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Phosphane-Free Hiyama Cross-Coupling of Aryl and Heteroaryl Halides Catalyzed by Palladium Nanoparticles in Ionic Liquids

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Palladium nanoparticles (NPs) 2–5 nm in size and preformed by thermal reduction in nitrile-functionalized 3-(3-cyanopropyl)-1-methyl-1*H*-imidazol-3-ium hexafluorophosphate {[CN-bmim]PF_6} act as an in situ catalyst for carbon–carbon bond-forming reactions of aromatic and heterocyclic halides with aryl- and vinyltrimethoxysilanes. A variety of biphenyl derivatives, substituted styrenes, and aromatic heterocycles were obtained in 76 to 98 % yield. We demonstrate for the first time the use of 1-butyl-3-methylimidazolium fluoride as an activator of the organosilanes with easy handling, storage, and workup in comparison to conventional fluorine sources such as tetrabutylammonium fluoride, which is indispensable for Hiyama coupling. Pd NPs immobilized in [CN-bmim]PF_6 gave high yields of the cross-coupled products at a low catalyst loading of only 4 mol-%, and the catalyst could be reused and recycled up to four times with only a slight loss in catalytic activity.

Introduction

Palladium-catalyzed cross-coupling reactions have emerged as a powerful tool for the construction of carbon–carbon and carbon–heteroatom bonds, especially for pharmaceuticals and agrochemicals.[1] Common catalysts such as $Pd(PPh_3)_4$ and precatalysts such as Pd–carbene complexes, phosphane–palladacycles, and Pd salts in the presence of an excess amount of PPh_3 are increasingly used in Heck and Suzuki reactions.[2] Phosphane and non-phosphane ligands stabilize Pd^0 and influence its catalytic activity in cross-coupling reactions with zinc-, boron-, tin-, and silicon-containing organometallics.[3] Of these materials, organosilanes as transmetalation reagents offer numerous advantages over organoboranes and organostannanes in terms of their low cost, ready availability, low toxicity, easy workup, and chemical stability.[4] Also, silicon waste generated from a reaction can be converted into harmless SiO_2 by facile incineration, and all of these points have made Hiyama coupling attractive from environmental and user-friendly points of view.[5] Hiyama coupling, as other coupling reactions, has been achieved by the combined use of a homogeneous Pd catalyst and a phosphane or an N-heterocyclic carbene ligand derived from an imidazolium salt.[6] Several of these ligands happen to be air and moisture sensitive, difficult to prepare, and expensive. Thus Pd catalysis by a ligand-free system is the simplest and cheapest alternative to these reactions. Recently, a few ligand-free Hiyama coupling reactions performed with homogeneous Pd catalysts such as $PdCl_2$, $Pd(OAc)_2$, and palladacycles or heterogeneous Pd nanoparticles (NPs), which are not commercially available, have been reported.[7] In a review, Reetz and de Vries suggested that the use of homeopathic doses of palladium (0.01–0.1 mol-%) could successfully promote a ligand-free Heck reaction with aryl iodides and bromides.[8] It was rationalized that low Pd concentrations suppress the formation of Pd black and keep all the metal available for catalysis.

The only limitation is that at low Pd concentrations the reaction proceeds slowly, whereas at higher concentrations Pd black is rapidly formed. However, in either case coupling does not occur with aryl chlorides. The existence and role of Pd NPs has been established in the Jeffery system, wherein tetraalkylammonium halides stabilize nanosized Pd colloids (1–5 nm) generated from $Pd(OAc)_2$ (5 mol-%) by forming a monomolecular layer around the metal core, which thereby prevents undesirable agglomeration and promotes phosphane-free Pd catalysis.[9] Ever since their inception, catalysis by Pd NPs has gained considerable attention owing to their high surface-to-volume ratio, which facilitates high turnover frequencies at low catalyst loadings, and this makes the overall process more economical and viable for industrial use.[10] NPs, however, are thermodynamically and kinetically unstable compared to the bulk material; hence, some kind of stabilization by way of polymers, surfactants, or dendrimers needs to be provided to prevent coalescence of the particles.[11] Dupont and co-workers demonstrated the preparation of transition-metal NPs from ionic liquids (ILs) without the use of additional stabilizers either by thermal decomposition of an organometallic precursor or by reduction of the precursor with hydrogen.[12] It has been

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proposed that ILs form preorganized structures as a result of cooperative hydrogen bonding between the cation and the anion, and this induces structural directionality and provides electrosteric stabilization to the NPs.[13] Although Pd-NP-catalyzed Heck, Suzuki, and Sonogashira couplings in imidazolium-based ILs have been reported, there have been no reports on IL-stabilized Pd NPs for Hiyama coupling.[14]

Herein, we report the catalytic activity of Pd NPs starting from a Pd^{II} precursor in 3-(3-cyanopropyl)-1-methyl-1*H*-imidazol-3-ium hexafluorophosphate {[CN-bmim]PF_6} for the Hiyama coupling of trimethoxyaryl- and vinylsilanes with aryl and heterocyclic halides in the presence of 1-butyl-3-methylimidazolium fluoride {[bmim]F} as the activator. The procedure accommodates various functional groups to yield a diverse range of biphenyl derivatives, substituted styrenes, and aromatic heterocycles. The method offers distinct advantages over conventional methods of coupling, as it occurs with a reusable nanocatalytic system and a highly convenient-to-handle silane activator, it is versatile in terms of substrate scope, the reaction is cleaner, and the products are obtained in high yields. To the best of our knowledge, this is the first example demonstrating the use of IL-stabilized Pd NPs as a catalyst for Hiyama cross-coupling reactions under phosphane-free conditions.

Results and Discussion

The ILs [CN-bmim]PF_6 (**1**), [bmim]F (**2**), and 1-butyl-3-methylimidazolium acetate {[bmim]OAc} (**3**) were synthesized by reported methods (Figure 1).[15] IL **1** was synthesized by a two-step procedure by heating 4-bromobutyronitrile with 1-methylimidazole at reflux. This resulted in the formation of viscous, yellow 3-(3-cyanopropyl)-1-methyl-1*H*-imidazol-3-ium bromide {[CN-bmim]Br}, which upon anion exchange with potassium hexafluorophosphate yielded **1** as a colorless liquid. ILs **2** and **3** were prepared by anion exchange of 1-butyl-3-methylimidazolium bromide {[bmim]Br} with AgF and NaOAc, respectively. The presence of fluorine in **2** was confirmed by ^{19}F NMR spectroscopy, which showed a singlet at $\delta = -121.8$ ppm. ILs **1**–**3** were obtained in more than 99% purity, as established by NMR spectroscopy (Supporting Information). The thermal degradation behavior of **2**, which is a liquid at room temperature, was determined by differential scanning calorimetry (DSC). Compound **2** displayed an exotherm at 91.4 °C corresponding to its decomposition temperature (Figure S2a, Supporting Information).

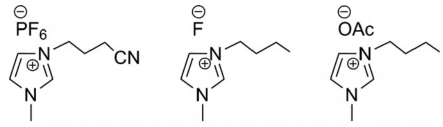
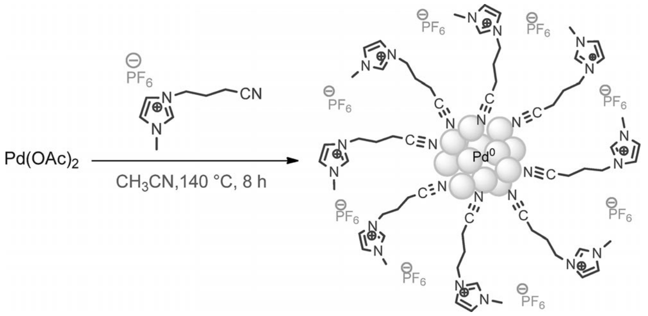


Figure 1. Ionic liquids used in the Pd-NP-catalyzed Hiyama coupling reactions.

The active Pd NP catalyst was prepared by a slightly modified literature procedure.[16] A solution of $Pd(OAc)_2$ in acetonitrile was added to **1**, and the contents were heated at 80 °C. After 2 h, the color of the solution changed from orange to yellow and finally to colorless, at which point acetonitrile was removed under reduced pressure. The residual contents were heated again at 140 °C for an additional 6 h, which resulted in a dark brown-black suspension of Pd^0 in **1** (Scheme 1). Formation of Pd NPs by thermolytic decomposition of $Pd(OAc)_2$ at 100 °C in polar solvents such as propylene carbonate has been reported to yield Pd NPs that are 8–10 nm in size.[17] In another report, basic ILs with tertiary aliphatic amines as pendant groups were shown to act as reducing agents in the redox process leading to the formation of Pd^0 NPs from $Pd(OAc)_2$.[18] To determine the role of ILs as reducing agents and stabilizers in the synthesis of the NPs, we screened other ILs such as [bmim]F (**2**) and [bmim]OAc (**3**) with $Pd(OAc)_2$ as the catalyst precursor. We found that no black-colored Pd^0 solution was obtained in ILs **2** and **3** at temperatures of 100 and 140 °C (Table 1, entries 1 and 2). However, in IL **1**, Pd NPs 25–50 nm in size (Table 1, entry 4) were isolated at 140 °C. This indicated that conversion of Pd^{II} into Pd^0 was not just a thermal decomposition of $Pd(OAc)_2$ but that it was the nitrile group on the imidazolium side chain that effected the reduction. The size and shape of the Pd NPs generated in **1** were determined by TEM, SEM, and dynamic light scattering (DLS), as shown in Figure 2. TEM images taken by drop casting the Pd[CN-bmim]PF_6 solution in hexane showed uniformly dispersed metal particles with an average diameter of around 2–5 nm. Similar results were obtained from SEM and DLS analyses, which showed particles to be in the range from 5 to 10 nm. The formation of Pd^0 was confirmed by energy-dispersive X-ray spectroscopy (EDAX; Figure S1a, Supporting Information) and powder X-ray diffraction (PXRD, Figure 2, a). The XRD pattern of the Pd NPs showed three planes at (111), (200), and (220) with lattice constant $a = 3.871$ Å. This could be readily indexed to crystalline Pd in terms of both the peak position and relative intensity and matched JCPDS file 87-0638.[19] The EDAX spectrum showed the presence of Pd, C, N, P, F, and Fe, which suggests the existence of IL **1**-stabilized Pd NPs. The size of the Pd NPs generated in both **1** and [CN-bmim]F was smaller with $Pd(OAc)_2$ as the precursor than with $PdCl_2$ (Table 1, entries 4–7). This is not unusual considering the lower solubility of $PdCl_2$ in ILs, which results in a more heterogeneous distribution, and this leads to larger sized Pd NPs. The formation of the NPs was followed by recording the UV/Vis spectrum at the start of the reaction and monitoring changes every 1 h (Figure S3, Supporting Information). It is well known that metal NPs absorb photons in the UV/Vis region as a result of coherent oscillation of the electrons in the conduction band induced by the interacting electromagnetic fields. However, Pd NPs do not show a pronounced peak owing to surface plasmon. Initially, the solution of $Pd(OAc)_2$ in [bmim]PF_6 and acetonitrile (brownish orange color) showed an absorption maximum at 240 nm. After 2 h, the color of the solution changed to yellow, and the appearance of a new peak at 260 nm was observed. This peak eventually disappeared when the color of the solution changed to dark brown, and a typical UV/Vis pattern indicative of the formation of Pd^0 NPs was observed.



Scheme 1. Synthesis of Pd NPs in **1**.

Table 1. Generation of Pd NPs in ionic liquids.[a]

Entry	Palladium precursor	Ionic liquid	*T* [°C]	Pd NPs [nm]
1	Pd(OAc)$_2$	**2**	100, 140	–
2	Pd(OAc)$_2$	**3**	100, 140	–
3	Pd(OAc)$_2$	[CN-bmim]F	100	–
4	Pd(OAc)$_2$	[CN-bmim]F	140	25–50
5	Pd(OAc)$_2$	**1**	140	2–5
6	PdCl$_2$	[CN-bmim]F	140	80–100
7	PdCl$_2$	**1**	140	20–25

[a] Palladium precursor (4 mg), ionic liquid (2.0 mL).

The preformed ligand-free Pd NPs generated in **1** were used as such for Hiyama coupling by diluting it with acetonitrile followed by the addition of the halide, silane, and activator. Optimization of the reaction conditions for the Hiyama coupling of iodo-, bromo-, and chlorobenzene with trimethoxyphenylsilane was carried out by varying the activator, catalyst ratio, time, and temperature (Table 2). The cross-coupling of iodobenzene with trimethoxyphenylsilane catalyzed by Pd NPs in **1** was investigated by using different activators such as CsF, KF, tetrabutylammonium fluoride (TBAF), NaOAc, [bmim]OAc, and [bmim]F. Although the reaction failed to occur with CsF, KF, and NaOAc, in the presence of TBAF biphenyl was obtained in 98% yield (Table 2, entries 1–4), and **2** and **3** (2.0 equiv.) afforded the product in 98 and 72% yield, respectively. This suggests that fluorine-based **2** is a better silyl activator than oxygen-based **3** (Table 2, entries 9 and 10). Optimization of the reaction conditions showed that trimethoxyphenylsilane (2 equiv.) and Pd(OAc)$_2$ (4 mol-%) in **1**/acetonitrile solution were required for the aryl iodide (1 equiv.) to yield 98% of the coupled product at 70 °C over 8 h.

The reaction was very clean and no side reaction such as homocoupling or reduction of iodobenzene was observed. A low catalyst loading of 4 mol-% of the Pd^{II} precursor was sufficient to catalyze the reaction by virtue of NP formation and stabilization by the ionic framework of **1**. However, upon decreasing the Pd concentration from 4 mol-% to 3 and 2 mol-%, the yield of biphenyl dropped to 82 and 50%, respectively (Table 2, entries 5 and 6). No product was observed in the absence of any palladium catalyst. With bromo- and chlorobenzene, the yield of the product was 98 and 82%, respectively, but the reactions required slightly elevated temperatures (Table 2, entries 13 and 15).

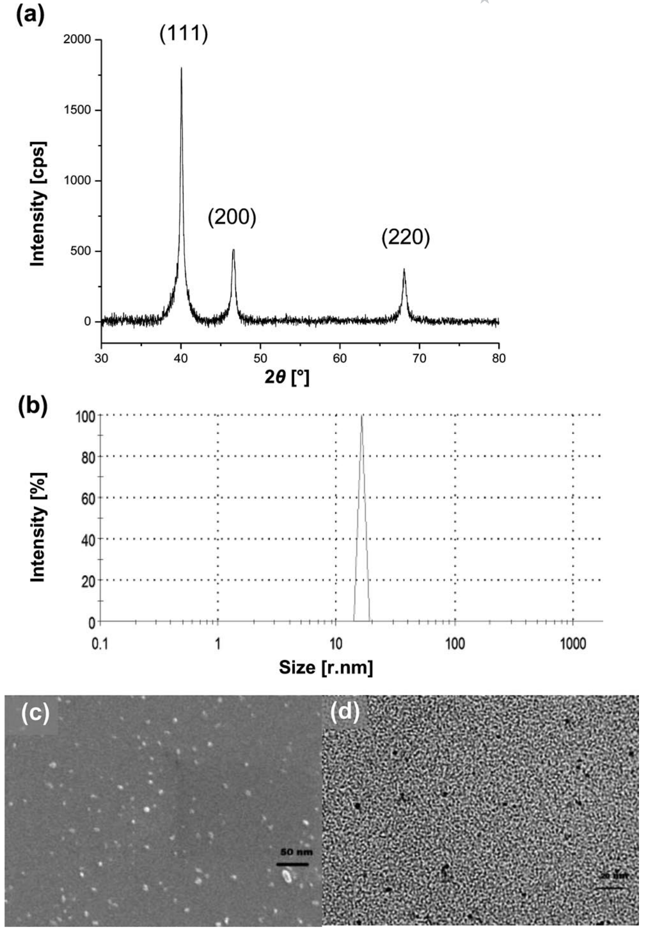
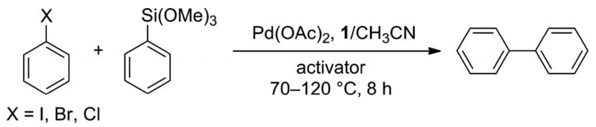


Figure 2. Characterization of the Pd NPs: (a) XRD image, (b) DLS showing intensity distributed particle size, (c) SEM image, (d) TEM image.

After the best reaction conditions were set, the scope of the Hiyama coupling was explored by screening different aryl halides and a few heterocyclic halides. Table 3 summarizes the reactions conducted under our optimized conditions to give C–C coupled products in yields ranging from 76 to 98%. Notably, if Pd(OAc)$_2$ (4 mol-%) was added directly to the reaction mixture containing bromobenzene (1.0 mmol), trimethoxyphenylsilane (2.0 mmol), [bmim]F (2.0 equiv.), IL **1** (2.0 mL), and CH$_3$CN (2.0 mL), no product was formed even after 8 h. It was only upon addition of triphenylphosphane (20 mol-%) to the reaction mixture that biphenyl was obtained in 90% yield. These results point towards the fact that Hiyama coupling with preformed Pd^0 NPs occurs under phosphane-free conditions, which is not possible if Pd(OAc)$_2$ is directly added to the reaction mixture. Both electron-rich and electron-deficient aryl iodides gave high yields of the products, and this portends minimal electronic influence. Nonetheless, the yield was slightly higher for substrates bearing electron-donating substituents such as –CH$_3$ and –OCH$_3$ in the *para* position

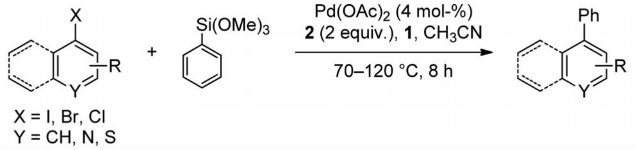
Table 2. Optimization of the catalytic conditions for the Hiyama coupling of aryl halides.[a]

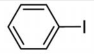
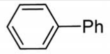
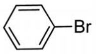
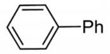
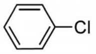
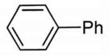
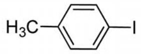
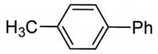
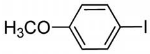
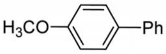
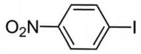
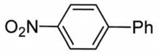
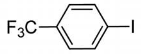
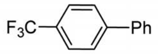
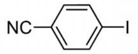
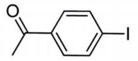
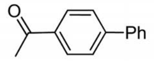
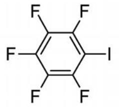
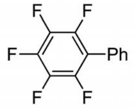
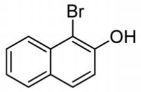
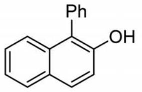
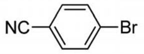
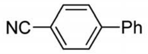
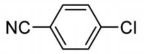
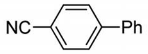
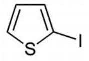
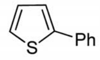
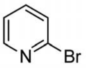
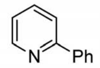
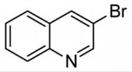
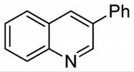


Entry	X	$Pd(OAc)_2$ [mol-%]	Activator (equiv.)	T [°C]	Yield[b] [%]
1	I	4.0	CsF (2.0)	70	–
2	I	4.0	KF (2.0)	70	–
3	I	4.0	NaOAc (2.0)	70	–
4	I	4.0	TBAF (2.0)	70	98
5	I	2.0	**2** (1.5)	70	50
6	I	3.0	**2** (1.5)	70	82
7	I	4.0	**2** (1.5)	70	90
8	I	7.0	**2** (1.5)	70	90
9	I	4.0	**2** (2.0)	70	98,76[c]
10	I	4.0	**3** (2.0)	70	72
11	I	4.0	**2** (3.0)	70	98
12	Br	4.0	**2** (2.0)	70	82[d]
13	Br	4.0	**2** (2.0)	80	98
14	Cl	4.0	**2** (2.0)	100	–
15	Cl	4.0	**2** (2.0)	120	82

[a] Reaction conditions: Aryl halide (1.0 mmol), arylsilane (2.0 mmol), preformed Pd NPs from $Pd(OAc)_2$ and **1** (2.0 mL), CH_3CN (2.0 mL), activator, 8 h. [b] Isolated yield. [c] CH_2Cl_2 was used as a cosolvent instead of CH_3CN. [d] Isolated yield after a reaction time of 24 h.

Table 3. Scope of the optimized Pd-NP-catalyzed coupling of aryl and heterocyclic halides with trimethoxyphenylsilane.[a]



Entry	Aryl halide	Product	Yield [%][b]
1			98 (91,[c] 86,[d] 80,[e] 70[f])
2			98,[g] 0,[h] 90[i]
3			82[j]
4			97
5			96
6			89
7			82
8			85
9			92
10			76
11			86
12			88
13			76
14			79
15			85
16			81

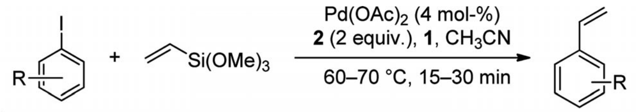
[a] Reaction conditions: aryl halide (1.0 mmol), trimethoxyphenylsilane (2.0 mmol), preformed Pd NPs from $Pd(OAc)_2$ (4.0 mol-%), [bmim]F (2.0 equiv.), **1** (2.0 mL), CH_3CN (2.0 mL), stirred at 70 °C for 8 h. [b] Isolated yield. [c] Yield after first recycle. [d] Yield after second recycle. [e] Yield after third recycle. [f] Yield after forth recycle. [g] Reaction performed at 80 °C. [h] Reaction with $Pd(OAc)_2$ (4 mol-%) added directly instead of preformed Pd NPs. [i] Reaction with $Pd(OAc)_2$ (4 mol-%) and PPh_3 (20 mol-%) added directly instead of preformed Pd NPs. [j] Reaction performed at 120 °C.

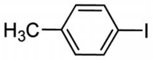
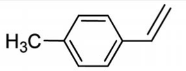
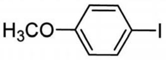
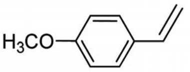
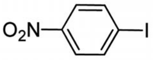
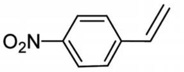
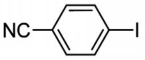
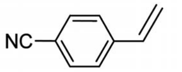
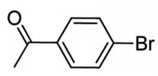
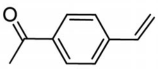
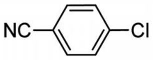
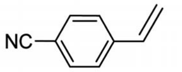
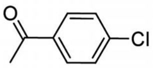
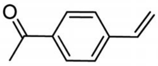
(Table 3, entries 4 and 5) than for substrates bearing electron-withdrawing substituents such as $–NO_2$, $–CF_3$, –CN, and $–COCH_3$ (Table 3, entries 6–9); the yield was particularly low with pentafluorophenyl iodide (Table 3, entry 10). Coupling occurred efficiently with heterocyclic halides as well to give the aromatic heterocycles in 79–85% yield (Table 3, entries 14–16).

The protocol was further extended to the Hiyama coupling of vinylsiloxanes to yield substituted styrenes. The vinylation reaction of aryl halides to yield styrenes has been mainly performed by using alkenyl stannanes and potassium trifluorovinylborates or through Heck coupling.[20] Cross-coupling with alkenylsilanes has found limited utility in styrene synthesis, as these compounds are less reactive and coupling has been achieved essentially only with aryl iodides. With aryl bromides and chlorides, only a few procedures involving the use of vinyltrialkoxysilanes have been reported. One involves the combination of $Pd(OAc)_2$, an imidazolium salt (3 mol-%), and TBAF at 80 °C.[21] The second route employs the use of π–allyl palladium chloride (2.5 mol-%), *N*-dicyclohexylphosphanyl-*N′*-methylpiperazine, and TBAF in DMF at 110 °C.[22] A more recent procedure describes fluoride-free coupling in aqueous sodium hydroxide by using tetrabutylammonium bromide (TBAB) as an additive under microwave and thermal conditions at 120 °C.[23] Results demonstrating the cross-coupling of trimethoxyvinylsilane with substituted aryl halides under our conditions are summarized in Table 4, and the reactions gave high yields of the products in the range from 81 to 98%. With aryl iodides, the reaction time was particularly short (15–30 min), whereas with bromide and chloride derivatives, a longer reaction time of 12 and 16 h, respectively, was required to achieve greater conversions.

Upon completion of the reaction, the products were extracted with diethyl ether, and **2** was removed by repeated washing with water to leave behind the catalyst immobilized in **1**. To the recovered Pd catalyst in **1**, fresh iodobenzene,

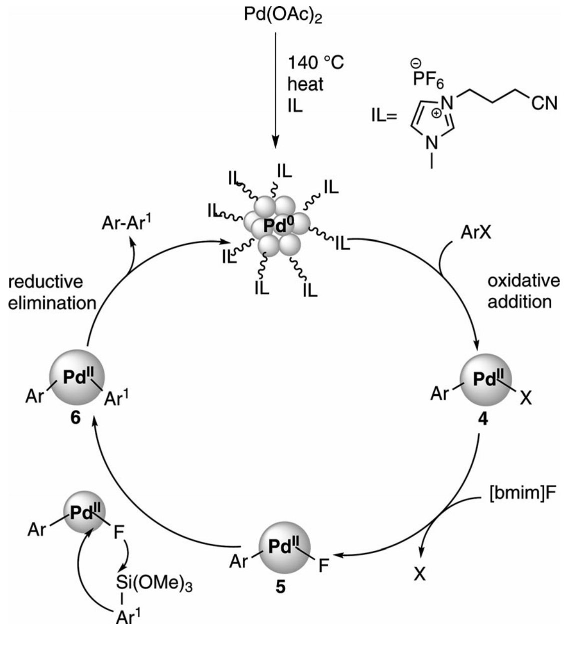
Table 4. Pd-NP-catalyzed Hiyama coupling of aryl iodides with trimethoxyvinylsilane.[a]



Entry	Aryl halide	Product	Yield [%][b]
1			98
2			98
3			97
4			98
5			86[c]
6			81[d]
7			75[d]

[a] Reaction condition: aryl halide (1.0 mmol), vinylsilane (2.0 mmol), preformed Pd NPs from $Pd(OAc)_2$ (4.0 mol-%), [bmim]F (2.0 equiv.), **1** (2.0 mL), CH_3CN (2.0 mL), stirred at 60–70 °C for 15–30 min. [b] Isolated yield. [c] Reaction carried out for 12 h. [d] Reaction carried out for 16 h.

trimethoxysilane, and **2** were added, and the contents were heated at 70 °C for 8 h to give biphenyl in 91% yield (Table 3, entry 1). Little deactivation of the catalyst was observed in subsequent catalytic runs. The reusability of the catalyst was checked up to four recycles, and biphenyl was obtained in 86, 80, and 70% yield in the second, third, and fourth cycles, respectively (Table 3, entry 1). Scheme 2 illustrates a possible mechanism for the reaction. Following the established mechanism, oxidative addition of the aryl halide to Pd^0 leads to the formation of aryl–Pd complex **4**. The agglomeration of these ligand-free Pd^0 species towards the catalytically inactive bulk material is avoided because IL **1** stabilizes the nanomeric structures responsible for the catalytic activity. Complex **4** undergoes transmetalation wherein the nucleophile is transferred to palladium in the presence of [bmim]F to produce intermediate complex **6**. Reductive elimination of **6** gives the coupled product and regenerates palladium(0) for the next catalytic cycle.



Scheme 2. Proposed mechanism for Hiyama coupling.

Conclusions

In summary, an effective protocol for the phosphane-free Hiyama coupling of aryl and heterocyclic halides with aryl- and vinylsilanes catalyzed by Pd NPs in nitrile-functionalized IL **1** was developed. Nitrile-functionalized ILs seem to be the best media for the generation and stabilization of the Pd NPs, and their usefulness is apparent upon catalyst recycling. Further, [bmim]F was employed for the first time as a silane activator with the advantages of being easy to handle, store, and remove during workup. In addition, under these conditions the formation of N-heterocyclic carbene palladium systems is avoided. The system allows easy isolation of the products with the recovery and reuse of the catalyst up to four times, which make the overall process highly economical and cost effective.

Experimental Section

Materials and Methods: Chemicals were either purchased or purified by standard techniques without special instructions. The products were purified by column chromatography on silica gel (230–400 mesh, SRL). ^1H NMR and ^{13}C NMR spectra were measured with a Bruker DPX-300 MHz spectrometer (^1H 300 MHz, ^{13}C 75 MHz) by using $CDCl_3$ and D_2O as the solvents and tetramethylsilane as the internal standard at room temperature. Chemical shifts are given in δ relative to TMS. The ESI-MS for **1**–**3** were performed with a MICROTOF-II mass instrument. High-resolution transmission electron microscope (HRTEM) experiments were conducted with a JEM 2100 F at an accelerating voltage of 200 KV. The scanning electron microscopy (SEM) image was captured with a Zeiss Evo series SEM model EVO 50. The size of the nanoparticles was determined by Malvern DLS. UV/Vis spectroscopy was recorded with a Lambda Bio 20, Perkin–Elmer. Powder XRD was taken with a powder X-ray diffractometer (Bruker). DSC analysis was carried out with a Q-100 DSC instrument (TA instruments, USA) in the temperature range from –50 to 500 °C at a heating rate of 10 °C min^{-1} under a N_2 atmosphere. Calibration was performed with indium as a standard, for which the melting point was determined as 156.6 °C well within the acceptable limit. GC–MS were recorded with a Perkin–Elmer Clarus 600C with a gas flow of 1.0 mL min^{-1} and a heating rate of 20 °C min^{-1} with an initial temperature of 50 °C and a final temperature of 310 °C.

Synthesis of 3-(3-Cyanopropyl)-1-methyl-1*H*-imidazol-3-ium Hexafluorophosphate {[CN-bmim]PF_6} (1): To 1-methyl-1*H*-imidazole

(2 mL, 1 equiv.), 4-bromobutyronitrile (2.5 mL, 1.2 equiv.) was added, and the reaction mixture was heated at reflux for 24 h at 70 °C. After completion of the reaction as monitored by TLC, the mixture was washed with diethyl ether and ethyl acetate to remove trace amounts of unreacted 4-bromobutyronitrile, and the pure product was obtained in 92% yield. Anion exchange was carried out by following a literature method. To a stirred solution of 3-(3-cyanopropyl)-1-methyl-1*H*-imidazol-3-ium bromide {[CN-bmim] Br; 2 mL, 1 equiv.} in water (5 mL) was added potassium hexafluorophosphate (1.6 g, 1 equiv.), and the contents were stirred for 24 h at room temperature. The reaction mixture was filtered through Celite to remove potassium bromide and water was evaporated at 55 °C under reduced pressure. IL **1** was dissolved in dichloromethane, dried with molecular sieves (4 Å) to remove any trace amounts of water, and finally concentrated under reduced pressure to obtain pure **1** in 80% yield.

Synthesis of Pd NPs: A solution of palladium acetate (4 mg, 0.04 mmol) and **1** (2 mL) in acetonitrile (5 mL) was stirred at 80 °C for 1 h. After 1 h, the color of the solution changed from reddish brown to yellow and finally turned colorless after 2 h. Acetonitrile was evaporated under reduced pressure, and the contents were vigorously stirred for another 6 h at 140 °C at which point the solution turned brownish-black. Pd NPs 2–5 nm in size were formed, and this was confirmed by UV, DLS, TEM, SEM, and PXRD. The catalyst immobilized in **1** was used as such for Hiyama coupling.

Characterization of Pd NPs: The formation of Pd nanoparticles was confirmed by UV, PXRD, and EDAX analysis. The size of the NPs was determined by DLS, TEM, and SEM. To prepare the sample for SEM/EDAX, the Pd NPs were centrifuged at 6000 rpm and washed with water and then with absolute ethanol to remove most of **1**. The precipitate was then redispersed in dry acetone and sonicated for about 1 h. The sample was prepared on a glass slide with the help of spin coating to get a uniform distribution of particles. The sample was then coated in a sputter coater (EMITECH K 550x) with a gold layer in vacuo. Samples for TEM were prepared by placing a drop of a colloidal dispersion of Pd[CN-bmim]PF$_6$ in hexane on the carbon-coated copper grid, followed by evaporation of the solvent at room temperature. DLS was recorded in acetonitrile at a sample concentration of 0.1 mg mL^{-1}.

General Procedure for Hiyama Coupling of Aryl and Heterocyclic Halides: Preformed Pd NPs were used as in situ catalysts for the coupling reaction. The aryl halide (1 mmol), trimethoxyphenylsilane (2 mmol), **2** (2 mmol), and acetonitrile (2 mL) were added to the catalytic solution of Pd NPs in **1**, and the contents were stirred under an argon atmosphere at 70 °C for 8 h. Upon completion of the reaction as monitored by TLC, the product was extracted with diethyl ether (5 × 5 mL). The organic layer was washed with brine, dried with MgSO$_4$, and concentrated in vacuo. Purification was done by silica gel column chromatography (ethyl acetate/hexane) to afford the C–C coupled products. All products obtained herein are known compounds, and their structures were confirmed by ^{1}H NMR and ^{13}C NMR spectroscopy and mass spectrometry (see the Supporting Information for full details).

Recycling Experiment: Upon completion of the reaction, the product was extracted with diethyl ether to leave behind Pd NPs immobilized in **1**. The reaction mixture was repeatedly washed with water (3 × 1 mL) to remove Si(OMe)$_3$F and residual **2**. As **1** is water immiscible, this limited the amount of Pd NPs leached. Finally, acetonitrile (2 mL) was added, and the contents were sonicated for 1 h and reused for the next reaction by addition of a fresh batch of reactants.

Supporting Information (see footnote on the first page of this article): Spectroscopic data for **1**–**3** and cross-coupled products, and characterization data for the Pd NPs.

Acknowledgments

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