

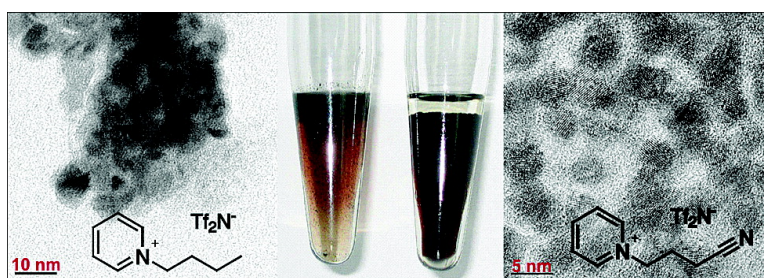
Article

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Nitrile-Functionalized Pyridinium Ionic Liquids: Synthesis, Characterization, and Their Application in Carbon–Carbon Coupling Reactions

Dongbin Zhao, Zhaofu Fei, Tilmann J. Geldbach, Rosario Scopelliti, and Paul J. Dyson*

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Abstract: A series of relatively low-cost ionic liquids, based on the *N*-butyronitrile pyridinium cation $[C_3CNpy]^+$, designed to improve catalyst retention, have been prepared and evaluated in Suzuki and Stille coupling reactions. Depending on the nature of the anion, these salts react with palladium chloride to form $[C_3CNpy]_2[PdCl_4]$ when the anion is Cl^- and complexes of the formula $[PdCl_2(C_3CNpy)_2][anion]_2$ when the anion is PF_6^- , BF_4^- , or $N(SO_2CF_3)_2^-$. The solid-state structures of $[C_3CNpy]Cl$ and $[C_3CNpy]_2[PdCl_4]$ have been established by single-crystal X-ray diffraction. The catalytic activity of these palladium complexes following immobilization in both *N*-butylpyridinium and nitrile-functionalized ionic liquids has been evaluated in Suzuki and Stille coupling reactions. All of the palladium complexes show good catalytic activity, but recycling and reuse is considerably superior in the nitrile-functionalized ionic liquid. Inductive coupled plasma spectroscopy reveals that the presence of the coordinating nitrile moiety in the ionic liquid leads to a significant decrease in palladium leaching relative to simple *N*-alkylpyridinium ionic liquids. Palladium nanoparticles have been identified as the active catalyst in the Stille reaction and were characterized using transmission electron microscopy.

Introduction

Ionic liquids are currently attracting considerable attention as an alternative reaction medium for homogeneous (molecular), heterogeneous (supported or nanoparticle), and enzymatic catalysis.¹ While the concept of biphasic catalysis has been around for many years, only few industrial biphasic processes are in operation.² This is partly due to the fact that separation of the product from the catalyst phase is rarely perfect, and that catalyst immobilization is seldom completely efficient. Both factors combined lead to levels of catalyst loss that cannot be sustained from an economic perspective. Furthermore, not all catalysts are sufficiently stable for extensive reuse, and the rapid deactivation of many homogeneous catalysts represents a major problem, which has even led to the proposition that attempts to recycle them could be futile.³ In the case of ionic liquids as immobilization media, ionic transition-metal catalysts are generally well retained during product separation, and many examples have been reported that illustrate their potential,⁴ although quantitative data is not always available. However, with uncharged catalysts, leaching can be high, and functionalized ligands may

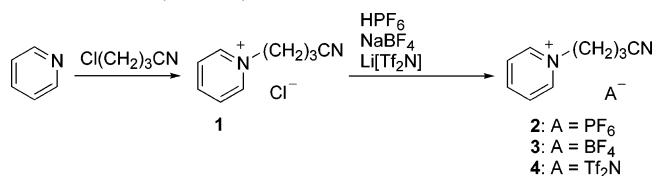
be required to prevent loss of the transition metal into the product phase.⁵

Task-specific ionic liquids that interact with a metal center and thereby facilitate retention of the catalyst could provide an alternative to ligand modification. Such task-specific ionic liquids have, for example, been used to extract metal ions from water.¹¹ It is therefore not unreasonable to conclude that the presence of appropriate coordinating groups in ionic liquids

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Scheme 1. Synthesis of the Nitrile-Functionalized Ionic Liquids 1–4: $\text{Tf}_2\text{N} = \text{N}(\text{SO}_2\text{CF}_3)_2$



might immobilize metal catalysts effectively, and such a strategy has been reported recently.⁶ A large number of ionic liquids bearing functional groups, such as amines,⁷ amides,⁸ ethers and alcohols,⁹ acids,¹⁰ urea and thiourea,¹¹ and fluoros chains,¹² are already known, most of which are tethered to imidazolium cations.

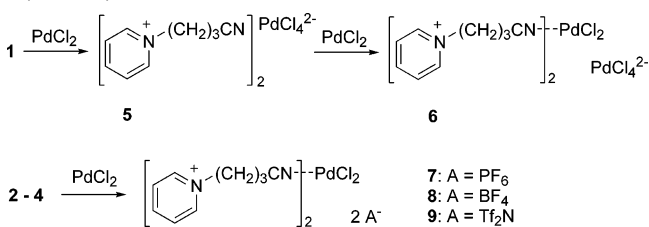
From the analysis of catalysts by electron microscopy, there is a growing body of evidence that in many carbon–carbon bonding formation reactions, the active catalysts are soluble nanoparticles, especially when simple metal salts, such as palladium(II) halides, are used as the precatalysts.¹³ The preparation and application of transition-metal nanoparticles immobilized in ionic liquids have been reported. Dupont and co-workers described the first example in which iridium nanoparticles prepared in $[\text{C}_4\text{C}_1\text{im}][\text{PF}_6]$ were shown to catalyze the hydrogenation of alkenes.¹⁴ Subsequently, the preparation of rhodium,¹⁵ platinum,¹⁶ and palladium¹³ colloids has been published, and these were found to be effective catalysts for the hydrogenation of alkenes and arenes. Thiol-functionalized ionic liquids can, for example, stabilize nanoparticles of gold and platinum.¹⁷ Pyridinium-based ionic liquids have been also used as solvents for various catalysis processes^{18–20} but are essentially unexplored as media for generating and stabilizing metal nanoparticles, although the presence of a functional group might facilitate their formation/stabilization.

In this paper, we report the synthesis of a series of nitrile-functionalized ionic liquids based on the *N*-butyronitrile pyridinium cation, $[\text{C}_3\text{CNpy}]^+$, and demonstrate their suitability as solvents for palladium-catalyzed biphasic Suzuki and Stille coupling reactions. In addition, a comparison of transmission electron microscopy (TEM) images of particles formed in situ in the Stille reaction reveals that the nitrile-functionalized ionic liquid exerts a superior nanoparticle-stabilizing effect compared to the nonfunctionalized ionic liquid.

Results and Discussion

The synthetic pathway leading to the *N*-butyronitrile pyridinium ionic liquids, $[\text{C}_3\text{CNpy}][\text{anion}]$, is summarized in Scheme 1. Quaternization of pyridine with 4-chlorobutyronitrile results in the formation of the chloride salt $[\text{C}_3\text{CNpy}]\text{Cl}$ 1 within

Scheme 2. Synthesis of Palladium Complexes 5–9: $\text{Tf}_2\text{N} = \text{N}(\text{SO}_2\text{CF}_3)_2$



24 h at 80 °C. Anion metathesis with either HPF_6 , NaBF_4 , or $\text{Li}(\text{Tf}_2\text{N})$ ($\text{Tf}_2\text{N} = \text{N}(\text{SO}_2\text{CF}_3)_2$) affords the salts $[\text{C}_3\text{CNpy}][\text{PF}_6]$ 2, $[\text{C}_3\text{CNpy}][\text{BF}_4]$ 3, and $[\text{C}_3\text{CNpy}][\text{Tf}_2\text{N}]$ 4, respectively, in high yield. Salts 1, 2, and 3 are solids at room temperature, but with melting points below 100 °C, they can nevertheless be classified as ionic liquids. Compound 4 is a liquid at room temperature with a melting point of -64.5 °C and a relatively low viscosity [170 mPa·s at 20 °C, cf. 50.1 mPa·s for $[\text{C}_4\text{py}][\text{Tf}_2\text{N}]$ at 20 °C].²¹

The pyridinium salts 1–4 were characterized using electro-spray ionization mass spectrometry (ESI-MS), IR,¹H and ¹³C NMR spectroscopy, and elemental analysis. The positive ion ESI mass spectra in methanol reveal a strong parent peak at m/z 174 corresponding to the pyridinium cation $[\text{C}_3\text{CNpy}]^+$. The nature of the anion can be deduced directly from the positive ion spectra since aggregates corresponding to $[\text{C}_3\text{CNpy}]_2\text{[anion]}^+$ are observed. The negative ion spectra also confirmed the identity of the appropriate anion. The ¹H and ¹³C NMR data of compounds 1–4 are of routine nature, with little change in the spectra with respect to the different anions present. In the ¹³C NMR, the nitrile carbon is observed between 123.0 and 120.5 ppm. The IR spectra show characteristic $\text{C}\equiv\text{N}$ vibrations between 2245 and 2246 cm^{-1} . In the case of 1, additional weak absorptions between 2862 and 2714 cm^{-1} are observed, which can be attributed to the presence of $\text{Cl}\cdots\text{H}-\text{C}$ hydrogen bonds. Such hydrogen bonding is well established from X-ray crystallography (vide infra).

Reactions of 1–4 with Palladium(II) Chloride. In acetonitrile, palladium(II) chloride reacts with 2 equiv of $[\text{C}_3\text{CNpy}]\text{Cl}$ 1 to form $[\text{C}_3\text{CNpy}]_2[\text{PdCl}_4]$ 5 (Scheme 2). Addition of a further equivalent of PdCl_2 to 5 in dichloromethane affords $[\text{PdCl}_2(\text{C}_3\text{CNpy})_2][\text{PdCl}_4]$ 6 over a period of several days. In the absence of coordinating anions, the reaction of PdCl_2 with 2 equiv of 2–4 in dichloromethane affords the complexes $[\text{Pd}(\text{C}_3\text{CNpy})_2\text{Cl}_2][\text{PF}_6]_2$ 7, $[\text{Pd}(\text{C}_3\text{CNpy})_2\text{Cl}_2][\text{BF}_4]_2$ 8, and $[\text{Pd}(\text{C}_3\text{CNpy})_2\text{Cl}_2][\text{N}(\text{SO}_2\text{CF}_3)_2]_2$ 9, respectively. Compounds 6–8 are yellow solids, whereas 9 can only be isolated as a highly viscous brown liquid. All of these new palladium complexes are air stable and do not decompose on washing with water or alcohols at room temperature, but they decompose in water and alcohols over prolonged periods of time. They are poorly soluble in chlorinated solvents, such as chloroform or dichloromethane, and degrade on contact with acetonitrile in that coordination of the pyridinium cation to the metal is lost, and the respective ionic liquid together with $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ is obtained.

Coordination of the nitrile to the palladium is clearly established using IR spectroscopy (it is not possible to use NMR as the few solvents which dissolve 5–9 cleave the metal–nitrile

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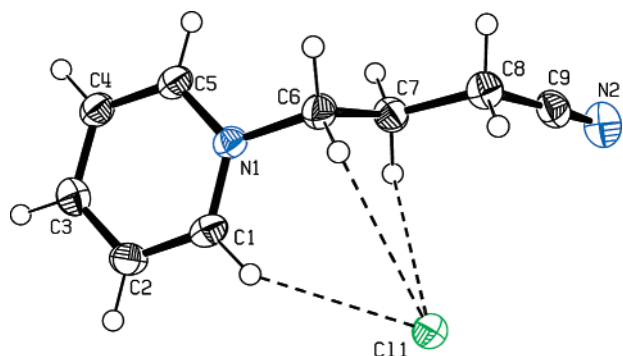


Figure 1. ORTEP representation of **1** showing some of the Cl–H interactions shorter than 3 Å; ellipsoids are drawn at the 50% probability level.

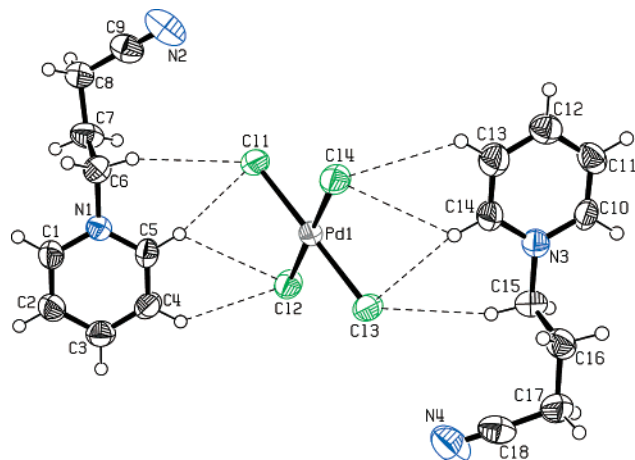


Figure 2. ORTEP representation of **5** showing some of the Cl–H interactions shorter than 3 Å; ellipsoids are drawn at the 50% probability level.

bond). The C≡N stretching frequency of the free nitrile in the pyridinium salts **1–5** is found in the range of 2244–2252 cm⁻¹, whereas interaction with the metal in **6–9** leads to a marked change in the ν_{C≡N} bands, which appear in the range of 2319–2326 cm⁻¹.

Solid-State Structures of 1 and 5. Single crystals of [C₃CNpy]Cl **1** and [C₃CNpy]₂[PdCl₄] **5** were obtained from acetonitrile following slow diffusion of diethyl ether, and their molecular structures have been determined by X-ray diffraction methods. Their structures are depicted in Figures 1 and 2, respectively, and key bond lengths are listed in Table 1. The organic cations in **1** and **5** exhibit a geometry that is in good agreement with that of the previously published pyridinium salts.²² Bond angles in the pyridinium rings range from 118.1(6) to 121.5(5)° and distances from 1.340(8) to 1.386(3) Å. The –CH₂–C≡N moiety is essentially linear with the C–N distance [1.139(3) Å in **1** and 1.128(7) and 1.128(8) Å in **5**] being found in the expected range.²³ The nitrile moiety in **1** lies almost in the same plane as the alkyl chain (deviation 10.5°), whereas in **5**, it is tilted out of plane by 117.1 and 118.4°, respectively. This difference is probably due to crystal packing effects, such as C≡N⋯π interactions. Distances from the nitrile nitrogen atom to the center of the pyridine ring of a nearby cation are 3.28 Å in **1** and 3.34 and 3.55 Å in **5**. The nitrile moiety points toward the center of the ring in **1** but is almost

Table 1. Selected Bond Lengths (angstroms) and Angles (deg) for **1** and **5**^a

	1	5	
Pd1–Cl1		2.3151(17)	
Pd1–Cl2		2.3116(17)	
Pd1–Cl3		2.3152(17)	
Pd1–Cl4		2.3145(17)	
N2–C9	1.139(3)	1.128(7)	1.128(8)*
N1–C1	1.343(3)	1.348(6)	1.354(6)*
N1–C5	1.352(3)	1.346(6)	1.353(7)*
C1–C2	1.383(3)	1.365(8)	1.359(9)*
C2–C3	1.386(3)	1.384(8)	1.385(8)*
C3–C4	1.384(3)	1.373(7)	1.375(8)*
C4–C5	1.374(3)	1.367(8)	1.340(8)*
C7–C8–C9	111.6(2)	114.0(5)	113.6(5)*
N2–C9–C8	178.1(3)	179.9(9)	179.9(9)*
C1–N1–C5	121.4(2)	121.0(5)	120.3(5)*
Cl1–Pd–Cl2		90.05(7)	
Cl2–Pd–Cl3		89.62(6)	
Cl3–Pd–Cl4		89.90(6)	
Cl4–Pd–Cl1		90.43(7)	

^aAsterisked (*) Bond Lengths Refer to the Second Pyridinium Cation in **5**.

parallel to the plane of the ring in **5**. The anion, [PdCl₄]²⁻, in **5** has a regular square planar geometry with Cl–Pd–Cl angles ranging between 89.62(6) and 90.43(7)°. The coordination plane of the [PdCl₄]²⁻ anion is tilted by 114.7 and 118.6° relative to the mean plane of the pyridine rings. Similar structures of the type [C_n-py][PdX₄], where C_n are long alkyl chains, have recently been reported and display comparable properties.²⁴ Furthermore, related paraquat salts of [PdCl₄]²⁻ are also known.²⁵

In both structures, the organic cation and the inorganic anion are held in place by extensive C–H⋯Cl interactions. In **1**, eight hydrogen contacts below 3 Å, which stem from five different cations and range between 2.609 and 2.931 Å, are observed. The [PdCl₄]²⁻ anion is close to 15 hydrogen atoms belonging to 6 different cations, with distances between 2.708 and 2.997 Å. Such hydrogen bonding is well established from imidazolium²⁶ and pyridinium^{22,24,25} halides and explains to some degree their markedly higher melting points relative to, for example, those of their BF₄⁻ derivatives.

Carbon–Carbon Coupling Reactions. Palladium-catalyzed carbon–carbon bond formation, such as in the Suzuki and Stille reactions, usually takes place in high yield under relatively mild conditions and tolerates a wide variety of functional groups on either coupling partner.²⁷ The development of biphasic (or multiphasic) systems for these types of reactions has received considerable attention,²⁸ and both Suzuki^{29,30} and Stille³¹ reactions have previously been studied in ionic liquids.

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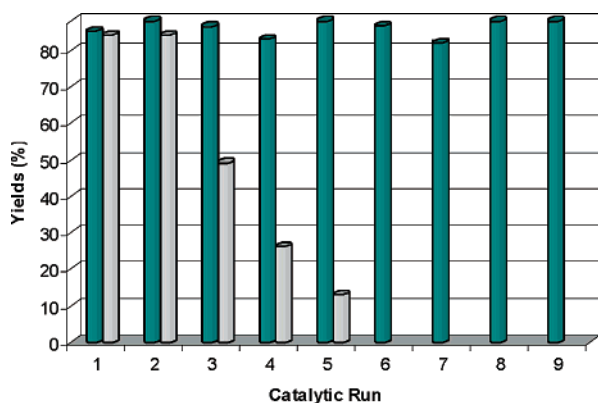
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Table 2. Suzuki Coupling Reactions between Iodobenzene and Phenylboronic Acid Conducted in **4** and $[C_4py][Tf_2N]^a$

precatalyst	ionic liquid	yield (%) ^b
5	4	86
6	4	85
7	4	88
8	4	81
9	4	85
9	$[C_4py][Tf_2N]$	84
$PdCl_2$	4	88

^a Conditions: iodobenzene (2.5 mmol), ionic liquid (5 mL), phenylboronic acid (2.75 mmol), Na_2CO_3 (5.28 mmol), water (2.5 mL), palladium complex (0.03 mmol), 110 °C, 12 h. ^b Yield corresponds to biphenyl determined by GC.

**Figure 3.** Recyclability in $[C_3CNpy][Tf_2N]$ **4** (green) and $[C_4py][Tf_2N]$ (grey) in the Suzuki reaction between phenylboronic acid and iodobenzene using **9** as the catalyst precursor.

The Suzuki reaction was evaluated using the palladium complexes **5–9** and $PdCl_2$ as precatalysts immobilized in either $[C_3CNpy][Tf_2N]$ **4** or in the nonfunctionalized ionic liquid $[C_4py][Tf_2N]$, employing conditions described previously.³² The performance of these catalyst precursors in the reaction between iodobenzene and phenylboronic acid is listed in Table 2.

The yields for all of the reactions are high, although it is worth noting that a relatively short reaction time was used; quantitative conversion can be obtained by increasing the reaction time. Under similar conditions, Welton showed that ~30% yield could be obtained after 6 h using $Pd(PPh_3)_4$ in $[C_4mim][BF_4]$ with arylbromide substrates, although under modified conditions, fast rates could be obtained.²⁹ We observed ~35% yield with bromobenzene and <1% yield with chlorobenzene. The nature of the palladium source does not seem to have a major effect on the kinetics of the reaction. The difference between the reactions conducted in the nitrile-functionalized ionic liquid **4** and $[C_4py][Tf_2N]$ becomes apparent in the recycling studies, which are summarized in Figure 3. After nine cycles with complex **9** as the catalyst precursor in the functionalized ionic liquid, there is no significant decrease in activity. However, if **9** is immobilized in $[C_4py][Tf_2N]$, the catalyst solution rapidly loses its activity to become completely inactive after the fifth cycle.

The superiority of the nitrile-functionalized system compared to the alkyl-pyridinium ionic liquid-based one appears to be

Table 3. Stille Reaction between Iodobenzene and Phenyltributylstannane Catalyzed by Palladium Complexes in Ionic Liquids^a

Pd source	ionic liquid	yield (%) ^b
5	4	62.1
6	4	58.3
7	4	43.9
8	4	43.7
9	4	48.9
5	$[C_4py][N(SO_2CF_3)_2]$	65.5
9	$[C_4py][N(SO_2CF_3)_2]$	56.0
$PdCl_2$	4	62.6

^a Conditions: iodobenzene (1.0 mmol), ionic liquid (1 mL), phenyltributylstannane (1.2 mmol), palladium complex (0.05 mmol), 80 °C, 12 h. ^b Yield corresponds to biphenyl determined by GC.

due to several factors. Inductive coupled plasma spectroscopy (ICP) was used to analyze the organic fractions after catalysis for palladium content. These analyses showed that while <5 ppm of palladium was lost from **4** into the organic phase, typically 28 ppm of palladium was lost from $[C_4py][Tf_2N]$. The difference in palladium loss does not fully account for the differences in recycling, and the catalyst must also be less stable in the unfunctionalized ionic liquid. It is conceivable to attribute the superior retention of the palladium complex in **4** to coordination of the palladium to the ionic liquid via the nitrile moiety, resulting in a higher capacity for immobilization of the palladium complex. It has been suggested that carbene complexes are the active catalytic species for the Suzuki reaction in imidazolium-based ionic liquids,³³ but the formation of carbenes from pyridinium-based ionic liquids is less likely. Attempts to identify the nature of the catalyst failed, which prevents delineation of the role of the nitrile group in the Suzuki reaction. In contrast, in the Stille reaction, some further insights could be gained. The results from the Stille coupling reaction between iodobenzene and phenyltributylstannane are compiled in Table 3.³⁴

The results are in keeping with the Suzuki reactions; for example, there is little difference between the catalytic activity in **4** or $[C_4py][Tf_2N]$ in the first batch; however, while activity remains essentially constant in **4**, activity decreases rapidly in $[C_4py][Tf_2N]$, as is clear from Figure 4. To assert that the active catalyst is colloidal, the nanoparticles isolated from $[C_3CNpy][Tf_2N]$ **4** after the Stille reaction were mixed with fresh **4**, and ultrasound was used to facilitate redispersion. The Stille reaction was carried out using the same procedure as before, affording 48% product, which is close to the yield obtained for the Stille reaction using the nanoparticles formed in situ.

The catalyst recycling experiments demonstrate the advantage of using the nitrile-functionalized ionic liquid as the biphasic catalyst support; with **4** as the catalyst support, the product yield is essentially unchanged, even in the ninth catalytic cycle, while in $[C_4py][Tf_2N]$, no activity is observed after six batches. Again, a much lower palladium content was found in the organic phase with **4** relative to $[C_4py][Tf_2N]$ (7 versus 46 ppm), indicating that the nitrile-functionalized ionic liquid facilitates catalyst retention and stability.

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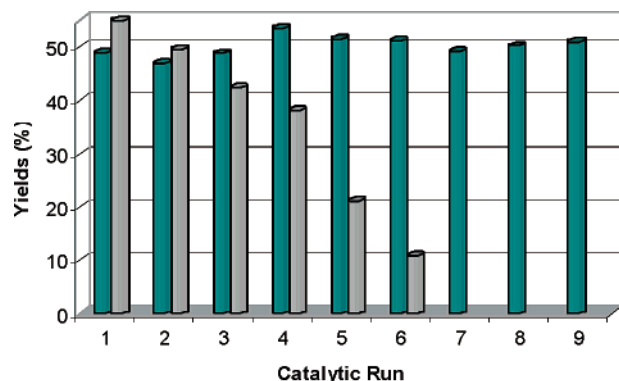


Figure 4. Recyclability of **9** in [C₃CNpy][Tf₂N] **4** (green) and [C₄py][Tf₂N] (grey) in the Stille reaction between phenyltributylstannane and iodobenzene using **9** as the catalytic precursor.

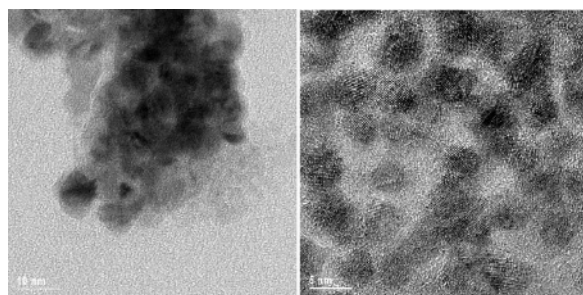


Figure 5. Comparison of TEM images of the palladium nanoparticles isolated after the Stille reaction from [C₄py][Tf₂N] (left) and [C₃CNpy][Tf₂N] (right).

In contrast to the Suzuki coupling, where no significant color change is observed in the course of the reaction, the ionic liquid–palladium complex solution rapidly turns black following the addition of phenyltributylstannane, which is indicative of nanoparticle formation. It proved possible to isolate the palladium nanoparticles from the Stille reactions, which were subsequently analyzed using transmission electron microscopy (TEM), and the TEM images are shown in Figure 5.

The nanoparticles obtained from [C₄py][Tf₂N] and [C₃CNpy][Tf₂N] **4** have a diameter of ~5 nm, but they exhibit different states. Whereas those from [C₄py][Tf₂N] are aggregated, nanoparticles generated in **4** are evenly distributed and the surface lattice can be clearly observed. Such microdissimilarity is in accordance with the macroappearance disparity of the two ionic liquid systems. The TEM images support the hypothesis that the nitrile-functionalized ionic liquid stabilizes the palladium colloid. The nitrile moiety could either weakly coordinate to the palladium surface or point away from the surface of the nanoparticle, thereby repelling proximal neighbors. In either case, agglomeration would be prevented and, ultimately, catalyst deactivation suppressed. The former hypothesis has been suggested previously for a different system.³⁵

Concluding Remarks

The nitrile-functionalized ionic liquid, [C₃CNpy][Tf₂N] **4**, is a considerably more-effective immobilization solvent for palladium-catalyzed Suzuki and Stille reactions than [C₄py][Tf₂N]. ICP analysis indicates that the nitrile-functionalized ionic liquid markedly reduces palladium leaching compared to the nonfunc-

tionized ionic liquid. In addition, TEM analysis of nanoparticles extracted from the catalysis solution directly shows the stabilizing effect of the nitrile-functionalized ionic liquid. Such task-specific ionic liquids may well prove to be decisive in transferring ionic liquids from the laboratory to production scale processes in C–C bond forming reactions. The [C₃CNpy][Tf₂N] ionic liquid described herein can be prepared from relatively inexpensive precursors, which provides further incentive for its deployment on a larger scale.

Experimental Section

All manipulations were carried out under a nitrogen atmosphere, using standard Schlenk techniques, using dried solvents. Reagents were purchased from Aldrich and used as received. IR spectra were recorded on a Perkin-Elmer FT-IR 2000 system. NMR spectra were measured on a Bruker DMX 400, with chemical shifts given in parts per million and coupling constants (*J*) in hertz. Electrospray ionization mass spectra (ESI-MS) were recorded on a ThermoFinnigan LCQ Deca XP Plus quadrupole ion trap instrument on samples diluted in methanol. Samples were infused directly into the source at 5 μL min⁻¹ using a syringe pump, and the spray voltage was set at 5 kV and the capillary temperature at 50 °C, as described previously.³⁶ Elemental analyses were carried out at the Institute of Chemical Sciences and Engineering (EPFL). Differential scanning calorimetry was performed using a SETARAM DSC 131. Inductively coupled plasma-atomic emission spectroscopy was conducted using a Perkin-Elmer Optima 3000 ICP-AE spectrometer. Intensities of spectral lines at 340.458 nm were measured in all samples and standards. The palladium level in the samples was determined by comparing the intensity of the spectral line with the palladium standard.

Crystallography. Data collection for the X-ray structure determination was performed on a mar345 IPDS diffractometer system using graphite-monochromated Mo Kα (0.71 070 Å) radiation and a low-temperature device [*T* = 140(2) K]. Colorless crystals of **1** and **5**, suitable for X-ray diffraction, were obtained by slow diffusion of diethyl ether into an acetonitrile solution of the compound at room temperature. Data reduction was performed using CrysAlis RED.³⁷ Structure solution and refinement were performed using the SHELX97 software package;³⁸ graphical representations of the structures were made with ORTEP32.³⁹ Structures were solved by direct methods and successive interpretation of the difference Fourier maps, followed by full-matrix least-squares refinement (against *F*²). An empirical absorption correction (DELABS)⁴⁰ was applied to **5**. All atoms were refined anisotropically. The contribution of the hydrogen atoms, in their calculated positions, was included in the refinement using a riding model. Relevant data concerning crystallographic data are compiled in Table 4.

Synthesis of [C₃CNpy]Cl **1.** A mixture of pyridine (7.90 g, 0.10 mol) and Cl(CH₂)₃CN (12.42 g, 0.12 mol) was stirred at 80 °C for 24 h, during which time, two phases formed. The reaction mixture was cooled to room temperature; acetonitrile (100 mL) and activated carbon (3 g) were added and the mixture stirred for 30 min. The solution was then reheated to 80 °C and filtered. The resulting product was crystallized upon cooling to 0 °C, washed with diethyl ether (3 × 30 mL), and dried under vacuum for 24 h to afford **1** as colorless solid: yield 16.8 g, 92%; mp 101 °C; ESI-MS (CH₃OH), positive ion 147 [C₃CNpy], negative ion 35 [Cl]; ¹H NMR (D₂O) δ 8.94 (d, 2H, ³*J*_{HH} = 5.6), 8.60 (m, 1H), 8.12 (m, 2H), 4.77 (t, 2H, ³*J*_{HH} = 7.2), 2.68 (t, 2H, ³*J*_{HH} = 6.8), 2.44 (m, 2H); ¹³C NMR (D₂O) δ 149.3, 147.5, 131.6, 123.0, 63.1, 29.2, 16.9; IR (cm⁻¹) ν 3030, 3002 (ν_{C–H} aromatic), 2933,

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Table 4. Crystallographic Data for Compounds **1** and **5**

	1	5
empirical formula	C ₉ H ₁₁ ClN ₂	C ₁₈ H ₂₂ Cl ₄ N ₄ Pd
formula weight	182.65	542.60
crystal system	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	8.074(3)	14.142(7)
<i>b</i> , Å	12.108(4)	10.421(5)
<i>c</i> , Å	10.505(2)	15.367(3)
α , deg	90	90
β , deg	112.46(2)	104.78(3)
γ , deg	90	90
<i>V</i> , Å ³	949.1(5)	2189.8(15)
<i>Z</i>	4	4
density, Mg/m ³	1.278	1.346
<i>T</i> , K	140	293
Θ range, deg	3.21 $\leq \Theta \leq$ 25.02	2.99 $\leq \Theta \leq$ 25.02
μ , mm ⁻¹	0.349	1.346
reflections measured	5684	13420
unique reflections [<i>I</i> > 2 σ (<i>I</i>)]	1626 (<i>R</i> _{int} = 0.0430)	3803 (<i>R</i> _{int} = 0.0658)
final <i>R</i> ₁ , w <i>R</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0528, 0.1301	0.0436, 0.0944

2862, 2714 (ν_{C-H} aliphatic), 2245 ($\nu_{C=N}$). Anal. Calcd for C₉H₁₁ClN₂: C, 59.18; H, 6.07; N, 15.34. Found: C, 59.14; H, 6.11; N, 15.31.

Synthesis of [C₃CNpy][PF₆]2**.** To a solution of **1** (5.46 g, 0.03 mol) in water (50 mL) was added HPF₆ (8.03 g, 60 wt %, 0.033 mol) at room temperature. After 10 min, the solid that had formed was collected by filtration, washed with ice-water (3 \times 15 mL), and then dried under vacuum: yield 6.13 g, 70%; mp 95 °C; ESI-MS (CH₃OH), positive ion 147 [C₃CNpy], negative ion 145 [PF₆]; ¹H NMR (CD₃CN) δ 8.72 (d, 2H, ³*J*_{HH} = 5.5), 8.53 (m, 1H), 8.07 (m, 2H), 4.60 (t, 2H, ³*J*_{HH} = 7.2), 2.55 (t, 2H, ³*J*_{HH} = 6.8), 2.32 (m, 2H); ¹³C NMR (CD₃CN) δ 149.2, 147.6, 131.6, 120.5, 63.1, 29.4, 16.6; IR (cm⁻¹) ν 3143, 3102 (ν_{C-H} aromatic), 2985, 2985 (ν_{C-H} aliphatic), 2246 ($\nu_{C=N}$). Anal. Calcd for C₉H₁₁F₆N₂P: C, 37.00; H, 3.79; N, 9.59. Found: C, 37.02; H, 3.75; N, 9.61.

Synthesis of [C₃CNpy][BF₄]3**.** A mixture of **1** (5.46 g, 0.03 mol) and NaBF₄ (3.62 g, 0.033 mol) in acetone (80 mL) was stirred at room temperature for 48 h. After filtration and removal of the solvents, the resulting pale yellow waxy solid was washed with THF and diethyl ether to give the product: yield 6.45 g, 92%; mp 62 °C; ESI-MS (CH₃OH), positive ion 147 [C₃CNpy], negative ion 87 [BF₄]; ¹H NMR (CD₃CN) δ 8.77 (d, 2H, ³*J*_{HH} = 5.5), 8.55 (m, 1H), 8.07 (m, 2H), 4.62 (t, 2H, ³*J*_{HH} = 7.2), 2.56 (t, 2H, ³*J*_{HH} = 6.8), 2.34 (m, 2H); ¹³C NMR (CD₃CN) δ 149.2, 147.7, 131.6, 120.7, 63.1, 29.5, 16.6; IR (cm⁻¹) ν 3142, 3079 (ν_{C-H} aromatic), 2970 (ν_{C-H} aliphatic), 2246 ($\nu_{C=N}$). Anal. Calcd for C₉H₁₁BF₄N₂: C, 46.20; H, 4.74; N, 11.97. Found: C, 46.21; H, 4.75; N, 12.01.

Synthesis of [C₃CNpy][N(SO₂CF₃)₂]4**.** To a solution of **1** (5.46 g, 0.03 mol) in water (50 mL) was added Li[N(SO₂CF₃)₂] (9.47 g, 0.033 mol) at room temperature in one portion, and the reaction mixture was stirred for 10 h, extracted with dichloromethane (200 mL), and dried with MgSO₄ overnight. The MgSO₄ was removed by filtration, and the solvent was removed under reduced pressure. The resulting hydrophobic liquid was washed with water (3 \times 10 mL) and dried in a vacuum: yield 9.22 g, 72%; mp -64.5 °C; ESI-MS (CH₃OH), positive ion 147 [C₃CNpy], negative ion 280 [N(SO₂CF₃)₂]; ¹H NMR (CD₃CN) δ 8.74 (d, 2H, ³*J*_{HH} = 5.5), 8.56 (m, 1H), 8.09 (m, 2H), 4.64 (t, 2H, ³*J*_{HH} = 7.2), 2.57 (t, 2H, ³*J*_{HH} = 6.8), 2.35 (m, 2H); ¹³C NMR (CD₃CN) δ 146.3, 147.7, 128.7, 121.5, 117.4, 60.2, 26.5, 13.72; IR (cm⁻¹) ν 3139, 3074 (ν_{C-H} aromatic), 2961 (ν_{C-H} aliphatic), 2252 ($\nu_{C=N}$), 1491 (δ_{C-F}), 1178 (ν_{N-SO_2}), 1133 ($\nu_{S=O}$). Anal. Calcd for C₁₁H₁₁N₃F₆S₂O₄: C, 30.92; H, 2.59; N, 9.83. Found: C, 31.02; H, 2.55; N, 9.86.

Synthesis of [(C₃CNpy)₂][PdCl₄]5**.** A reaction mixture of PdCl₂ (177 mg, 1.0 mmol) and **1** (364 mg, 2.00 mmol) in acetonitrile (5 mL) was heated at 80 °C for 4 h. After removal of the solvent, the resulting

orange solid was washed with dichloromethane (2 \times 2 mL) and dried under vacuum to give the product: yield 536 mg, 99%; mp 165 °C; ¹H NMR (DMSO-*d*₆) δ 9.16 (d, 2H, ³*J*_{HH} = 5.6), 8.63 (m, 1H), 8.18 (m, 2H), 4.72 (t, 2H, ³*J*_{HH} = 7.2), 2.67 (t, 2H, ³*J*_{HH} = 6.8), 2.29 (m, 2H); ¹³C NMR (DMSO-*d*₆) δ 149.5, 148.5, 131.6, 122.9, 62.9, 29.7, 16.9. IR (cm⁻¹) ν 3121, 3051 (ν_{C-H} aromatic), 2988, 2972, 2926, 2901 (ν_{C-H} aliphatic), 2244 ($\nu_{C=N}$). Anal. Calcd for C₁₈H₂₂Cl₄N₄Pd: C, 39.84; H, 4.09; N, 10.33. Found: C, 39.87; H, 4.04; N, 10.29.

Synthesis of [(C₃CNpy)₂PdCl₂][PdCl₄]6**.** PdCl₂ (177 mg, 1.0 mmol) was added to a suspension of **5** (543 mg, 1.0 mmol) in dichloromethane (5.0 mL). The reaction mixture was stirred at room temperature for 3 days, during which time, the orange color of the suspension disappeared and a light yellow suspension formed. The resulting yellow solid was collected by centrifugation filtration, washed with dichloromethane (2 \times 2 mL), and dried under vacuum to give the product: yield 687 mg, 95%; mp 110 °C dec; ¹H NMR (DMSO-*d*₆) δ 9.15 (d, 2H, ³*J*_{HH} = 5.6), 8.63 (m, 1H), 8.18 (m, 2H), 4.71 (t, 2H, ³*J*_{HH} = 7.2), 2.67 (t, 2H, ³*J*_{HH} = 7.2), 2.29 (m, 2H); ¹³C NMR (DMSO-*d*₆) δ 149.3, 148.5, 131.6, 122.9, 62.9, 29.6, 16.9; IR (cm⁻¹) ν 3130, 3057 (ν_{C-H} aromatic), 2962, 2937 (ν_{C-H} aliphatic), 2319 ($\nu_{C=N}$). Anal. Calcd for C₁₈H₂₂Cl₆N₄Pd₂: C, 30.03; H, 3.08; N, 7.78. Found: C, 30.05; H, 3.09; N, 7.69.

Synthesis of Complexes 7–9. A typical procedure included a reaction mixture of PdCl₂ (177 mg, 1.0 mmol) and **2** (584 mg, 2.00 mmol) in dichloromethane (5.0 mL) and was stirred at room temperature for 4 days. The resulting yellow solid was collected by centrifugation filtration, washed with dichloromethane (2 \times 2 mL), and dried under vacuum to give the product. Complexes **8** and **9** were prepared using the same procedure.

Compound 7, [(C₃CNpy)₂PdCl₂][PF₆]2**:** yield 98%; mp 150 °C; ¹H NMR (DMSO-*d*₆) δ 9.08 (d, 2H, ³*J*_{HH} = 5.8), 8.61 (m, 1H), 8.16 (m, 2H), 4.65 (t, 2H, ³*J*_{HH} = 7.2), 2.64 (t, 2H, ³*J*_{HH} = 7.2), 2.28 (m, 2H); ¹³C NMR (DMSO-*d*₆) δ 149.2, 148.4, 131.6, 122.9, 63.0, 29.5, 16.9; IR (cm⁻¹) ν 3138, 3098, 3071 (ν_{C-H} aromatic), 2987, 2972, 2901 (ν_{C-H} aliphatic), 2326 ($\nu_{C=N}$). Anal. Calcd for C₁₈H₂₂Cl₂F₁₂N₄Pd₂: C, 28.39; H, 2.91; N, 7.36. Found: C, 28.42; H, 2.95; N, 7.29.

Compound 8, [(C₃CNpy)₂PdCl₂][BF₄]2**:** yield 95%; mp 131 °C; ¹H NMR (DMSO-*d*₆) δ 9.07 (d, 2H, ³*J*_{HH} = 5.5), 8.61 (m, 1H), 8.16 (m, 2H), 4.65 (t, 2H, ³*J*_{HH} = 7.2), 2.63 (t, 2H, ³*J*_{HH} = 7.2), 2.27 (m, 2H); ¹³C NMR (DMSO-*d*₆) δ 149.2, 148.4, 131.6, 122.9, 63.0, 29.5, 16.9; IR (cm⁻¹) ν 3138, 3092, 3069 (ν_{C-H} aromatic), 2987, 2901 (ν_{C-H} aliphatic), 2326 ($\nu_{C=N}$). Anal. Calcd for C₁₈H₂₂B₂Cl₂F₈N₄Pd: C, 33.50; H, 3.44; N, 8.68. Found: C, 33.47; H, 3.45; N, 8.62.

Compound 9, [(C₃CNpy)₂PdCl₂][N(SO₂CF₃)₂]2**:** yield 99%, viscous liquid; ¹H NMR (DMSO-*d*₆) δ 8.74 (d, 2H, ³*J*_{HH} = 5.6), 8.57 (m, 1H), 8.09 (m, 2H), 4.64 (t, 2H, ³*J*_{HH} = 7.2), 2.57 (t, 2H, ³*J*_{HH} = 6.8), 2.35 (m, 2H); ¹³C NMR (D₂O) δ 146.3, 147.8, 128.7, 121.5, 60.2, 26.5, 13.7; IR (cm⁻¹) ν 3122, 3051, 3038 (ν_{C-H} aromatic), 2962 (ν_{C-H} aliphatic), 2319 ($\nu_{C=N}$), 1492 (δ_{C-F}), 1177 (ν_{N-SO_2}), 1131 ($\nu_{S=O}$). Anal. Calcd for C₂₂H₂₂Cl₂F₁₂N₆O₈PdS₄: C, 25.60; H, 2.15; N, 8.14. Found: C, 25.62; H, 2.21; N, 8.19.

Typical Suzuki C–C Coupling Procedure. To a 20 mL two-necked flask fitted with a septum and reflux condenser was added iodobenzene (2.5 mmol, 1 equiv) with ionic liquid (5 mL). Then, phenylboronic acid (335 mg, 2.75 mmol, 1.1 equiv), Na₂CO₃ (560 mg, 5.28 mmol, 2.1 equiv), water (2.5 mL), and finally the appropriate palladium complex (0.03 mmol, 1.2 mol % based on iodobenzene) were added. The mixture was heated to 110 °C and stirred vigorously for 12 h. The mixture was cooled to room temperature and extracted with diethyl ether (3 \times 15 mL). The combined extracts were washed with brine and water and then dried with MgSO₄. The biphenyl product was obtained by filtering the solution followed by removal of solvent. The product was characterized by GC and ¹H NMR. The ionic liquid phase was washed with diethyl ether and put under vacuum overnight prior to the next catalytic cycle. The samples for ICP analysis were prepared by evaporating diethyl ether extract (5 mL) following addition of 65%

HNO₃ (500 mL).⁴¹ The mixture was stirred at room temperature for 2 days and evaporated to dryness again. The residue was dissolved in 15 mL of 2% HNO₃ aqueous solution.

Typical Stille C–C Coupling Procedure. To a 20 mL two-neck flask fitted with a septum and reflux condenser were added iodobenzene (204 mg, 1.0 mmol) and the appropriate palladium complex (0.05 mmol) with ionic liquid (1.0 mL). The mixture was heated to 80 °C and phenyltributylstannane (0.39 mL, 1.2 mmol) added. After it was stirred for 12 h at 80 °C, the reaction mixture was allowed to cool to room temperature, and the product was extracted with diethyl ether (3 × 10 mL). The combined organic layers were washed with saturated aqueous potassium fluoride (3 × 30 mL), then dried over MgSO₄, filtered, and concentrated in a vacuum. The remaining ionic liquid solution was washed with water and dried in a vacuum overnight for further catalytic cycles. The ICP analysis samples were prepared in the same way to that described for the Suzuki reaction.

TEM Sample Preparation. A reaction mixture containing ionic liquid **4** or [C₄py][N(SO₂CF₃)₂] (1.0 mL) was taken after the catalysis,

and ethanol (2.0 mL) was added. The mixture was centrifuged, and the nanoparticles were collected at the bottom of the centrifugation vessel. They were then suspended in ethanol (2 mL) and centrifuged, and the ethanol was decanted. This process was repeated four times. Finally, the ethanol/nanoparticle suspension was deposited on a carbon-coated copper grid (500 mesh) and dried at ambient temperature. The TEM images were obtained on a PHILIPS CM 300 transmission electron microscope.

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Supporting Information Available: X-ray crystallographic data of **1** and **5** and X-ray crystallographic file for **1** and **5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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