elmer FT-IR 2000 system. GC analyses were carried out on a Varian Chrompack CP-3380 equipped with a capillary column (25 m × 0.25 mm, using N_2 as carrier gas). Viscosities were measured with a Brookfield DV-II+ viscometer on 0.50 mL of sample. The temperature of the samples was maintained to 21 °C by means of an external temperature controller. Inductively coupled plasma spectroscopy was conducted using a Perkin-Elmer Optima 2000DV instrument. Intensities of spectral lines at 340.458 nm were measured in all samples and standards. The palladium level in the sample was determined by comparing the intensity of the spectral line with the palladium standards.

Preparation of Ionic Polymer 1. $LiTf_2N$ (2.87 g, 10 mmol) was added to poly(1-methyl-3-(4-vinylbenzyl)imidazolium chloride) (2.35 g, 10 mmol) in water (10 mL). The mixture was stirred at room temperature for 24 h during which time a solid formed. The solid was collected by filtration, washed with water (2 × 5 mL) and dried under vacuum to afford the product. Yield: 91%. ^1H NMR (CD_3CN): 8.20 (1 H, s), 7.55 (1 H, br), 7.53 (1 H, br), 7.34 (2 H, br), 7.02 (2 H, br), 6.86 (1 H, m), 5.23 (3 H, br), 3.43 ppm (3 H, br). FTIR: ν (cm^{-1}) 3023 (C—H aromatic), 2920 (C—H alkyl), 1611 (C═C aromatic).

Preparation of IP—IL. Ionic polymer **1** (0.24 g) was dissolved in acetonitrile (50 mL) over a period of 8 h at RT. IL **2** (48 g) was then added in one portion and it was stirred for additional 2 h. Removal of the acetonitrile under vacuum afforded the IP—IL solution. The viscosity of IP—IL with the polymer **1** concentration of 0.5% (w/w) is 185 cP; If the concentration of the polymer is 1:100 (w/w), the viscosity of the resulting gel is 600 cP (the viscosity of pure IL **2** is 160 cP; see reference 21).

Preparation of NP—IP—IL. $PdCl_2$ (0.15 mmol) was added to IP—IL (30 mL) at RT, the reaction mixture was stirred for 2 h at 80 °C during which time an orange solution formed. After cooling to RT, $NaBH_4$ (0.8 mmol) was added. The reaction mixture was stirred at RT for 24 h, washed with water (2 × 6 mL) and dried under vacuum to afford a black solution containing Pd NPs with diameter 5.0 nm.

Preparation of NP—IP—IL—2. $PdCl_2$ (0.25 mmol) was added to a mixture of NP—IP—IL (10 mL) at RT, and the reaction mixture was stirred for 2 h at 80 °C. After cooling to RT, $NaBH_4$ (0.8 mmol) was added. The reaction mixture was stirred at RT for 24 h, washed with water (2 × 6 mL) and dried under vacuum to afford a black solution containing Pd NPs with diameter 16.0 nm. The thus obtained black solution (1.0 mL) was diluted in pure IL **2** (5.0 mL) affording the NP—IP—IL—**2**.

Suzuki Coupling Reactions. To a 10 mL two-necked flask fitted with a septum and reflux condenser, aryl halide (0.5 mmol, 1 equiv) was mixed with NP—IP—IL (1 mL). Next, phenylboronic acid (0.55 mmol, 1.1 equiv), Na_2CO_3 (112 mg, 1.05 mmol, 2.1 equiv), and water (0.5 mL) were added. The mixture was heated to 100 °C and stirred vigorously. After reaction, the mixture was cooled and the product was extracted with diethyl ether (3 × 5 mL). The combined extracts were washed with brine and water (3 × 5 mL) and dried with $MgSO_4$ overnight. The extract was filtered and evaporated to dryness and the products were analyzed by GC and ^1H NMR.

Stille Coupling Reactions. To a 10 mL two-necked flask fitted with a septum and reflux condenser, aryl halide (1.0 mmol, 1 equiv) and organostannane (1.2 mmol, 1.2 equiv) were mixed with NP—IP—IL (1.0 mL). The mixture was heated to 80 °C and stirred vigorously. After reaction the mixture was cooled and the product extracted with diethyl ether (3 × 5 mL). The combined extracts were washed with brine and water (3 × 5 mL) and dried with $MgSO_4$ overnight. The extract was filtered and evaporated to dryness and the products were analyzed by GC. Prior to reuse NP—IP—IL was washed with diethyl ether (3 × 5 mL) and placed under vacuum for 18 h. Samples for ICP analysis was prepared according to a literature method.[42] In brief, the combined diethyl ether extracts (15 mL) were evaporated to dryness, 65% HNO_3 (10 mL) and 37% HCl (30 mL) were added to the residue. The mixture was heated for 5 h. After removal of the solvent, the residue was added to perchloric acid (10 mL, 71%). The mixture was stirred at reflux for 3 h and evaporated to dryness again. The residue was dissolved in 10 mL of 2% HNO_3 aqueous solution for analysis.

Heck Coupling Procedure. To a 10 mL two-necked flask fitted with a septum and reflux condenser, aryl halide (1.0 mmol, 1 equiv), ethyl acrylate (1.5 mmol, 1.5 equiv), and tributylamine (1.5 mmol, 1.5 equiv) were mixed with NP—IP—IL (1 mL). The mixture was heated to 80 °C and stirred vigorously. After reaction the mixture was cooled to RT and the products extracted with diethyl ether (3 × 5 mL). The combined extracts were washed with brine and water (3 × 5 mL) and dried with $MgSO_4$. The extract was filtered and evaporated to dryness and the products were analyzed by GC.

TEM Sample Preparation. A sample (0.1 mL) of NP—IP—IL (or NP—IP—IL—**2**) was diluted in acetone (1.0 mL), and the suspension was deposited on a carbon coated copper grid (500 mesh) and dried at ambient temperature. TEM images were obtained on a PHILLIPS CM 20 transmission electron microscope. The size distribution is estimated from measuring 200 particles.

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