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Synthesis and Characterization of Pyrazolyl-Functionalized Imidazolium-Based Ionic Liquids and Hemilabile (Carbene)palladium(II) Complex Catalyzed Heck Reaction

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Neat reactions of 1-(pyrazolylmethyl)imidazole with an excess of alkyl or polyfluoroalkyl halides at 100 °C followed by subsequent metathetical reactions with $LiN(SO_2CF_3)_2$ or KPF_6 at 25 °C gave rise to a series of monoquaternary salts **3a**–**3k**. These salts can be also prepared through treatment of 1-alkylimidazole with 1-(chloromethyl)pyrazole hydrochloride in the presence of base, followed by anion exchange with $LiN(SO_2CF_3)_2$ or KPF_6. Their phase-transition temperature, thermal stability, density and solubility in common solvents have been investigated. Most of the bis(trifluoromethanesulfon)amide salts are room-temperature ionic liquids. The effect of anions and of alkyl substituents bonded to the imidazolium cation on the physicochemical properties was examined. Using 3-butyl-1-(pyrazolylmethyl)imidazolium chloride (**2d**), the precursor of 3-butyl-1-(pyrazolylmethyl)-imidazolium bis(trifluoromethanesulfon)amide (**3d**), as a reactant, a hemilabile (N-heterocyclic carbene)palladium(II) complex **4** was synthesized through a (carbene)silver(I) transfer reagent. It was characterized by single-crystal X-ray diffraction analysis. The catalytic activity and recyclability of **4** in **3d** were preliminarily evaluated by consecutive Heck reactions using different substrates.

Introduction

With ever-increasing environmental awareness, much effort has been directed toward the reduction or replacement of traditional volatile organic solvents as the reaction media in the green chemistry focus area.[1–3] Among various environmentally benign media, such as water, ionic liquids, perfluoroalkyl-containing solvents and supercritical fluids, ionic liquids have been emerging as promising and attractive "green" alternatives in organic synthesis and catalysis.[3–9] In many cases, ionic liquids are good solvents for a wide range of inorganic, organic, and organometallic compounds and have been demonstrated to be ideal immobilizing reagents for various classical transition metal catalyst precursors.[4] Some catalytic transformations can provide high reaction rates and specific chemo-selectivities in the media; however, catalysts were often leached from common ionic liquids, which results in the loss of catalytic activity in the following cycle. Subsequent experiments showed that adding other materials, such as phosphane[5] and nitrogen-containing ligands[6] to ionic liquids can combine different types of stabilizing effects, leading to more stable and recyclable catalytic species. Very recently, this was further addressed by metal-containing ionic liquids in which ionic liquids serve as both solvent and catalyst. Under these conditions, the problem of catalyst leaching is negligible, thus providing a very neat way of conducting the reactions.[7–9] Nonetheless, further development of organic chemistry and catalysis may require the exploration of new types of ionic liquid catalytic systems for specific applications.

N-Heterocyclic carbenes have been extensively employed in homogeneous catalysis because of the formation of strong metal–carbon bonds.[10] Current interest was focused on the development of catalysts for new chemical transformations or catalytic systems with improved performance for known reactions. In this context, the kinetically inert coordination groups, such as pyridyl,[11] pyrazolyl,[12] oxazolyl[13] and phosphane,[14] were often attached to a strongly bonded imidazolyl ring to form the hemilabile ligands[11–13] which give a relatively well-defined active system. Various strategies have also been developed for the preparation of these types of pre-catalysts.[11–15] However, they were usually employed in volatile organic solvents. In these cases, the recovery and reuse of catalysts were difficult. The quest for successful strategies to solve the problem is of great importance in practical terms. Inspired by the excellent efficiency of metal complex catalysts with pendant imidazolium tags,[16] we reasoned that if the ligands of the catalyst precursors possess skeleton structures like the ionic liquid, leaching of catalysts could be avoided due to the increase of ionophilicity and electrostatic action towards ionic

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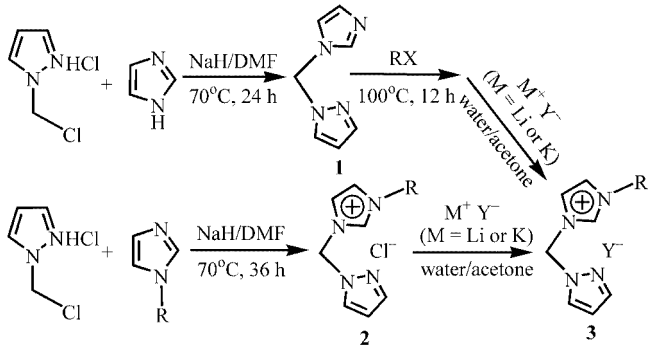
liquids. As a result, activity and recyclability can be improved greatly. Continuing our research in functionalized phosphane-free ionic liquids,[8,12] in this paper, we wish to report the syntheses and characterization of a series of pyrazolyl-functionalized imidazolium-based ionic liquids. In addition, Heck cross-coupling reaction was preliminarily evaluated using a pyrazolyl-functionalized hemilabile (carbene)palladium(II) complex in the ionic liquid possessing a similar skeleton structure.

Results and Discussion

Pyrazolyl-functionalized ionic liquids **3a**–**3k** were prepared by two different routes summarized in Scheme 1. One is the reaction of 1-(chloromethyl)pyrazole hydrochloride with 1-alkylimidazole in the presence of base, followed by metathetical reaction with lithium bis(trifluoromethanesulfon)amide ($LiNTf_2$) or potassium hexafluorophosphate (KPF_6); the other is the reaction of 1-(chloromethyl)pyrazole hydrochloride with imidazole in the presence of base to produce the neutral compound **1**.



Scheme 1.

Subsequent mono-quaternization reactions with alkyl halides under appropriate conditions followed by metathesis with $LiNTf_2$ or KPF_6 gave rise to the target ionic liquids. The first route is an ideal method for commercially available and cheaper alkylimidazoles, such as methylimidazole and butylimidazole. While the latter is a good alternative for expensive alkylimidazoles, especially for ionic liquids with polyfluoroalkyl substituents. In this work, the ionic liquids with methyl and butyl substituents (**3a**, **3d**, **3h** and **3i**) were prepared from **2a** or **2d** using the first route. The remainder was synthesized using the second one.

As noted for 1-(chloromethyl)-3,5-dimethylpyrazole,[17] we found that 1-(chloromethyl)pyrazole is more sensitive to water. Thus, the hydrochloride salt of 1-(chloromethyl)pyrazole was used as starting material and the reactions were carried out under anhydrous conditions. The reaction products, 1-(pyrazolymethyl)imidazole (**1**) and ionic liquids **3a**–**3k**, are stable to air and water. The melting point and decomposition temperatures of **1** are 85 and 232 °C, respectively.

Compounds **3a**–**3k** were characterized by ^1H, ^{13}C, ^{19}F NMR and elemental analyses. The ^1H and ^{13}C NMR spectra have common features, with minimal or no change in the chemical shifts of the signals of the imidazolium and pyrazolyl parent rings in **3a**–**3k**, which indicates that *N*-substituents and anions have little impact on them. The chemical shifts of signals of the protons of the methylene bridge (–NCH_2N–) and the acidic proton of the imidazolium ring in **3a**–**3k** appear in the range from δ = 6.51 to 6.71 ppm and from δ = 9.05 to 9.42 ppm, respectively, which are shifted down-field compared to the corresponding shifts δ = 6.11 ppm and 7.65 ppm in **1**. It should be pointed out that **3g** with a 1*H*,1*H*,2*H*,2*H*-perfluorohexyl substituent shows only one set of signals in its ^1H and ^{13}C NMR spectra, which is very different from its symmetric analog of methylene-bridged bis(imidazolium) compound.[18] The ^{19}F NMR spectra were employed to monitor the progress of metathesis reactions when introducing fluoro-containing anions into ionic liquids that contain polyfluoroalkyl substituents. Resonance bands regarding the fluorine atoms of the NTf_2 and PF_6 anions are in the range from δ = –79.8 to –79.9 and from δ = –70.8 to –74.0 ppm, respectively. The relative areas of anions were compared with those of the polyfluoroalkyl substituents on the imidazolium cation in **3c**, **3e**, **3g** and **3j** to determine completion of reactions.

Phase-transition temperatures (midpoint of glass transition and/or melting point) for **3a**–**3k** were determined by differential scanning calorimetry (DSC). The relationship between their structures and melting points is seen in Table 1. The anion exhibits a crucial influence on their melting points. With constant *N*-substituents on the cation, changing NTf_2 in **3a**–**3f** to PF_6 in **3h**–**3k** gave rise to a marked increase in the respective melting points.

Table 1. Thermal properties and density of **3a**–**3k**.

Compd.	R	Y	T_m [°C][a]	T_d [°C][b]	Density[c]
3a	CH_3	NTf_2	–34[d]	279	1.61
3b	$(CH_2)_2CH_3$	NTf_2	–56[d]	285	1.57
3c	$(CH_2)_2CF_3$	NTf_2	–35[d]	283	1.69
3d	$(CH_2)_3CH_3$	NTf_2	–62[d]	288	1.51
3e	$(CH_2)_3CF_3$	NTf_2	–42[d]	276	1.62
3f	$(CH_2)_5CH_3$	NTf_2	–55[d]	273	1.42
3g	$(CH_2)_2(CF_2)_3CF_3$	NTf_2	44	267	1.75
3h	CH_3	PF_6	66	248	1.65
3i	$(CH_2)_3CH_3$	PF_6	–36[d]	259	1.49
3j	$(CH_2)_3CF_3$	PF_6	75	254	1.58
3k	$(CH_2)_5CH_3$	PF_6	79	256	1.39

[a] Melting point. [b] Thermal degradation. [c] Determined at 25 °C. [d] Glass transition temperature.

The NTf_2 salts are liquids at room temperatures with the exception of the 1*H*,1*H*,2*H*,2*H*-perfluorohexyl-substituted salt **3g** (44 °C). However, the melting points of PF_6 salts are > 25 °C except for butyl-substituted salt **3i** (–36 °C). Nonetheless, all of salts can be classified as ionic liquids since their melting points are < 100 °C.[19] The N substituents on the imidazolium ring also affect phase-transition temperatures of the salts. For salts paired with NTf_2 and

PF_6, as the alkyl chains are changed from methyl to butyl to hexyl, the melting points vary from –34 (**3a**) to –62 (**3d**) to –55 °C (**3f**) and from 66 (**3h**) to –36 (**3i**) to 79 °C (**3k**), respectively. This suggests poorer packing in the crystal lattice as the flexibility of the N substituents on the imidazolium ring increases. As is usually the case, trifluoropropyl-, trifluorobutyl- and 1*H*,1*H*,2*H*,2*H*-perfluorohexyl-substituted salts **3c**, **3e**, **3g** and **3j** have higher melting points than those with propyl, butyl and hexyl substituents.

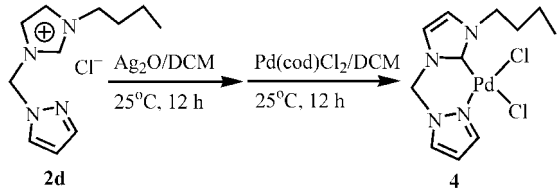
The thermal stabilities of **3a**–**3k** were determined by thermogravimetric analysis (TGA). As shown in Table 1, the anion demonstrates a major influence. The thermal degradation temperatures of NTf_2 and PF_6 salts are in the range 267–288 and 248–259 °C, respectively. The ionic liquids paired with NTf_2 are thermally more stable than their PF_6 analogs. However, the change of *N*-substituents does not essentially influence their decomposition temperature.

The densities of **3a**–**3k** are in the range from 1.39 to 1.75 g cm^{-3} (Table 1). As the alkyl substituents on the imidazolium ring increase in length, the density is decreased. Not surprisingly, the densities of salts bearing fluoroalkyl chains (**3c**, **3e**, **3g** and **3j**) are higher than those of their congeners bearing non-fluoroalkyl chains, and the density increases with increase in the number of fluorine atoms. The 1*H*,1*H*,2*H*,2*H*-perfluorohexyl-substituted salt **3g** has the highest density (1.75 g cm^{-3}), and the hexyl-substituted salts **3f** and **3k** have the lowest density. Anions have no obvious effect on the density. Thus, densities of the pyrazolyl-functionalized imidazolium-based ionic liquids appear to be a function of both the type and bulkiness of alkyl and fluoroalkyl groups.

All of the salts are soluble in ethyl acetate, acetone, methanol, ethanol, and DMF, and they are partially soluble in $CHCl_3$ and CH_2Cl_2. They are immiscible with water and nonpolar solvents, such as alkanes (hexane and pentane) and diethyl ether. In general, the solubilities of the pyrazolyl-functionalized imidazolium-based ionic liquids were quite similar to those of imidazolium-based ionic liquids containing NTf_2 and PF_6 anions.[20]

Syntheses and Structural Characterization of Palladium(II) Compound 4

(Carbene)silver(I) complexes are known to be effective carbene transfer reagents for the synthesis of (carbene)-palladium(II) complexes.[11,13,15] The use of the transfer reagents is particularly important when the imidazolium precursors contain groups that are sensitive to strong bases which are necessary to form the free carbene. In 3-butyl-1-(pyrazolylmethyl)imidazolium chloride (**2d**), the acidic protons in the methylene bridge limit the use of a strong base. Therefore, complex **4** was prepared via a (carbene)silver(I) intermediate (Scheme 2). Treatment of **2d** with Ag_2O in CH_2Cl_2 at 25 °C for 12 h and subsequent addition of $Pd(cod)Cl_2$ with stirring at 25 °C for an additional 12 h gave rise to **4**. Compound **4** is stable in air and moisture.



Scheme 2.

The formation of **4** was supported by the absence of the singlet resonance at δ = 9.59 ppm which would arise from the imidazolium C2–H in the ^{1}H NMR spectrum, where the signal of its precursor **2d** was found. In the ^{13}C NMR spectrum, the signal for the carbene carbon atom of **4** appears at δ = 164.9 ppm, which is a characteristic peak for a (carbene)metal complex.[11,15]

In order to learn more about the coordination mode and conformation of the (carbene)palladium complex, the single-crystal X-ray structure of **4** was determined. As shown in Figure 1, the palladium(II) center is in a distorted square-planar geometry and is coordinated by two Cl anions and one carbene carbon atom and one pyrazolyl nitrogen atom from **2d**. The *cis* angles are in the range from 86.84(14) to 93.44(11)°. The deviation of the palladium(II) center from the square-plane is 0.0076 Å. The Pd1–Cl1 bond *trans* to the carbene carbon atom [2.3598(10) Å] is significantly longer than the Pd1–Cl2 bond *trans* to the pyrazolyl nitrogen atom [2.2732(11) Å], demonstrating the greater *trans* influence of the strongly σ-donating N-heterocyclic carbene ligand.[21] The Pd1–C8 and Pd1–N1 bond lengths are 1.970(4) and 2.042(3) Å, respectively. Compound **2d** serves as a chelating ligand through its carbene carbon atom and pyrazolyl nitrogen atom coordinating to the palladium(II) center which results in a six-membered metallocycle with boat-like conformation. The imidazolium ring is not coplanar with the pyrazolyl ring, with the dihedral angle between them being 60°. There are no other short contacts or worthwhile weak interactions among adjacent molecules.

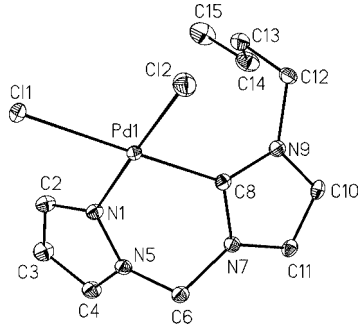


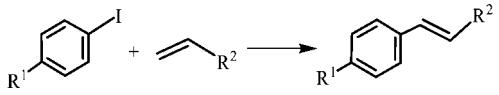
Figure 1. Crystal structure of **4** with thermal ellipsoids at 30% probability.

Palladium(II)-Catalyzed Heck Cross-Coupling Reactions in Ionic Liquid 3d

Because complex **4** was found to have good solubility and stability in ionic liquid **3d** which possesses a similar

skeleton structure, the Heck cross-coupling reaction, a powerful and reliable reaction to test new catalytic systems and C–C bond formation in organic synthesis, was evaluated using **4** as a pre-catalyst immobilized in ionic liquid **3d** according to reported methods.[7a,8a,9a] The cross-coupling reactions between aryl iodides and *n*-butyl acrylate were initially performed with a catalyst loading of 2.0 mol-% in the presence of Na_2CO_3 at 120 °C. The corresponding coupled products were obtained in excellent isolated yields (Entries 1–5, Table 2). The electron-donating (Me, MeO) and electron-withdrawing (F, NO_2) substituents on aryl iodides have no obvious effect on the yields. Similar results were also observed in consecutive coupling reactions between aryl iodide and styrene (Entries 6–10, Table 2). It is noteworthy that the catalytic solution was recycled five times with different reactants in the two cases, and no detectable loss of catalytic activity was observed.

Table 2. Recyclability in the Heck coupling reaction of aryl iodides and vinyl compounds.[a]



Entry	Cycle	R^1	R^2	Yield[b]
1	1	H	CO_2Bu	93
2	2	Me	CO_2Bu	92
3	3	MeO	CO_2Bu	90
4	4	F	CO_2Bu	95
5	5	NO_2	CO_2Bu	92
6	1	H	Ph	94
7	2	Me	Ph	88
8	3	MeO	Ph	90
9	4	F	Ph	91
10	5	NO_2	Ph	93

[a] All reactions were carried out using 1.0 mmol of aryl iodides, 1.25 mmol of olefin, 1.5 mmol of Na_2CO_3, 2.0 mol-% of catalyst and 3.0 g og ionic liquid at 120 °C for 12 h. [b] Isolated yield (%).

This suggests that the pyrazolyl-functionalized (carbene)-palladium(II) precursor is effectively immobilized in the ionic liquid **3d**. All coupled products were easily separated from the catalyst and ionic liquid by simple extraction with diethyl ether. After extracting the products from the catalytic solution, the resulting solution was washed with water and dried under vacuum before new substrates were charged. In the processes, the catalyst leaching problem was negligible owing to similarity of skeleton structure between ionic liquid and catalyst precursor.[9b]

Conclusions

A family of pyrazolyl-functionalized imidazolium-based ionic liquids bearing alkyl and polyfluoroalkyl substituents were synthesized. The relationship between their structures and phase-transition temperatures, thermal stabilities as well as densities was determined. A hemilabile pyrazolyl-functionalized (N-heterocyclic carbene)palladium complex **4** was synthesized and was employed as a catalyst precursor for the consecutive Heck cross-coupling reactions in the ionic liquid **3d**. The catalytic solution showed high stability and catalytic activity in the absence of phosphane ligands. The outstanding activity and recyclability of the catalytic system are based on the similarity of skeleton structure between the palladium catalyst **4** and the ionic liquid **3d**, which precluded the leaching of catalysts during product separation and recycling experiments. This has demonstrated that the hemilabile (carbene)palladium(II) complex catalyzed organic reactions can be performed effectively in the ionic liquid possessing a similar skeleton structure. In summary, this work suggests a promising pathway toward design and synthesis of highly stable and active phosphane-free catalytic systems.

Experimental Section

General: 1-(Chloromethyl)pyrazole hydrochloride was prepared as previously reported.[22] DMF was distilled prior to use. The other chemicals were obtained commercially and were used as purchased. A standard Schlenk line system was used for handling the air- and moisture-sensitive reactions under nitrogen. ^1H, ^{13}C and ^{19}F NMR spectra were recorded with spectrometers at 300, 75 and 282 MHz, respectively, with [D_6]acetone as locking solvent except where otherwise indicated. Chemical shifts are reported in ppm relative to the appropriate standard: $CFCl_3$ for ^{19}F and TMS for ^1H and ^{13}C NMR spectra. MS data were determined using an appropriate instrument; M^+ is the mass of the cation. Densities of solid salts were measured at room temperature with a Micromeritics Accupyc 1330 gas pycnometer. Densities of ionic liquids were measured at room temperature with a pycnometer. Differential scanning calorimetry (DSC) measurements were performed with a calorimeter equipped with an auto-cool accessory and calibrated using indium. The following procedure was used in experiments for each sample: cooling from 40 °C to –80 °C and heating to 400 or 500 °C at 10 °C/min. The transition temperature, T_m, was taken as the peak maximum. Thermogravimetric analysis (TGA) measurements were carried out by heating samples at 10 °C/min from room temperature to 500 °C in a dynamic nitrogen atmosphere (flow rate = 70 mL/min). Thin-layer chromatography (TLC) analysis was performed with Al-backed plates pre-coated with silica gel and examined under UV (254 nm). Flash column chromatography was executed on silica gel (60–200 μm, 60 A). Elemental analyses were performed with a CE-440 Elemental analyzer.

X-ray Crystallography: Crystals of compound **4** 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.[23] Data for **4** were collected at 89(2) K with 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 using ω-scans of 0.3° per frame for 10 s, and a full sphere of data was collected. A total of 2400 frames were collected with a final resolution of 0.83 Å. Cell parameters were retrieved using SMART[24] software and refined using SAINTPlus[25] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.[26] The structure was solved by direct methods and refined by the least-squares method on F^2 using the SHELXTL program package.[27] The structure was solved in the space group $P\bar{1}$ (# 2) by analysis of systematic absences. All non-hydrogen atoms were refined anisotropically. No decomposition was observed dur-

ing data collection. CCDC-617712 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 1-(Pyrazolylmethyl)imidazole (1): This synthesis is a modification of a literature procedure.[22] A solution of imidazole (6.81 g, 100 mmol) in dry DMF (20 mL) was added slowly to a stirred solution of sodium hydride (4.2 g, 105 mmol) in DMF (50 mL). The mixture was stirred under nitrogen at 80 °C for 1 h and then cooled to room temperature. A mixture of 1-(chloromethyl)pyrazole hydrochloride (15.2 g, 100 mmol) and sodium hydride (4.2 g, 105 mmol) in dry DMF (50 mL) was added carefully to the reaction mixture, which was stirred at 70 °C for 24 h. After cooling to room temperature, the inorganic salt was removed by filtration through Celite and washed with acetone (3 × 10 mL). The combined solutions were concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford a colorless solid. Yield: 8.5 g (57%). ^{1}H NMR ($CDCl_3$): δ = 7.65 (s, 1 H, NC*H*N), 7.54 (d, J = 1.5 Hz, 1 H, C$H_{4,5\text{-imidazole}}$), 7.48 (d, J = 2.4 Hz, 1 H, C$H_{4,5\text{-imidazole}}$), 7.05 (d, J = 1.4 Hz, 2 H, C$H_{3,5\text{-pyrazole}}$), 6.30 (t, J = 2.1 Hz, 1 H, C$H_{4\text{-pyrazole}}$), 6.11 (s, 2 H, NCH_2N) ppm. ^{13}C NMR ($CDCl_3$): δ = 141.2, 136.8, 130.5, 128.9, 118.5, 107.6, 60.7 ppm. GC-MS (EI): m/z (%) = 148 (57) [M^+ + 1].

Synthesis of 3-Methyl-1-(pyrazolylmethyl)imidazolium Chloride (2a): 1-(Chloromethyl)pyrazole hydrochloride (0.76 g, 5.0 mmol) was added slowly to a solution of sodium hydride (0.21 g, 5.2 mmol) in dry DMF (20 mL) at 0 °C, and then 1-methylimidazole (2.05 g, 11 mmol) in dry DMF (10 mL) was added to the reaction mixture without delay. The mixture was heated at 70 °C for 36 h. After cooling to room temperature, the resulting solution was filtered and washed with acetone (3 × 10 mL). After the removal of the solvent in the combined solution under reduced pressure, the residue was purified by flash chromatography on silica gel to afford a colorless solid. Yield: 0.60 g (61%). ^{1}H NMR (CD_3CN): δ = 9.81 (s, 1 H, NC*H*N), 8.33 (d, J = 2.4 Hz, 1 H, C$H_{4,5\text{-imidazolium}}$), 7.77 (d, J = 1.7 Hz, 1 H, C$H_{4,5\text{-imidazolium}}$), 7.55 (d, J = 1.7 Hz, 1 H, C$H_{3,5\text{-pyrazole}}$), 7.40 (d, J = 1.6 Hz, 1 H, C$H_{3,5\text{-pyrazole}}$), 6.74 (s, 2 H, NCH_2N), 6.30 (t, J = 2.1 Hz, 1 H, C$H_{4\text{-pyrazole}}$), 3.85 (s, 3 H, NCH_3) ppm. ^{13}C NMR (CD_3CN): δ = 142.6, 138.3, 132.6, 124.7, 122.8, 108.0, 62.3, 37.1 ppm.

Synthesis of 3-Butyl-1-(pyrazolymethyl)imidazolium Chloride (2d): Compound **2d** was synthesized from reaction of 1-(chloromethyl)-pyrazole hydrochloride and 1-butylimidazole according to the procedure described for **2a**. Yield: 0.70 g (58%). ^{1}H NMR (CD_3CN): δ = 9.59 (s, 1 H, NC*H*N), 8.20 (d, J = 2.5 Hz, 1 H, C$H_{4,5\text{-imidazolium}}$), 7.67 (d, J = 1.8 Hz, 1 H, C$H_{4,5\text{-imidazolium}}$), 7.58 (d, J = 1.6 Hz, 1 H, C$H_{3,5\text{-pyrazole}}$), 7.40 (d, J = 1.7 Hz, 1 H, C$H_{3,5\text{-pyrazole}}$), 6.60 (s, 2 H, NCH_2N), 6.33 (t, J = 2.1 Hz, 1 H, C$H_{4\text{-pyrazole}}$), 4.15 (t, J = 7.3 Hz, 2 H, NCH_2CH$_2$), 1.80 (quint, J = 7.3 Hz, 2 H, NCH$_2$CH_2), 1.26 (sext, J = 7.5 Hz, 2 H, CH_2CH$_3$), 0.91 (t, J = 7.3 Hz, 3 H, CH$_2$CH_3) ppm. ^{13}C NMR (CD_3CN): δ = 142.7, 137.6, 132.6, 123.5, 122.9, 108.0, 62.4, 50.5, 32.3, 19.9, 13.6 ppm.

General Method for the Synthesis of 3a, 3d, 3h and 3i from 2a and 2d: To a stirred solution of **2a** or **2d** (1.0 mmol) in water (10 mL) and acetone (10 mL) was added slowly $LiN(SO_2CF_3)_2$ (0.43 g, 1.5 mmol) or KPF_6 (0.28 g, 1.5 mmol). The reaction mixture was stirred at 25 °C for 5 h. The acetone was evaporated under reduced pressure, and the water layer was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with water (3 × 10 mL), once with saturated $Na_2S_2O_3$ solution (5 mL), and then dried with anhydrous Na_2SO_4. The solvent was removed in vacuo to give desired product.

General Method for Synthesis of 3a–3k from 1: 1-(Pyrazolylmethyl)-imidazole (**1**) (0.15 g, 1 mmol) and an alkyl halide (1.5 mmol) were placed in a 20-mL Pyrex glass tube. After the samples were cooled to –195 °C, the tube was evacuated and sealed. The reaction mixture was stirred at 100 °C for 12 h. After cooling and carefully opening the tube, the volatile materials were removed under reduced pressure. The residue was dissolved in water (10 mL) and acetone (10 mL), then $LiN(SO_2CF_3)_2$ (0.43 g, 1.5 mmol) or KPF_6 (0.28 g, 1.5 mmol) was added slowly. The reaction mixture was stirred at 25 °C for 5 h. The acetone was evaporated under reduced pressure, and the water layer was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with water (3 × 10 mL), once with saturated $Na_2S_2O_3$ solution (5 mL), and then dried with anhydrous Na_2SO_4. The solvent was removed in vacuo to give **3a**–**3k**.

3-Methyl-1-(pyrazolylmethyl)imidazolium Bis(trifluoromethanesulfon)amide (3a): Pale-yellow liquid; yield: 0.40 g (90%). ^{1}H NMR: δ = 9.23 (s, 1 H, NC*H*N); 8.03 (s, 1 H, C$H_{4,5\text{-imidazolium}}$), 7.85 (s, 1 H, C$H_{4,5\text{-imidazolium}}$), 7.72 (s, 1 H, C$H_{3,5\text{-pyrazole}}$), 7.61 (s, 1 H, C$H_{3,5\text{-pyrazole}}$), 6.69 (s, 2 H, NC$H_2$N), 6.37 (s, 1 H, C$H_{4\text{-pyrazole}}$), 4.08 (s, 3 H, NC$H_3$) ppm. ^{13}C NMR: δ = 142.8, 137.2, 131.9, 125.3, 122.9, 120.9 (q, J = 319.1 Hz), 108.2, 62.9, 37.0 ppm. ^{19}F NMR: δ = –79.9 (s, 6 F) ppm. $C_{10}H_{11}F_6N_5O_4S_2$ (443.02): calcd. C 27.09, H 2.50, N 15.80; found C 27.24, H 2.49, N 15.93.

3-Propyl-1-(pyrazolylmethyl)imidazolium Bis(trifluoromethanesulfon)amide (3b): Pale-yellow liquid; yield: 0.43 g (92%). ^{1}H NMR: δ = 9.30 (s, 1 H, NC*H*N), 8.04 (s, 1 H, C$H_{4,5\text{-imidazolium}}$), 7.87 (s, 1 H, C$H_{4,5\text{-imidazolium}}$), 7.80 (s, 1 H, C$H_{3,5\text{-pyrazole}}$), 7.63 (s, 1 H, C$H_{3,5\text{-pyrazole}}$), 6.71 (s, 2 H, NC$H_2$N), 6.39 (t, J = 2.0 Hz, 1 H, C$H_{4\text{-pyrazole}}$), 4.38 (t, J = 7.2 Hz, 2 H, NCH_2CH$_2$), 1.97 (sext, J = 6.9 Hz, 2 H, NCH$_2$CH_2), 0.95 (t, J = 7.4 Hz, 3 H, CH$_2$CH_3) ppm. ^{13}C NMR: δ = 142.3, 137.3, 131.9, 124.3, 123.2, 120.9 (q, J = 319.3 Hz), 109.3, 63.1, 50.9, 31.2, 10.8 ppm. ^{19}F NMR: δ = –79.8 (s, 6 F) ppm. $C_{12}H_{15}F_6N_5O_4S_2$ (471.05): calcd. C 30.57, H 3.21, N 14.86; found C 30.47, H 3.10, N 14.82.

1-(Pyrazolylmethyl)-3-(3,3,3-trifluoropropyl)imidazolium Bis(trifluoromethanesulfon)amide(3c): Pale-yellow liquid; yield: 0.46 g (88%). ^{1}H NMR: δ = 9.47 (s, 1 H, NC*H*N), 8.06 (d, J = 2.2 Hz, 1 H, C$H_{4,5\text{-imidazolium}}$), 7.96 (s, 1 H, C$H_{4,5\text{-imidazolium}}$), 7.64 (s, 2 H, C$H_{3,5\text{-pyrazole}}$), 6.76 (s, 2 H, NC$H_2$N), 6.40 (t, J = 1.8 Hz, 1 H, C$H_{4\text{-pyrazole}}$), 4.82 (t, J = 6.9 Hz, 2 H, NCH_2CH$_2$), 3.06–3.16 (m, 2 H, NCH$_2$CH_2) ppm. ^{13}C NMR: δ = 143.5, 142.4, 131.9, 126.7 (q, J = 274.2 Hz), 123.6, 123.1, 120.9 (q, J = 319.3 Hz), 109.3, 63.2, 34.5 (q, J = 43.8 Hz), 10.4 ppm. ^{19}F NMR: δ = –65.9 (t, J = 10.7 Hz, 3 F), –79.9 (s, 6 F) ppm. $C_{12}H_{12}F_9N_5O_4S_2$ (525.02): calcd. C 27.43, H 2.30, N 13.33; found C 27.88, H 2.23, N 13.38.

3-Butyl-1-(pyrazolylmethyl)imidazolium Bis(trifluoromethanesulfon)amide (3d): Pale-yellow liquid; yield: 0.46 g (95%). ^{1}H NMR: δ = 9.32 (s, 1 H, NC*H*N), 8.03 (d, J = 2.4 Hz, 1 H, C$H_{4,5\text{-imidazolium}}$), 7.87 (d, J = 1.6 Hz, 1 H, C$H_{4,5\text{-imidazolium}}$), 7.82 (d, J = 1.7 Hz, 1 H, C$H_{3,5\text{-pyrazole}}$), 7.62 (d, J = 1.5 Hz, 1 H, C$H_{3,5\text{-pyrazole}}$), 6.71 (s, 2 H, NCH_2N), 6.39 (t, J = 2.1 Hz, 1 H, C$H_{4\text{-pyrazole}}$), 4.42 (t, J = 7.3 Hz, 2 H, NCH_2CH$_2$), 1.93 (quint, J = 7.3 Hz, 2 H, NCH$_2$CH_2), 1.37 (sext, J = 7.5 Hz, 2 H, CH_2CH$_3$), 0.93 (t, J = 7.4 Hz, 3 H, CH$_2$CH_3) ppm. ^{13}C NMR: δ = 142.9, 137.2, 132.0, 124.1, 123.2, 120.9 (q, J = 319.3 Hz), 108.2, 63.1, 50.7, 32.5, 19.9, 13.6 ppm. ^{19}F NMR: δ = –79.9 (s, 6 F) ppm. $C_{13}H_{17}F_6N_5O_4S_2$ (485.06): calcd. C 32.17, H 3.53, N 14.43; found C 32.18, H 3.51, N 14.41.

1-(Pyrazolylmethyl)-3-(4,4,4-trifluorobutyl)imidazolium Bis(trifluoromethanesulfon)amide (3e): Pale-yellow liquid; yield: 0.50 g (92%). ^{1}H NMR: δ = 9.23 (s, 1 H, NC*H*N), 7.92 (d, J = 1.9 Hz, 1 H, C$H_{4,5\text{-imidazolium}}$), 7.75 (d, J = 1.1 Hz, 1 H, C$H_{4,5\text{-imidazolium}}$), 7.51 (s, 2 H, C$H_{3,5\text{-pyrazole}}$), 6.58 (s, 2 H, NC$H_2$N), 6.27 (t, J = 2.1 Hz, 1 H, C$H_{4\text{-pyrazole}}$), 4.44 (t, J = 6.7 Hz, 2 H, NCH_2CH$_2$), 2.13–2.30 (s, 4 H, CH_2CH_2CF$_3$) ppm. ^{13}C NMR: δ = 142.8, 137.4, 132.0, 127.9 (q, J = 273.8 Hz), 124.0, 123.2, 120.9 (q, J = 319.1 Hz), 108.2, 63.1, 49.5, 30.8 (q, J = 29.3 Hz), 23.5 (q, J = 3.2 Hz) ppm. ^{19}F NMR: δ = –66.9 (t, J = 10.6 Hz, 3 F), –79.9 (s, 6 F) ppm. $C_{13}H_{14}F_9N_5O_4S_2$ (539.03): calcd. C 28.95, H 2.62, N 12.98; found C 29.15, H 2.13, N 12.78.

3-Hexyl-1-(pyrazolylmethyl)imidazolium Bis(trifluoromethanesulfon)amide (3f): Pale-yellow liquid; yield: 0.49 g (96%). ^{1}H NMR: δ = 9.20 (s, 1 H, NC*H*N), 8.02 (d, J = 2.4 Hz, 1 H, C$H_{4,5\text{-imidazolium}}$), 7.78 (s, 1 H, C$H_{4,5\text{-imidazolium}}$), 7.74 (s, 1 H, C$H_{3,5\text{-pyrazole}}$), 7.61 (d, J = 1.5 Hz, 1 H, C$H_{3,5\text{-pyrazole}}$), 6.65 (s, 2 H, NCH_2N), 6.37 (t, J = 1.8 Hz, 1 H, C$H_{4\text{-pyrazole}}$), 4.35 (t, J = 7.3 Hz, 2 H, NCH_2CH$_2$), 1.93 (quint, J = 6.8 Hz, 2 H, NCH$_2$CH_2), 1.27–1.34 (m, 6 H, CH_2CH_2CH_2CH$_3$), 0.85 (t, J = 6.7 Hz, 3 H, CH$_2$CH_3) ppm. ^{13}C NMR: δ = 142.1, 136.0, 131.1, 123.1, 122.1, 120.1 (q, J = 319.4 Hz), 107.4, 62.1, 50.0, 30.8, 29.7, 25.4, 22.0, 13.2 ppm. ^{19}F NMR: δ = –79.8 (s, 6 F) ppm. $C_{15}H_{21}F_6N_5O_4S_2$ (513.09): calcd. C 35.09, H 4.12, N 13.64; found C 35.10, H 4.09, N 13.43.

3-(1*H*,1*H*,2*H*,2*H*-Perfluorohexyl)-1-(pyrazolylmethyl)imidazolium Bis(trifluoromethanesulfon)amide (3g): Colorless solid; yield: 0.58 g (86%). ^{1}H NMR: δ = 9.42 (s, 1 H, NC*H*N), 8.03 (s, 1 H, C$H_{4,5\text{-imidazolium}}$), 7.94 (s, 1 H, C$H_{4,5\text{-imidazolium}}$), 7.87 (s, 1 H, C$H_{3,5\text{-pyrazole}}$), 7.62 (s, 1 H, C$H_{3,5\text{-pyrazole}}$), 6.70 (s, 2 H, NC$H_2$N), 6.38 (t, J = 1.5 Hz, 1 H, C$H_{4\text{-pyrazole}}$), 4.85 (t, J = 7.1 Hz, 2 H, NCH_2CH$_2$), 3.03–3.15 (m, 2 H, NCH$_2$CH_2) ppm. ^{13}C NMR: δ = 142.9, 141.6, 137.9, 132.0, 124.3, 123.3, 120.6 (q, J = 370.5 Hz), 110.1–124.2 (m), 108.3, 63.2, 43.2 (t, J = 5.1 Hz), 31.6 (t, J = 21.1 Hz) ppm. ^{19}F NMR: δ = –79.9 (s, 6 F), –82.0 (t, J = 9.9 Hz, 3 F), –114.60 (quint, J = 7.8 Hz, 2 F), –125.0 (s, 2 F), –126.6 (quint, J = 6.3 Hz, 2 F) ppm. $C_{15}H_{12}F_{15}N_5O_4S_2$ (675.01): calcd. C 26.67, H 1.79, N 10.37; found C 26.70, H 1.80, N 10.72.

3-Methyl-1-(pyrazolylmethyl)imidazolium Hexafluorophosphate (3h): Colorless solid, yield: 0.37 g (84%). ^{1}H NMR: δ = 9.09 (s, 1 H, NC*H*N); 8.02 (d, J = 2.3 Hz, 1 H, C$H_{4,5\text{-imidazolium}}$), 7.76 (d, J = 1.8 Hz, 1 H, C$H_{4,5\text{-imidazolium}}$), 7.65 (d, J = 1.7 Hz, 1 H, C$H_{3,5\text{-pyrazole}}$), 7.60 (d, J = 1.6 Hz, 1 H, C$H_{3,5\text{-pyrazole}}$), 6.63 (s, 2 H, NCH_2N), 6.37 (t, J = 2.1 Hz, 1 H, C$H_{4\text{-pyrazole}}$), 4.04 (s, 3 H, NCH_3) ppm. ^{13}C NMR: δ = 142.8, 137.6, 132.0, 125.2, 122.7, 108.2, 62.8, 36.8 ppm. ^{19}F NMR: δ = –71.5 to –74.0 (d, J = 706.4 Hz, 6 F) ppm. $C_8H_{11}F_6N_4P$ (308.16): calcd. C 31.18, H 3.60, N 18.18; found C 31.70, H 3.57, N 18.11.

3-Butyl-1-(pyrazolylmethyl)imidazolium Hexafluorophosphate (3i): Pale-yellow liquid; yield: 0.32 g (91%). ^{1}H NMR: δ = 9.17 (s, 1 H, NC*H*N), 7.93 (d, J = 2.4 Hz, 1 H, C$H_{4,5\text{-imidazolium}}$), 7.74 (d, J = 1.7 Hz, 1 H, C$H_{4,5\text{-imidazolium}}$), 7.69 (d, J = 1.7 Hz, 1 H, C$H_{3,5\text{-pyrazole}}$), 7.51 (d, J = 1.5 Hz, 1 H, C$H_{3,5\text{-pyrazole}}$), 6.57 (s, 2 H, NCH_2N), 6.27 (t, J = 2.1 Hz, 1 H, C$H_{4\text{-pyrazole}}$), 4.30 (t, J = 7.3 Hz, 2 H, NCH_2CH$_2$), 1.82 (quint, J = 7.5 Hz, 2 H, NCH$_2$CH_2), 1.25 (sext, J = 7.5 Hz, 2 H, CH_2CH$_3$), 0.82 (t, J = 7.4 Hz, 3 H, CH$_2$CH_3) ppm. ^{13}C NMR: δ = 142.9, 137.2, 132.1, 124.1, 123.1, 108.2, 63.1, 50.7, 32.6, 20.0, 13.6 ppm. ^{19}F NMR: δ = –71.4 to –73.9 (d, J = 706.4 Hz, 6 F) ppm. $C_{11}H_{17}F_6N_4P$ (350.11): calcd. C 37.72, H 4.89, N 16.00; found C 37.92, H 4.80, N 15.87.

1-(Pyrazolylmethyl)-3-(4,4,4-trifluorobutyl)imidazolium Hexafluorophosphate (3j): Colorless solid; yield: 0.35 g (87%). ^{1}H NMR: δ = 9.14 (s, 1 H, NC*H*N), 7.92 (d, J = 2.1 Hz, 1 H, C$H_{4,5\text{-imidazolium}}$), 7.71 (d, J = 1.8 Hz, 1 H, C$H_{4,5\text{-imidazolium}}$), 7.70 (d, J = 1.7 Hz, 1 H, C$H_{3,5\text{-pyrazole}}$), 7.50 (d, J = 1.5 Hz, 1 H, C$H_{3,5\text{-pyrazole}}$), 6.54 (s, 2 H, NCH_2N), 6.26 (t, J = 2.1 Hz, 1 H, C$H_{4\text{-pyrazole}}$), 4.41 (t, J = 7.1 Hz, 2 H, NCH_2CH$_2$), 2.13–2.28 (m, 4 H, CH_2CH_2CF3) ppm. ^{13}C NMR: δ = 142.8, 137.3, 132.0, 127.9 (q, J = 273.8 Hz), 123.9, 123.2, 108.2, 63.0, 49.4, 30.8 (q, J = 29.1 Hz), 23.5 (q, J = 3.2 Hz) ppm. ^{19}F NMR: δ = –66.8 (t, J = 10.6 Hz, 3 F), –70.8 to –73.3 (d, J = 707.5 Hz, 6 F) ppm. $C_{11}H_{14}F_9N_4P$ (404.08): calcd. C 32.69, H 3.49, N 13.86; found C 32.78, H 3.37, N 13.39.

3-Hexyl-1-(pyrazolylmethyl)imidazolium Hexafluorophosphate (3k): Colorless solid; yield: 0.35 g (93%). ^{1}H NMR: δ = 9.05 (s, 1 H, NC*H*N), 7.92 (d, J = 2.4 Hz, 1 H, C$H_{4,5\text{-imidazolium}}$), 7.67 (d, J = 2.2 Hz, 1 H, C$H_{4,5\text{-imidazolium}}$), 7.62 (d, J = 1.8 Hz, 1 H, C$H_{3,5\text{-pyrazole}}$), 7.49 (d, J = 1.6 Hz, 1 H, C$H_{3,5\text{-pyrazole}}$), 6.51 (s, 2 H, NCH_2N), 6.26 (t, J = 2.1 Hz, 1 H, C$H_{4\text{-pyrazole}}$), 4.25 (t, J = 7.4 Hz, 2 H, NCH_2CH$_2$), 1.82 (quint, J = 7.2 Hz, 2 H, NCH$_2$CH_2), 1.13–1.25 (m, 6 H, CH_2CH_2CH_2CH$_3$), 0.73 (t, J = 7.0 Hz, 3 H, CH$_2$CH_3) ppm. ^{13}C NMR: δ = 142.8, 137.0, 132.0, 123.9, 122.9 108.2, 62.9, 50.8, 31.7, 30.4, 26.3, 22.9, 14.1 ppm. ^{19}F NMR: δ = –71.3 to –73.8 (d, J = 706.4 Hz, 6 F) ppm. $C_{13}H_{21}F_6N_4P$ (378.14): calcd. C 41.27, H 5.60, N 14.81; found C 41.53, H 5.46, N 14.71.

Synthesis Procedure for [3-Butyl-1-(pyrazolylmethyl)imidazol-2-ylidene]palladium Dichloride (4): A mixture of **2d** (0.48 g, 2.0 mmol) and silver(I) oxide (0.24 g, 1.05 mmol) in dichloromethane (20 mL) was stirred at 25 °C for 12 h. The reaction mixture was filtered through Celite and washed with CH_2Cl_2 (3 × 3 mL). The solvent of the combined solutions was removed in vacuo until ca. 10 mL remained. Then Pd(cod)Cl$_2$ (0.57 g, 2 mmol) in 10 mL of CH_2Cl_2 was added to the resulting solution and the mixture stirred at 25 °C for 12 h. After this time, it was filtered through Celite and washed with CH_2Cl_2 (3 ×3 mL). The combined solutions were concentrated under reduced pressure to leave a yellow solid, which was recrystallized from CH_2Cl_2/Et$_2$O (3 mL/10 mL), washed with hexane, and dried in vacuo to leave a yellow powder. Yield: 0.68 g (89%). ^{1}H NMR ([D$_6$]DMSO): δ = 8.06 (d, J = 2.4 Hz, 1 H, C$H_{4,5\text{-imidazol}}$), 7.77 (d, J = 1.6 Hz, 1 H, C$H_{4,5\text{-imidazol}}$), 7.44 (d, J = 1.5 Hz, 1 H, C$H_{3,5\text{-pyrazole}}$), 7.33 (d, J = 1.5 Hz, 1 H, C$H_{3,5\text{-pyrazole}}$), 6.51 (s, 2 H, NCH_2N), 6.77 (t, J = 2.1 Hz, 1 H, C$H_{4\text{-pyrazole}}$), 4.34 (t, J = 7.3 Hz, 2 H, NCH_2CH$_2$), 1.70 (quint, J = 7.0 Hz, 2 H, NCH$_2$CH_2), 1.12 (sext, J = 7.1 Hz, 2 H, CH_2CH$_3$), 0.82 (t, J = 7.3 Hz, 3 H, CH$_2$CH_3) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 164.9, 143.8, 133.6, 122.5, 121.7, 107.1, 62.4, 49.4, 32.6, 19.0, 13.4 ppm. $C_{11}H_{16}Cl_2N_4Pd$ (379.98): calcd. C 34.62, H 4.23, N 14.68; found C 35.35, H 4.19, N 14.05.

General Procedures for the Heck Cross-Coupling Reactions in Ionic Liquid 3d: The palladium(II) complex **4** (7.6 mg, 0.02 mmol) was dissolved in **3d** (3.0 g), and the solvent was degassed under reduced pressure at 60 °C for 1 h before nitrogen was introduced. The aryl iodide (1.0 mmol), the olefin (1.25 mmol) and Na_2CO_3 (1.5 mmol) were subsequently added under nitrogen. The resulting mixture was stirred at 120 °C for 12 h. The product was extracted from the reaction mixture by the addition of diethyl ether (3 mL), and followed by decanting the diethyl ether solution of the product. This was repeated three more times (3 × 3 mL). The combined organic layers were concentrated by rotary evaporation. The residue was purified by flash chromatography on silica gel to give the desired product. The ionic liquid containing the Pd^{II} catalyst was washed with water (3 × 3 mL), then dried under reduced pressure at 60 °C for 4 h to remove traces of water and other volatile materials, and employed for the next cycle.

Supporting Information (see footnote on the first page of this article): Spectroscopic data of coupled products for Heck cross-coupling reaction.

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