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Basic Ionic Liquids: Facile Solvents for Carbon–Carbon Bond Formation Reactions and Ready Access to Palladium Nanoparticles

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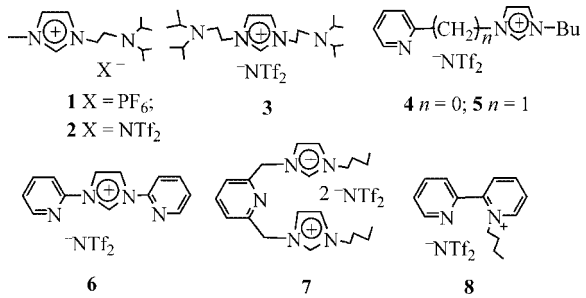
A basic ionic liquid was selected to serve as both the solvent and base for Heck, "copper-free" Sonogashira reactions, and for homocoupling reactions of terminal alkynes. The ionic liquids with tertiary aliphatic amines are effective solvents for these reactions. Under reflux conditions, eight equivalent basic ionic liquids and $Pd(OAc)_2$ in THF or acetone produced palladium colloids with diameters of (2.6 ± 0.3) or (3.7 ± 0.5) nm, respectively. Preliminary results for Knoevenagel condensations are also reported.

Introduction

As environmentally benign solvents, ionic liquids that do not emit volatile organic chemicals (VOCs) have attracted enormous attention as media for green syntheses, and they have also been used successfully to realize many important reactions.[1–2] The Heck reaction has been studied extensively in ionic liquids,[3] where Pd^{II} complexes or Pd^0 nanoparticles act as catalysts. A recent study[4] described the catalytic cycle of palladium colloids in Heck reactions: a palladium precursor can act as a reservoir for a catalytically active Pd^0 species (Pd colloids or highly active forms of low-coordinated Pd^0 species) that undergoes oxidative addition of the aryl halide on the surface with subsequent detachment to generate a homogeneous Pd^{II} species. The main catalytic cycle is initiated by oxidative addition of iodobenzene to the Pd^0 species, which is followed by the reversible coordination of the olefin to the oxidative addition product. The Pd^0 formed in the main catalytic cycle, after β hydride and reductive elimination steps, can either continue in the catalytic cycle or fall back to the nanoparticle reservoir.[4] In these cases, a base, such as K_2CO_3, $NaHCO_3$, NaOAc, triethylamine, or tetrabutylammonium acetate, etc., must be added. Although the consumption of one equivalent of base is inevitable, we believe that a basic ionic liquid acting as both the solvent and base would make the procedure much easier to handle. This is essentially important for Sonogashira reactions where normally a large excess of organic base, e.g. triethylamine, DBU, or piperidine, is required, which causes an additional environmental burden. Moreover, ionic liquids have been proven to be excellent media for syntheses of nanoparticles, nanorods, and nanowires,[5] whose preparation include chemical reduction of transition-metal salts with various reagents, e.g., hydrogen, hydrazine, borohydrides, or alcohols, in the presence of stabilizers, such as special ligands, polymers, or surfactants of the type $R_4N^+ X^-$. There are few reports where amines are used as reducing agents.[6]

Results and Discussion

In this work, eight basic ionic liquids (ILs) (Scheme 1) were employed as both the solvent and base for coupling reactions in which the basic part can be categorized into two series:[7,8] tertiary aliphatic amines **1**–**3** and pyridines



Scheme 1. Structures of basic ionic liquids.

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Table 1. Thermal properties of basic ionic liquids.

Ionic liquid	T_m/T_g	T_d
1	32	289
2	–50	301
3	42	278
4	–	360
5	–70	362
6	75	393
7	–53	401
8	–58	308

4–**7** and **8**.[8] As shown in Table 1, most of the basic ionic liquids have good thermal stabilities.

The structure of **1** was also established by X-ray crystallography (Figure 1); the closest cation contact is 3.166 Å, which approaches the van der Waals distance, and interactions appear to be largely coulombic. The diisopropylamino group bends closely to the imidazolium plane; calculations at the B3LYP/6-311+G(d,p) level show that this configuration is lower in energy by 3.04 kcal than that possessing a dihedral angle (N5–C7–C8–N9) of 180° (Figure 2).[9] In addition, no significant inter- or intramolecular hydrogen bonds were observed as a result of the low charge density ($\rho < 1$) of each fluorine on the anion (PF_6^-).[10]

The Heck reaction of iodobenzene and butyl acrylate was conducted in ionic liquids **1**–**8** at 110 °C with the use of 1 mol-% palladium acetate as the catalyst (Table 2).

After eight hours, almost quantitative conversions and selectivities were found when ionic liquids **1**, **2**, and **3** were used as solvents. The reaction became much slower with the use of **5** or **7**, whereas no reaction occurred in **4**, **6**, or **8**, where the nitrogen base was weaker. These results indicate that for Heck reactions the ionic liquids having aliphatic tertiary amine pendants are superior to the ones substituted with a pyridine functionality. The catalytic system described above can be readily recovered for further use simply by washing with a $NaHCO_3$ solution. After five recycles, no obvious loss in catalytic activity was observed. By using **3** and **5**, owing to their strong affinity for the product, a

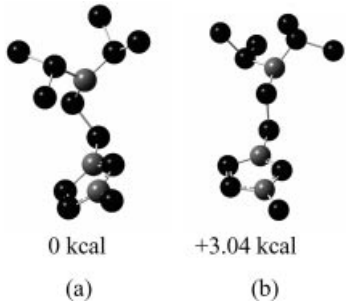
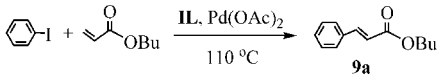


Figure 2. Calculated energies of two structures at the B3LYP/6-311+G** level of theory [dihedral angle N5–N7–C8-N9 in (a) single crystal 69.6°; in (b) 180°].

Table 2. Heck reactions with the use of different ionic liquids.



IL	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Conv. [%]	100	100	100	0	41	0	5	0

lengthy procedure was required to extract the product totally from the ionic liquid phase. Because **2** is a liquid with low viscosity at room temperature, it was chosen as the solvent for C–C bond formation reactions, e.g. Heck and Sonogashira reactions, and Knoevenagel condensations.

Initial attempts to synthesize the carbene–palladium complex [**1**/$Pd(OAc)_2$, 8:1] in THF or acetone resulted in stable palladium colloids measuring (2.6 ± 0.3) or (3.7 ± 0.5) nm, respectively. The tertiary aliphatic amine may act as a reducing agent in the redox process leading to the formation of the nanoparticles (Figure 3). Just as with tetraalkylammonium acetate[11] or the corresponding trialkylborate hydride,[12] this basic ionic liquid can act as both the stabilizer and the reductant for nanometal particles. The reaction rate of bromobenzene is much slower than that of iodobenzene in the current system. Interestingly, when these

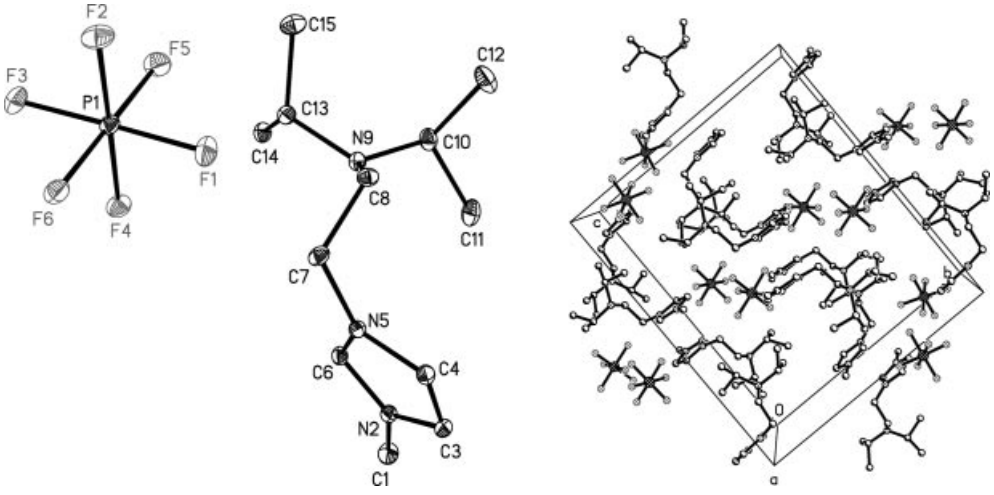


Figure 1. Thermal ellipsoid plot (30%) (left) and packing diagram (right) of **1**.

nanoparticles were preprepared, they showed similar reactivity to the carbene complex[13] for Heck reactions (Table 3). However, the nanocolloid is not stable at high temperature where it agglomerates to form palladium black under the Heck reaction conditions described above.

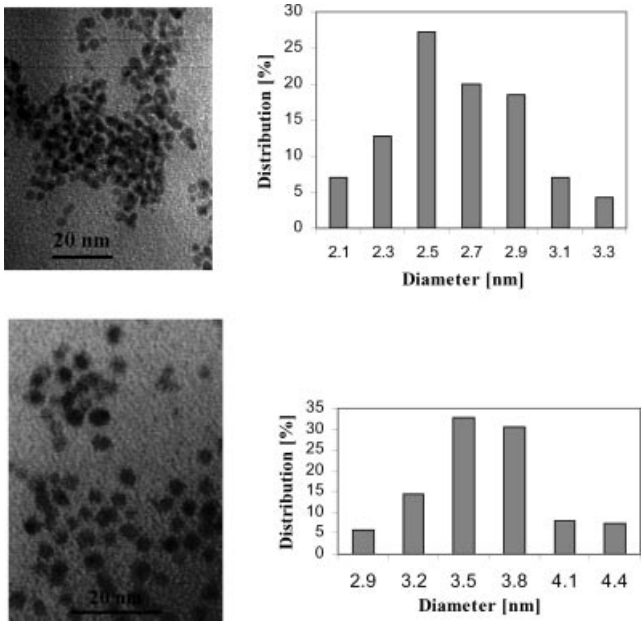
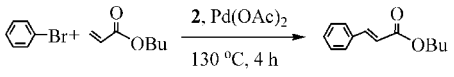
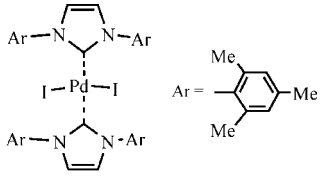


Figure 3. TEM and size distribution of Pd nanoparticles formed in THF (upper) and acetone (lower).

Table 3. Heck reactions with the use of different catalysts.



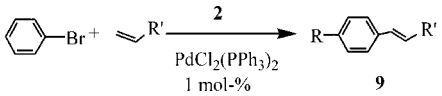
Pd catalyst	$Pd(OAc)_2$	$Pd(PPh_3)_2Cl_2$	Dicarbene-Pd	Nano Pd
Conv. [%]	17	79	21	25



Dicarbene–Pd complex

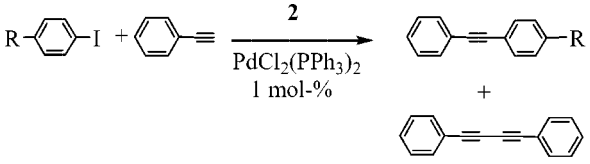
Further studies show that $PdCl_2(PPh_3)_2$ exhibits better reactivity than $Pd(OAc)_2$, carbene complex, or palladium colloid for bromoarenes. As shown in Table 4, with both electron-donating or electron-withdrawing groups in the *para* position, after 10 h the substituted iodo- and bromoarenes were transformed almost quantitatively into cinnamate analogues or stilbene. By using $PdCl_2(PPh_3)_2$ as the catalyst, the palladium colloid was not observed by TEM after the Heck reaction. However, the ^{31}P NMR spectroscopic resonance band of the catalyst $Pd(PPh_3)_2Cl_2$ had shifted from 23.8 to 24.4 ppm, which may indicate the formation of the carbene/Pd/PPh_3 complex during the reaction.[14]

Table 4. Heck reactions for bromobenzenes with the use of **2** as the solvent.

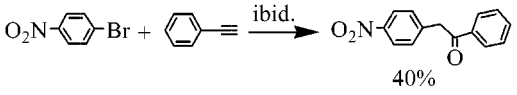


Entry	R	R′	Product	Yield [%]
1	Me	COOBu	**9b**	90
2	NO_2	COOBu	**9c**	84
3	MeO	COOBu	**9d**	88
4	H	Ph	**9e**	86
5	H	OAc	**9e**	84

A palladium-catalyzed Sonogashira coupling reaction[15] was also investigated with the use of **2** as the solvent. The most commonly used catalytic systems for Sonogashira reactions include $PdCl_2(PPh_3)_2$, together with CuI as the cocatalyst and large amounts of amines as the solvents or cosolvents. Frequently the presence of CuI can initiate side reaction including the oxidative homocoupling reactions of alkynes. Therefore, several "copper-free" Sonogashira procedures have been reported.[16] We found that **2**/$PdCl_2(PPh_3)_2$ with a small amount of piperidine or methanol[17] was also an effective system for the this transformation, where CuI was unnecessary. Unfortunately, the homocoupling of alkynes as byproducts was still observed in 10–40% yield. For 1-bromo-4-nitrobenzene, a keto derivative that hydrolyzed from the Sonogashira product was isolated in 40% yield,



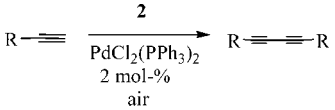
Yield: 80% (R = H), 71% (R = MeO), 67% (R = Me), 63 % (R = F)



By using the same catalytic system in the open air, the alkynes readily underwent homocoupling reactions in good yields with the exception of 1-hexyne. The ionic liquids can be recycled at least six times without significant loss of reactivity (Table 5).

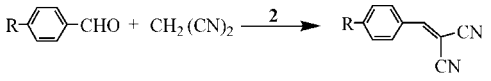
It was reported that the Knoevenagel condensation proceeds efficiently in recyclable [bmim]PF_6 and [bmim]BF_4 without any catalyst in 1 to 24 h.[18] We found that **2** was a more efficient solvent than either of these ionic liquids, e.g., the condensation of aldehyde with malononitrile is completed in less than 10 min. When [bmim]NTf_2 was used as the solvent, less than 20% conversion was observed for the condensation of benzaldehyde with malononitrile after 2 h. This compares favorably with ionic liquid [bmim]OH,[19] as the basic ionic liquids described in this work can be recycled more easily.

Table 5. Recyclable homocoupling reactions of alkynes.[a]



	R					
	C_6H_5	4-*n*Bu-C_6H_4	4-*t*Bu-C_6H_4	4-F-C_6H_4	*n*-C_4H_9	Cy(OH)[b]
Cycle	1	2	3	4	5	6
Yield[c]	93	88	90	92	45[d]	82

[a] All reactions were carried out by using 2 mmol of alkyne, 20 mol-% of piperidine, 2 mol-% of catalyst, and 2 g of ILs at 25 °C for 8 h. [b] 1-Ethynylcyclohexanol. [c] Isolated yield. [d] Conversion based on GC–MS.



Yield: 86 % (R = H), 87 % (R = CH_3), 83 % (R = NO_2), 89 % (R = Cl), 83 % [R = $N(CH_3)_2$]

In conclusion, the new basic ionic liquids with tertiary aliphatic amines are effective solvents and internal bases for Heck and Sonogashira reactions, Knoevenagel condensations, and reagents for the preparation of palladium nanoparticles.

Experimental Section

General: All the reagents used were analytical reagents purchased from commercial sources and used as received. ^{1}H, ^{19}F, and ^{13}C NMR spectra were recorded with a Bruker spectrometer. Chemical shifts are reported in ppm relative to the appropriate standard, $CFCl_3$ for ^{19}F and $SiMe_4$ for ^{1}H and ^{13}C NMR spectra. Differential scanning calorimetry (DSC) data were recorded in the range of –80 to 450 °C with a heating rate of 10 °C min^{-1}. TEM was conducted with a JEOL 1200 EX II Transmission Electron Microscope. XRD was performed with a Siemens D5000 X-ray Diffractometer.

X-ray Crystallography: Crystals of compound **1** were removed from the flask and covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and placed in the low-temperature nitrogen stream. Data for **1** were collected at 86(2) K by using a Bruker/Siemens SMART APEX instrument (Mo-K_α radiation, λ = 0.71073 Å) equipped with a Cryocool NeverIce low temperature device. Data were measured by using omega scans of 0.3° per frame for 15 s, and a full sphere of data was collected. A total of 2450 frames were collected with a final resolution of 0.83 Å. The first 50 frames were recollected at the end of data collection to monitor for decay. Cell parameters were retrieved by using SMART[20] software and refined by using SAINT Plus[21] on all observed reflections. Data reduction and correction for Lp and decay were performed by using the SAINT Plus software. Absorption corrections were applied by using SADABS.[22] The structure was solved by direct methods and refined by least-squares method on F^2 by using the SHELXTL program package.[23] The structure was solved in the space group *Pbca* (#61) by analysis of systematic absences. All atoms were refined anisotropically. No decomposition was observed during data collection. CCDC-631928 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of Ionic Liquids

1-(2′-Diisopropylamino)ethyl-3-methylimidazolium Hexafluorophosphate (1) or Bis(trifluoromethanesulfonyl)amide (2): Prepared according to a similar procedure.[7a] *N*-methylimidazole (4.0 g, 49 mmol) was added to a solution of 2-(diisopropylamino)ethyl chloride hydrochloride (7.0 g, 40.7 mmol) in ethanol (50 mL), and the mixture was heated at reflux for 12 h. After the reaction was complete, the solvent was removed under reduced pressure, and the residue was washed with THF to leave a white powder. Yield: 10.4 g (95%). The solid (5.0 g, 17.7 mmol) was dissolved in water (20 mL) and NaOH (0.71 g, 17.7 mmol) was added. After stirring for 15 min, dichloromethane (30 mL) and KPF_6 (3.3 g, 18 mmol) were added, stirred for a further 30 min, and the aqueous phase was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layer was dried with Na_2SO_4. After evaporation of the solvent, the desired product was obtained (6.1 g, yield 97%). Data for **1**: ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 0.86 [d, ^3J = 6.6 Hz, 12 H, -CH(CH_3)$_2$], 2.75 (t, ^3J = 5.9 Hz, 2 H, -CH$_2$CH_2N), 2.97 [sept, ^3J = 6.6 Hz, 2 H, -NCH(CH$_3$)$_2$], 3.87 (s, 3 H, CH$_3$), 4.11 (t, ^3J = 5.9 Hz, 2 H, imidazolium-CH_2CH$_2$-), 7.63 (s, 1 H, 4-H or 5-H on imidazolium), 7.70 (s, 1 H, 4-H or 5-H on imidazolium), 8.97 (s, 1 H, 2-H on imidazolium) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 21.6, 36.7, 45.8, 48.6, 50.3, 124.1, 124.2, 138.0 ppm. ^{19}F NMR (282 MHz, [D$_6$]DMSO): δ = –70.3 (d, ^1J = 704.5 Hz) ppm. MS (EI+): *m*/*z* (%) = 210 (39.7) [M]$^+$, 128 (36.4) [M – methylimidzole]$^+$, 114 (61.59) [(*i*C$_3$H$_7$)$_2$NCH$_2$]$^+$, 82 (100) [methyl imidazole]$^+$. $C_{12}H_{24}F_6N_3P$ (355.303): calcd. C 40.56, H 6.81, N 11.83; found C 40.69, H 7.00, N 11.90. Data for **2**: ^{1}H NMR (300 MHz, [D$_6$]-DMSO): δ = 0.87 [d, ^3J = 6.6 Hz, 12 H, -CH(CH_3)$_2$], 2.76 (t, ^3J = 5.9 Hz, 2 H, -CH$_2$CH_2N), 2.97 [sept, ^3J = 6.6 Hz, 2 H, -NCH-(CH$_3$)$_2$], 3.88 (s, 3 H, CH$_3$), 4.11 (t, ^3J = 5.9 Hz, 2 H, imidazolium-CH_2CH$_2$-), 7.63 (s, 1 H, 4-H or 5-H on imidazolium), 7.71 (s, 1 H, 4-H or 5-H on imidazolium), 8.98 (s, 1 H, 2-H on imidazolium) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 21.6, 36.7, 45.8, 48.6, 50.3, 120.9 (q, J = 319.4 Hz), 124.1, 124.2, 138.0 ppm. ^{19}F NMR (282 MHz, [D$_6$]DMSO): δ = –79.7 (s) ppm. $C_{14}H_{24}F_6N_4O_4S_2$ (490.485): calcd. C 34.28, H 4.93, N 11.42; found 34.65, H 4.92, N 11.58.

1,3-Bis(2′-diisopropylamino)ethylimidazolium Bis(trifluoromethanesulfonyl)amide (3): Prepared as described for **1**. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.95 [d, ^3J = 6.6 Hz, 24 H, -CH(CH_3)$_2$], 2.93 (t, ^3J = 5.9 Hz, 4 H, -CH$_2$CH_2N), 3.08 [sept, ^3J = 6.6 Hz, 4 H, -NCH(CH$_3$)$_2$], 4.32 (t, ^3J = 5.9 Hz, 4 H, imidazolium-CH_2-CH$_2$-), 7.72 (s, 2 H, 4-H and 5-H on imidazolium), 7.93 (s, 1 H, 2-H on imidazolium) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 20.8, 45.8, 48.6, 50.4, 120.9 (q, J = 319.4 Hz), 123.7, 137.0 ppm. ^{19}F NMR (282 MHz, CDCl$_3$): δ = –79.7 (s) ppm. MS (EI+): *m*/*z* (%) = 323 (15.6) [M]$^+$, 128 (100) [(*i*C$_3$H$_7$)$_2$NCH$_2$CH$_2$]$^+$, 114 (39.7) [(*i*C$_3$H$_7$)$_2$NCH$_2$]$^+$.

1-Butyl-3-(2-pyridinyl)imidazolium Bis(trifluoromethanesulfonyl)-amide (4): Prepared according to the literature,[24] followed by metathesis reaction with $LiNTf_2$. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.00 (t, ^3J = 7.4 Hz, 3 H, CH$_3$), 1.48 (sext, ^3J = 7.5 Hz, 2 H, -CH$_2$CH$_2$CH_2CH$_3$), 2.06 (qui, ^3J = 7.5 Hz, 2 H, -CH$_2$-CH_2CH$_2$CH$_3$), 4.52 (t, ^3J = 7.4 Hz, 2 H, Im-CH_2CH$_2$CH_2CH$_3$), 7.64 (ddd, J = 7.1, 4.8, 0.8 Hz, 1 H), 7.99 (t, J = 1.9 Hz, 1 H), 8.01 (dt, J = 8.0, 0.8 Hz, 1 H), 8.18 (td, J = 7.8, 1.8 Hz, 1 H), 8.44 (t, J = 1.9 Hz, 1 H), 8.64 (d, J = 7.8 Hz, 1 H), 9.84 (s, 1 H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 13.6, 19.9, 32.5, 51.1, 114.9, 120.36, 120.9 (q, J = 319.4 Hz), 124.6, 126.2, 135.3, 141.3, 146.8,

150.3 ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –79.6 (s) ppm. MS (EI+): *m*/*z* (%) = 202 (100) $[M]^+$, 146 (24.5) $[M - C_4H_8]^+$, 78 (6.8) $[Py]^+$.

1-Butyl-3-(2-pyridinylmethyl)imidazolium Bis(trifluoromethanesulfonyl)amide (5): A modified literature procedure was used.[24b] To 2-(bromomethyl) pyridine hydrobromide (2 g, 8 mmol) dissolved in methanol (30 mL) was added sodium hydrogen carbonate (1 equiv.) to neutralize hydrobromide. After stirring for 30 min at room temperature, 1-butylimidazole (0.95 g, 8 mmol) was added, and the solution was stirred at 25 °C for 12 h. Methanol was then evaporated under reduced pressure, and the residue was dissolved in water and extracted several times with ether. To the aqueous phase was added $LiNTf_2$. The resulting oily product was washed with water and dried in vacuo. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.97 (t, ^3J = 7.4 Hz, 3 H, CH_3), 1.41 (sext, ^3J = 7.5 Hz, 2 H, -$CH_2CH_2CH_2CH_3$), 1.96 (qui, ^3J = 7.4 Hz, 2 H, -CH_2CH_2-CH_2CH_3), 4.40 (t, ^3J = 7.4 Hz, 2 H, Im-$CH_2CH_2CH_2CH_3$), 5.68 (s, 2 H, CH_2), 7.40 (dd, *J* = 7.5, 4.9 Hz, 1 H), 7.56 (d, *J* = 7.7 Hz, 1 H), 7.77–7.79 (m, 2 H), 7.87 (td, *J* = 7.7, 1.7 Hz, 1 H), 8.58 (d, *J* = 4.9 Hz, 1 H), 9.19 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.6, 19.9, 32.6, 50.4, 54.7, 120.9 (q, *J* = 318.6 Hz), 123.1, 123.6, 124.3, 124.7, 137.5, 138.4, 150.7, 153.9 ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –79.7 (s) ppm. MS (EI+): *m*/*z* (%) = 216 (100) $[M]^+$, 160 (31.5) $[M - C_4H_8]^+$, 92 (36.8) [M – butylimidazole]$^+$.

1,3-Bis(2-pyridinyl)imidazolium Bis(trifluoromethanesulfonyl)amide (6): Prepared according to the literature,[25] followed by metathesis reaction with $LiNTf_2$. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.73 (td, *J* = 5.5, 2.0 Hz, 2 H), 8.22–8.27 (m, 4 H), 8.68 (d, *J* = 1.5 Hz, 2 H), 8.72 (d, *J* = 4.3 Hz, 2 H), 10.53 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 115.5, 120.9 (q, *J* = 319.5 Hz), 121.4, 126.8, 133.5, 141.5, 147.3, 150.5 ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –79.6 (s) ppm. MS (EI+): *m*/*z* (%) = 223 (100) $[M]^+$, 78 (29.9) $[Py]^+$.

1,1′-[2,6-Pyridinediylbis(methylene)]-bis(3-butyl)imidazolium Bis-[bis(trifluoromethanesulfonyl)amide] (7): Prepared according to the literature,[26] followed by metathesis reaction with $LiNTf_2$. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.96 (t, ^3J = 7.4 Hz, 6 H, CH_3), 1.41 (sext, ^3J = 7.5 Hz, 4 H, -$CH_2CH_2CH_2CH_3$), 1.96 (qui, ^3J = 7.5 Hz, 4 H, -$CH_2CH_2CH_2CH_3$), 4.42 (t, ^3J = 7.3 Hz, 4 H, Im-$CH_2CH_2CH_2CH_3$), 5.71 (s, 4 H, CH_2), 7.59 (d, ^3J = 7.8 Hz, 2 H, H on pyridine), 7.78 (d, ^3J = 1.6 Hz, 2 H, H on imidazolium), 7.83 (d, ^3J = 1.6 Hz, 2 H, H on imidazolium), 8.00 (t, ^3J = 7.8 Hz, 1 H, H on imidazolium), 9.19 (s, 2 H, H on imidazolium) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.6, 19.9, 32.7, 50.5, 54.4, 120.9 (q, *J* = 319.6 Hz), 123.1, 123.5, 124.5, 137.5, 140.0, 154.5 ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –79.8 (s) ppm. MS (EI+): *m*/*z* (%) = 296 (6.5) $[M - C_4H_9]^+$, 230 (87.7) $[M - C_4H_8$ – imidazole$]^+$, 106 (31.8) [M – (butylimidazole)$_2$]$^+$, 82 (100) [methylimidazole]$^+$.

Heck Reactions: Iodobenzene (2.0 mmol), butyl acrylate (3.0 mmol), and ionic liquids (1.5 g) as well as $Pd(OAc)_2$ or $PdCl_2(PPh_3)_2$ (0.02 mmol) were placed in a 25-mL flask, and stirred at 130 °C under an atmosphere of nitrogen for 4 h. The mixture was cooled to room temperature and extracted with diethyl ether/hexane (5:1) until TLC showed no more product in the extracting solvent. The organic phases were combined and the solvent was removed. The residue was purified by column chromatography to isolate the cinnamate derivatives.

Sonogashira Reactions: Iodobenzene (1.0 mmol), phenylacetylene (1.2 mmol), and ionic liquids (1.5 g) as well as $PdCl_2(PPh_3)_2$ (0.01 mmol) and piperidine (20 mol-%) were placed in a 25-mL Schlenk tube, frozen in liquid nitrogen, and then sealed under vacuum. After stirring at room temperature for 20 h, the mixture was extracted with hexane until TLC showed no more product in the extracting solvent.

Homocoupling Reaction of Alkynes: Phenylacetylene (2 mmol) and ionic liquids (1.5 g) as well as $PdCl_2(PPh_3)_2$ (0.04 mmol) and piperidine (20 mol-%) were placed in a 25-mL Schlenk tube open to the air and stirred 8 h. The mixture was extracted with hexane until TLC showed no more product in the extracting solvent.

Knoevenagel Condensation: Phenylaldehyde (1 mmol), malononitrile (1.1 mmol) and ionic liquids (1.5 g) were placed in a 25-mL flask and stirred at 40 °C for several minutes. The mixture was extracted with hot toluene until TLC showed no more product in the extracting solvent.

Recycling Experiment of Ionic Liquids after Coupling Reactions: After the product was extracted, the solvent residue (ionic liquids + catalyst) of the coupling reaction was dissolved in CH_2Cl_2. It was then washed with $NaHCO_3$ and dried with $NaSO_4$; the ionic liquid was thus recycled after evaporation of CH_2Cl_2.

Supporting Information (see footnote on the first page of this article): ^1H NMR spectra of all compounds.

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