Efficient Heck reactions catalyzed by a highly recyclable palladium(II) complex of a pyridyl-functionalized imidazolium-based ionic liquid†

Ruihu Wang, Ji-Chang Xiao, Brendan Twamley and Jean'ne M. Shreeve*

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The reactions of 2-(2-pyridyl)imidazole with alkyl iodides at 25 °C in the presence of base gave rise to 1-alkyl-2-(2-pyridyl)imidazole. Subsequent neat reactions with alkyl or polyfluoroalkyl halides at 100 °C, followed by anion exchange with $LiN(SO_2CF_3)_2$, generated the mono-quaternary ionic liquids **3a–3l**. All of them have excellent thermal stability and wide liquid range. Most of the salts with asymmetric *N*-substituents are liquid at room temperature. The effect of *N*-substituent variation and symmetry on NMR, TGA and DSC is discussed. Reaction of **3f** with palladium(II) chloride produced a mononuclear palladium ionic liquid complex **4**, the structure of which was confirmed by single-crystal X-ray diffraction analysis. The Heck cross-coupling reactions using **4** in ionic liquid **3f** demonstrated excellent stability and recyclability.

Introduction

Room temperature ionic liquids are currently attracting considerable attention as alternative media to conventional volatile solvents in organic synthesis and catalysis owing to their specific physical and chemical properties.[1–9] One of the amazing features is that they can be well-tailored to meet particular requirements through variation and modification of cationic and/or anionic components. Recent advances in ionic liquid research provide another route for achieving carefully designed compounds, in which various functional groups, such as nitrile,[3] thiocyanate,[4] silyl,[5] hydroxyl,[6] thiols,[7] and fluoroalkyl[8] groups, were bonded to cationic cores of ionic liquids as substituents. These functionalized ionic liquids exhibit wider ranges of physical and chemical properties that could be useful for some applications due to excellent synergetic effects between cationic cores and functional groups.

Of the various types of ionic liquids available, imidazolium-based compounds have been extensively employed as reaction media in transition-metal catalyzed organic reactions, since the catalysts can be easily immobilized and recovered in the media.[3–9] As a consequence, much interest has been focused on the rational design and tuning of imidazolium-based ionic liquids through introducing functional groups into their side chains.[3–8] Experimental studies suggested that *in situ* formation of metal carbene precursors was involved during the catalytic process in the imidazolium-based salts, stabilizing and activating the metal centers.[9] However, in some cases, the strong acidity at C-2 of the imidazolium ring gave rise to arylimidazolium salts and other side-products.[9a,10] This drawback was avoided by using 2-methylimidazolium-based ionic liquids, but metal catalysts could not be efficiently trapped into the ionic liquids even in the presence of other supporting ligands.[11] It was envisaged that ionic liquids incorporating an appropriate coordinating group at C-2 of the imidazolium core might serve as both ligand and solvent to the metal catalysts. This strategy was initially implemented by introducing a diphenylphosphine group at C-2 of the imidazolium cation.[12] However, the resulting salt was not an ionic liquid and, therefore, had to be dissolved in another ionic liquid for effective use in catalysis. Moreover, phosphine-containing ionic liquids are sensitive to air and moisture. Thus, development of functionalized phosphine-free ionic liquids is of great importance for catalyst recycling. As an extension of our research into fluorine-containing ionic liquid systems,[8b] we became interested in the use of ionic liquids containing coordinating groups as reaction media.[13] Herein, we wish to report a series of imidazolium-based ionic liquids functionalized by a 2-pyridyl group at C-2 and to demonstrate the preliminary results in their use as a ligand and solvent for palladium(II)-catalyzed Heck cross-coupling reactions. For comparison, an uncoordinated phenyl-functionalized analogue, 1-butyl-2-phenyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide (**6**), was also investigated.

Results and discussion

The synthetic pathway for ionic liquids **3a–3l** is depicted in Scheme 1. 2-(2-Pyridyl)imidazole (**1**) was easily prepared by the reaction of 2-pyridylcarboxaldehyde, glyoxal and concentrated aqueous NH_3.[14] Subsequent alkylation reactions of 2-(2-pyridyl)imidazole with alkyl iodides in DMF and aqueous NaOH solution gave rise to 1-alkyl-2-(2-pyridyl)imidazole (**2a–2c**). In **2a–2c**, two basic nitrogen atoms from imidazolyl and pyridyl rings are available for quaternization. Usually, the imidazoyl nitrogen atom has stronger donor ability[15] and is more easily quaternized than the pyridyl nitrogen atom. Thus, a pyridyl coordination center will remain after monoquaternization under appropriate conditions. Thus, treatment of **2a–2c** with alkyl halides under neat conditions at 100 °C gave the monoquaternary salts, and subsequent anion exchange with lithium bis(trifluoromethanesulfonyl)amide led to

Department of Chemistry, University of Idaho, Moscow, Idaho, 83844-2343, USA. E-mail: jshreeve@uidaho.edu

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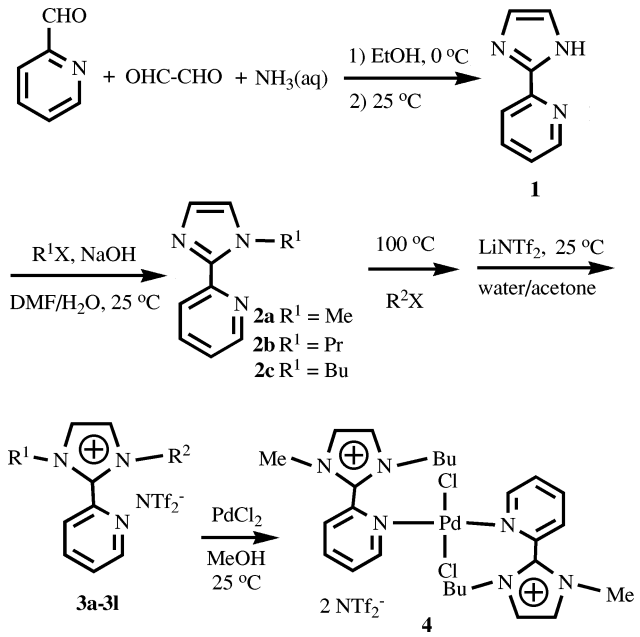


Scheme 1

the formation of ionic liquids **3a–3l** in high yields. Following similar procedures, a phenyl-functionalized ionic liquid, 1-butyl-2-phenyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide (**6**), was synthesized using 2-phenylimidazole as a starting material (Scheme 2).

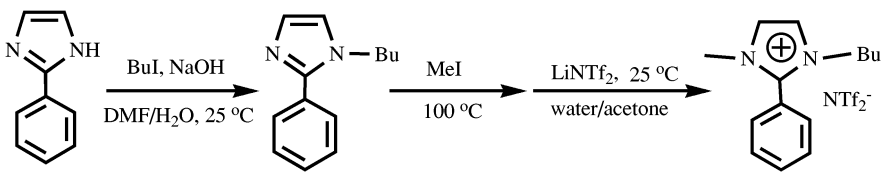
All of the ionic liquids are stable in air. Solid probe mass spectrometry was used to characterize the (2-pyridyl)imidazolium-based cations diluted in methanol or acetone. In all cases, strong peaks indicative of the parent cations were observed (Table 1).

For the ionic liquids with the same *N*-substituents ($R^1 = R^2$, **3a–3c**), the protons of both the imidazolium ring and the two alkyl chains show only a single set of signals in the ^{1}H NMR spectra, which indicates the equivalence of alkyl groups and substituted imidazolium ring supporting the symmetric structures. This is also reflected in their ^{13}C NMR spectra, where only one resonance is observed for C-4 and C-5 of the imidazolium ring. For the remainder of the compounds (**3d–3l**), due to the asymmetric substitution of the imidazolium nitrogen atoms, two ^{1}H NMR resonance patterns appear for the protons of the imidazolium ring, and two ^{13}C NMR resonances are found for C-4 and C-5 of the imidazolium ring. There is minimal or no change in the chemical shift of the protons of the (2-pyridyl)imidazolium parent ring in the two types of compounds. In ^{19}F NMR spectra, the variation of alkyl substituents has no obvious effects on the chemical shift of the anion.

All of the ionic liquids are soluble in CH_2Cl_2, ethyl acetate and acetone, but they are immiscible with water and solvents of low polarity, such as ethyl ethers and alkanes. The immiscibility with water, reflecting the absence of hydrogen bonds of the cation and anion due to the C-2-functionalization of the imidazolium ring and the hydrophobic ability of NTf_2, makes the compounds easily purifiable by simple washing with water to remove water-soluble impurities.

It has been recognized that impurities in ionic liquids, notably residual halides and water arising from the preparation process, strongly influence their chemical and physical properties.[16] In this work, the absence of halides was tested using $AgNO_3$.[3b] The water content is negligible after vacuum drying because of the hydrophobicity of the salts.

The key criterion for evaluation of an ionic liquid is its melting point. For the imidazolium-based salts, the influence of structural variation of cation and/or anion on melting point has been well



Scheme 2

Table 1 Physical properties of **3a–3l** and **4**

Compound	R^1	R^2	T_g/°C [a]	T_d/°C [b]	M [c]
3a	CH_3	CH_3	−32	367	174
3b	$(CH_2)_2CH_3$	$(CH_2)_2CH_3$	60[d]	372	230
3c	$(CH_2)_3CH_3$	$(CH_2)_3CH_3$	41[d]	388	258
3d	CH_3	CH_2CH_3	−45	370	188
3e	CH_3	$(CH_2)_2CH_3$	−52	384	202
3f	CH_3	$(CH_2)_3CH_3$	−59	398	216
3g	CH_3	$(CH_2)_5CH_3$	−60	381	244
3h	$(CH_2)_2CH_3$	$(CH_2)_3CF_3$	−50	382	298
3i	$(CH_2)_3CH_3$	CH_2CH_3	−62	379	230
3j	$(CH_2)_3CH_3$	$(CH_2)_2CH_3$	58[d]	397	244
3k	$(CH_2)_3CH_3$	$(CH_2)_3CF_3$	−52	383	312
3l	$(CH_2)_3CH_3$	$(CH_2)_5CH_3$	−63	379	286
4	CH_3	$(CH_2)_3CH_3$	116[d]	305	216

[a] Glass transition temperature. [b] Thermal degradation. [c] Mass of cation in MS. [d] Melting point.

investigated.[17,18] Generally, low symmetry, weak intermolecular interactions (such as suppressing hydrogen bonds) and a good charge distribution over cation and/or anion tend to produce salts with lower melting points.[18] In **3a–3l**, a better charge delocalization and the suppression of hydrogen bonds by C-2 pyridyl substitution likely result in lower melting points.

Melting points or glass transition temperatures of **3a–3l** were determined by differential scanning calorimetry (DSC). All of the salts fall in the ionic liquid class since their melting points are below 100 °C.[19] The correlation between melting points and alkyl substituents of cations is clearly observed in Table 1. For the compounds with the same *N*-substituents (**3a–3c**), as the alkyl groups are changed from methyl to propyl to butyl, the melting points vary from −32 to 60 to 41 °C, in which the relatively low melting point of **3a** is somewhat surprising.[13b] For the asymmetric ionic liquids **3d–3l**, all with a methyl substituent, the increase of length and flexibility of the other alkyl group results in lower melting points. This suggests poorer packing into the crystal lattice as the alkyl group is elongated. However, with a constant butyl substituent, varying the other alkyl substituent from methyl to ethyl to propyl to butyl to hexyl led to a discontinuous change from −59 to −62 to 58 to 41 to −63 °C. The melting point of the propyl- and butyl-substituted asymmetric salt **3j** is in the middle of that for the *N*-propyl- and butyl-substituted symmetric salts **3b** and **3c**, which shows the synergetic effect of cationic symmetry and effect of *N*-substitutents on the melting point. Generally, a decrease in cation symmetry contributes to poorer packing in the crystalline lattice, which leads to lower melting points. Thus, it is not surprising that changing the non-fluorinated alkyl chain in **3c** and **3j** to a fluorinated alkyl chain in **3k** and **3h** results in a great decrease in the melting points.

The thermal stability of ionic liquids **3a–3l** was determined by thermogravimetric analysis (TGA). The thermal degradation of these ionic liquids occurs in the range 367–398 °C, which is higher than the decomposition temperatures of the ionic liquids bearing side-chain functional groups.[3,6,8] There is no clear relation between decomposition temperature and *N*-substituents; thus the variation of alkyl or polyfluroalkyl substituents on the cation has little effect on the stability of the corresponding salts. The wide liquid range of **3a–3l** is quite impressive. For example, the liquid range of **3f** is −57 to 398 °C. This gives them potential for use in a wide variety of applications in which large liquid range and high thermal stability are required.[20]

The viscosity of ionic liquids is usually governed by van der Waals interactions and hydrogen bonds. The viscosity of **3f** (360 mPa s at 25 °C, 51 mPa s at 60 °C) is much higher than that of imidazolium-based analogues.[18a] Obviously, the increase of the van der Waals attraction dominates over the decrease of hydrogen bonding and better charge delocalization. Moreover, the viscosity of pyridyl-functionalized **3f** is slightly higher than that of phenyl-functionalized **6** (228 mPa s at 25 °C, 36 mPa s at 60 °C). Similar cases have also observed in ionic liquids bearing side-chain coordination groups.[3a]

The coordinating ability of the ionic liquids was examined briefly. Reaction of $PdCl_2$ with **3f** in methanol for 12 h at 25 °C gave rise to a mononuclear palladium(II) complex **4** as an air-stable pale-yellow solid. In the ^1H and ^{13}C NMR spectrum of **4**, downfield shifts are observed for the pyridylimidazolium parent ring when compared with those of **3f**. The melting point of **4** is 116 °C, and thus it is not an ionic liquid.[19] The thermal decomposition temperature (305 °C) is lower than that of the corresponding ionic liquid **3f** (398 °C). Solid-probe positive-ion mass spectrometry showed that its cation (*m*/*z* 216) is the parent ion.

The crystal structure of **4** was determined by single-crystal X-ray diffraction. As shown in Fig. 1, the palladium(II) center is in a distorted square-planar geometry and is coordinated by two *trans* pyridyl nitrogen atoms of **3f** and two *trans* chloride ions, with *cis*-angles ranging from 88.00(7) to 92.00(7)°. The Pd–N_{py} and Pd–Cl bond distances are 2.030(2) and 2.2970(8) Å, respectively. Palladium(II) lies on an inversion center, **3f** serves as a monodentate ligand, and the dihedral angle between the pyridyl and imidazolyl rings is 68.9°. There are no other short contacts or significant weak interactions between adjacent molecules.

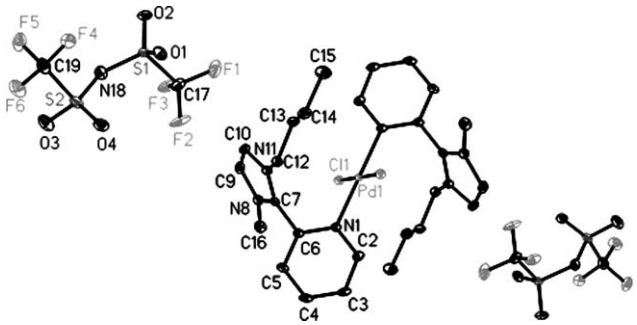


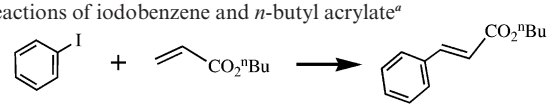
Fig. 1 Crystal structure of mononuclear palladium(II) complex **4**.

Palladium-catalyzed Heck cross-coupling reactions in ionic liquid 3f

Since the ionic liquids can coordinate with $PdCl_2$ to form stable palladium(II) complexes, it seems feasible that palladium(II) catalyst precursors could be effectively immobilized in the corresponding ionic liquids during catalysis and product separation.[3,13] Recent research demonstrated that these types of palladium-containing ionic liquids could be reused more than ten times without significant loss of catalytic activity,[3,13] and could even lead to the activation of aryl chlorides.[13a] In our work, the Heck cross-coupling reaction was initially evaluated using pyridyl-functionalized ionic liquid **3f** and phenyl-functionalized ionic liquid **6** as reaction solvents in the presence of **4**. As expected, the coupling reaction of iodobenzene and *n*-butyl acrylate in **3f** could be performed successfully 10 times without detectable loss of catalytic activity (Table 2, entry 1). Using the same protocols, the Heck reaction in **6** could also be carried out 10 times (Table 2, entry 2); this is ascribed to the similarity of the skeletons of **6** and **4**, allowing the catalyst precursor **4** to be efficiently trapped in **6**. This has been confirmed by using metal complexes with pendant imidazolium tags to catalyze organic reactions in ionic liquids.[21] However, when the Heck reaction was examined using $PdCl_2$ instead of **4** under similar conditions, palladium black was formed during the first cycle, the catalytic solution lost its activity after two cycles and become completely inactive after six cycles (Table 2, entry 3).

To further test the scope and recyclability of **4** in **3f**, a more versatile and practical method was applied to the coupling reactions between aryl halides and vinyl compounds (Table 3),

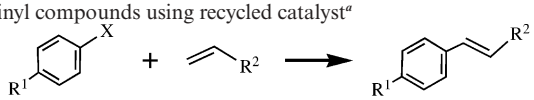
Table 2 GC Yields (%) of Heck coupling reactions of iodobenzene and *n*-butyl acrylate[a]



Entry	IL	Cat.	Cycle no.									
			1	2	3	4	5	6	7	8	9	10
1	**3f**	**4**	>99	>98	>98	>99	>99	>99	>99	>99	>98	>99
2	**6**	**4**	>98	>99	>99	>99	>99	>98	>98	>99	>99	>98
3	**6**	$PdCl_2$	>99	>98	81	46	17	<5	—	—		

[a] All reactions were carried out using 1.0 mmol aryl iodide, 1.25 mmol *n*-butyl acrylate, 1.5 mmol Et_3N, 2 mol% catalyst and 3.0 g ionic liquid at 120 °C for 3 h.

Table 3 Isolated yields of Heck cross-coupling reactions of aryl halides with vinyl compounds using recycled catalyst[a]



Entry	Cycle	R^1	R^2	X	Yield (%)
1	1	H	$CO_2{}^nBu$	I	93
2	2	Me	$CO_2{}^nBu$	I	94
3	3	MeO	$CO_2{}^nBu$	I	91
4	4	F	$CO_2{}^nBu$	I	93
5	5	H	$CO_2{}^nMe$	I	91
6	6	H	$CO_2{}^nBu$	Br	62
7	7	MeO	$CO_2{}^nBu$	Br	47
8	8	CF_3	$CO_2{}^nBu$	Br	89
9	9	NO_2	$CO_2{}^nBu$	Br	90
10	10	H	Ph	Br	65
11	11	CH_3CO	Ph	Br	91
12	12	F	Ph	Br	85
13	13	NO_2	Ph	Br	88
14	14	H	$CO_2{}^nBu$	I	92

[a] All reactions were carried out using 1.0 mmol aryl halide, 1.25 mmol vinyl compound, 1.5 mmol Et_3N, 2 mol% **4** and 3.0 g of **3f** at 120 °C for 5 h.

wherein each subsequent cycle was carried out with a different substrate. A high isolated yield was obtained for aryl iodides bearing electron-withdrawing and electron-donating groups (Table 3, entries 1–5). No appreciable difference in yields between activated and deactivated aryl iodides was found. However, the electronic nature of the aryl bromides has a clear effect on the coupling reactions. For example, the coupling reaction of electron-rich 4-bromoanisole with *n*-butyl acrylate and styrene provided 47% isolated yield (entry 7), but for electron-neutral bromobenzene, the desired coupled product was obtained in 62% isolated yield (entry 6). Interestingly, the Heck reactions between electron-deficient aryl bromides and vinyl compounds occurred smoothly under identical conditions (entries 8, 9, 11–13).

All coupled products were easily separated from the catalyst and ionic liquid solvent by simple extraction with ether. After extracting the products from the catalytic solution, the resulting solution was washed with water to remove ammonium salts and dried under vacuum before new substrates were charged. It is noteworthy that the catalytic solution could be recycled fourteen times with different reactants, with no apparent loss of catalytic activity.

Conclusions

The outstanding recyclability and activity of catalyst precursor **4** in the corresponding ionic liquid **3f** results from a highly synergetic effect between the imidazolium and pyridyl groups, *i.e.*:

1) Ionic liquids can serve as both solvent and ligand. Thus, the palladium center can be efficiently immobilized in ionic liquids by coordination with the pyridyl group during the catalytic process, which prevents the formation of palladium black and catalyst decomposition.

2) Since the imidazolium is functionalized by pyridyl at C-2, the formation of arylimidazolium salts and other detrimental side-products is precluded.

3) Perhaps most importantly, the palladium catalyst is part of the ionic liquid in the catalytic system. As a consequence, it is easily lost during extraction of the products.[3a]

In summary, we have developed a family of imidazolium-based ionic liquids functionalized by pyridyl at C-2. The correlation between their structures and melting points, thermal stabilities, solubility as well as viscosity was determined. The role of the pyridyl group in these properties is shown. All of them display high thermal stabilities and a wide liquid range. Their reactions with palladium(II) chloride easily gave rise to palladium(II) ionic liquid complexes. Heck cross-coupling reactions of the palladium compounds in the corresponding ionic liquids showed excellent recyclability. Hence, this work has not only demonstrated that the functionalized ionic liquids have a superior capacity to immobilize and recycle the catalyst when serving as both solvent and ligand, but also provides a promising pathway toward the design and synthesis of functionalized ionic liquids for particular applications, which greatly enlarges the scope of application of ionic liquids.

Experimental

All the reagents were purchased from commercial sources and used without further purification. 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 on a Bruker AMX 300 spectrometer at 300, 75 and 282 MHz, respectively, using deuterated acetone as the locking solvent except where otherwise indicated. Chemical shifts were reported in ppm relative to the appropriate standard: $CFCl_3$ for ^{19}F, and TMS for ^1H and ^{13}C NMR spectra. GC/MS spectra were determined

using an appropriate instrument. Mass spectra (Shimadzu GCMS-QP5050) for ionic compounds were determined by insertion using a solid probe (EI). Viscosity was measured on MINIVIS II instrument. Differential scanning calorimetry (DSC) (TA Instruments Q10) measurements were performed using 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^{-1}. The transition temperature, T_m, was taken as the peak maximum. Thermogravimetric analysis (TGA) (TA Instruments Q50) was carried out by heating samples at 10 °C min^{-1} from room temperature to 500 °C in a dynamic nitrogen atmosphere (flow rate = 70 mL min^{-1}). 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 on a CE-440 Elemental analyzer.

Synthesis of 2-(2-pyridyl)imidazole (1)

This synthesis is a slight modification of the literature procedure.[14] An ice-cold solution of 2-pyridinecarboxaldehyde (187 mmol, 20 g) in ethanol (20 mL) was added to an ice-cold solution of 40% aqueous glyoxal (27 mL) in ethanol (20 mL), and then ice-cold concentrated aqueous NH_3 (64 mL) was added without delay. The yellow–brown solution was held at 0 °C for 1 h, and was then allowed to stir for 5 h at 25 °C. Most of the ethanol was removed under reduced pressure, and the resulting solution was extracted several times with ethyl ether. The combined solution was evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel to give a colorless solid. Yield: 11.4 g (42%). ^{1}H NMR ($CDCl_3$): δ 8.46–8.48 (m, 1H), 8.18–8.21 (m, 1H), 7.72–7.78 (m, 1H), 7.18–7.23 (m, 2H), 7.08 (s 1H), ^{13}C NMR ($CDCl_3$): δ 148.7, 148.5, 146.3, 137.3, 130.4, 123.1, 120.1, 117.6; GC–MS (EI) m/z (%) 144 ($M^+ - 1$, 100).

General procedures for the preparation of 1-alkyl-2-(2-pyridyl)imidazoles 2a–2c

A mixture of 2-(2-pyridyl)imidazole (5.8 g, 40 mmol) and 35% aqueous NaOH (6.0 ml) in DMF (30 ml) was stirred for 1 h at 25 °C. Alkyl iodide (52 mmol) was then added slowly, and the mixture stirred overnight at 25 °C. The resulting solution was poured into H_2O (30 ml), and extracted with chloroform (3 × 20 mL). The combined organic layers were washed with H_2O (3 × 20 mL), and dried over Na_2SO_4. After evaporating the solvent, the residue was purified by flash chromatography on silica gel to give **2a–2c**.

1-Methyl-2-(2-pyridyl)imidazole (2a). Pale-yellow liquid, yield: 82%. ^{1}H NMR ($CDCl_3$): δ 8.30–8.32 (m, 1H), 7.94–7.97 (m, 1H), 7.43–7.49 (m, 1H), 6.88–6.93 (m, 2H), 6.70 (s, 1H), 3.83 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 151.3, 147.7, 144.3, 135.9, 127.6, 123.9, 122.0, 121.7, 35.7; GC–MS (EI) m/z (%): 158 ($M^+ - 1$, 100).

1-Propyl-2-(2-pyridyl)imidazole (2b). Pale-yellow liquid, yield: 75%. ^{1}H NMR ($CDCl_3$): δ 8.52–8.54 (m, 1H), 8.12–8.15 (m, 1H), 7.66–7.72 (m, 1H), 7.13–7.17 (m, 1H), 7.08 (s 1H), 6.97 (s, 1H), 4.53 (t, 2H, J = 7.3 Hz), 1.79 (sextet, 2H, J = 7.4 Hz), 0.87 (t, 3H, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$): δ 151.0, 148.2, 144.5, 136.4, 128.1, 123.2, 122.7, 122.2, 49.9, 24.5, 11.0; GC–MS (EI) m/z (%): 186 ($M^+ - 1$, 100).

1-Butyl-2-(2-pyridyl)imidazole (2c). Pale-yellow liquid, yield: 89%. ^{1}H NMR ($CDCl_3$): δ 8.53–8.55 (m, 1H), 8.13–8.17 (m, 1H), 7.68–7.74 (m, 1H), 7.16–7.19 (m, 1H), 7.09 (s 1H), 6.98 (s, 1H), 4.59 (t, 2H, J = 7.3 Hz), 1.76 (quintet, 2H, J = 7.3 Hz), 1.32 (sextet, 2H, J = 7.4 Hz), 0.89 (t, 3H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$): δ 151.0, 148.2, 144.4, 136.4, 128.2, 123.1, 122.7, 122.2, 48.0, 33.3, 19.8, 13.6; GC–MS (EI) m/z (%) 201 (M^+, 27).

General procedures for the preparation of 3a–3l

1-Alkyl-2-(2-pyridyl)imidazole (1 mmol) and alkyl halide (1.5 mmol) were placed in a Pyrex glass tube. After cooling the samples to −195 °C, the tube was evacuated and sealed. The reaction mixture was then stirred at 100 °C for 24 h. After cooling and carefully opening the tube, the volatile materials were removed under reduced pressure. The residue was dissolved in a mixture of water (10 ml) and acetone (10 ml), and then $LiN(SO_2CF_3)_2$ (0.43 g, 1.5 mmol) was added. The reaction mixture was stirred at 25 °C for 5 h. The acetone was evaporated under reduced pressure, and the water layer was extracted three times with ethyl acetate (3 × 10 ml). The combined organic layer was washed three times with water (3 × 10 ml), once with saturated $Na_2S_2O_3$ solution (10 ml), and then was dried over anhydrous Na_2SO_4. After removing the solvent *in vacuo*, the products were washed with CH_2Cl_2 (3 ml) and were filtered to remove any inorganic salts. The solvent was removed again *in vacuo* to give **3a–3l**.

1-Methyl-2-pyridyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide (3a). Pale-yellow liquid, yield: 86%. ^{1}H NMR: δ 8.82–8.84 (m, 1H), 8.02–8.08 (m, 1H), 7.90 (d, 1H, J = 7.9 Hz), 7.58–7.62 (m, 1H), 7.42 (s, 2H), 3.86 (s, 6H); ^{13}C NMR: δ 151.0, 142.7, 140.7, 138.2, 127.4, 126.8, 123.7, 121.0 (q, J = 319.4 Hz), 36.5; ^{19}F NMR: δ −79.8 (s, 6F); MS (solid probe) (EI) m/z (%) 174 (M^+, 100), Anal. Calcd for $C_{12}H_{12}F_6N_4O_4S_2$ (454.37): C, 31.72; H, 2.66; N 12.33. Found: C, 31.50; H, 2.60; N, 12.29.

1-Propyl-2-pyridyl-3-propylimidazolium bis(trifluoromethanesulfonyl)amide (3b). Colorless solid, yield: 88%. ^{1}H NMR: δ 8.91–8.93 (m, 1H), 8.15–8.21 (m, 1H), 8.02–8.05 (m, 1H), 7.87 (s, 2H), 7.73–7.78 (m, 1H), 4.22 (t, 4H, J = 7.2 Hz), 1.81 (sextet, 4H, J = 7.3 Hz), 0.82 (t, 6H, J = 7.4 Hz); ^{13}C NMR: δ 152.0, 143.4, 142.2, 139.1, 128.0, 127.7, 123.4, 121.8 (q, J = 319.0 Hz), 51.2, 23.8, 10.6; ^{19}F NMR: δ −79.9 (s, 6F); MS (solid probe) (EI) m/z (%) 230 (M^+, 100), Anal. Calcd for $C_{16}H_{20}F_6N_4O_4S_2$ (510.08): C, 37.65; H, 3.95; N 10.98. Found: C, 37.60; H, 3.97; N, 10.84.

1-Butyl-2-pyridyl-3-butylimidazolium bis(trifluoromethanesulfonyl)amide (3c). Colorless solid, yield: 95%. ^{1}H NMR: δ 8.94–8.97 (m, 1H), 8.20–8.26 (m, 1H), 8.07–8.11 (m, 1H), 7.94 (s, 2H), 7.78–7.82 (m, 1H), 4.29 (t, 4H, J = 7.5 Hz), 1.81 (quintet, 2H, J = 7.4 Hz), 1.26 (sextet, 2H, J = 7.6 Hz), 0.80 (t, 3H, J = 7.3 Hz); ^{13}C NMR: δ 152.1, 143.5, 142.4, 139.2, 128.1, 127.8, 123.5, 121.0 (q, J = 319.4 Hz), 49.6, 32.6, 19.8, 13.4; ^{19}F NMR: δ −79.8 (s, 6F); MS (solid probe) (EI) m/z (%) 258 (M^+, 100), Anal. Calcd for $C_{18}H_{24}F_6N_4O_4S_2$ (538.11): C, 40.15; H, 4.49; N 10.40. Found: C, 40.10; H, 4.37; N, 10.38.

1-Ethyl-2-pyridyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide (3d). Pale-yellow liquid, yield: 90%. ^{1}H NMR: δ 8.76–8.84 (m, 1H), 8.00–8.05 (m, 1H), 7.85–7.92 (m, 1H), 7.58 (d, 1H, $J = 2.1$ Hz), 7.43 (d, 1H, $J = 1.2$ Hz), 7.14–7.21 (m, 1H), 4.14 (q, 2H, $J = 7.4$ Hz), 3.80 (s, 3H), 1.41 (t, 3H, $J = 7.3$ Hz); ^{13}C NMR: δ 151.1, 142.8, 141.9, 138.3, 127.4, 126.9, 124.0, 121.5, 121.0 (q, $J = 319.2$ Hz), 44.9, 36.4, 15.1; ^{19}F NMR: δ −79.8 (s, 6F); MS (solid probe) (EI) m/z (%) 188 (M^+, 100), Anal. Calcd for $C_{13}H_{14}F_6N_4O_4S_2$ (468.04): C, 33.33; H, 3.01; N 11.96. Found: C, 33.34; H, 3.03; N, 11.70.

1-Propyl-2-pyridyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide (3e). Pale-yellow liquid, yield: 87%. ^{1}H NMR: δ 8.92–8.94 (m, 1H), 8.17–8.23 (m, 1H), 8.05–8.08 (m, 1H), 7.87 (d, 1H, $J = 1.7$ Hz), 7.83 (d, 1H, $J = 1.2$ Hz), 7.74–7.79 (m, 1H), 4.29 (t, 2H, $J = 7.3$ Hz), 3.98(s, 3H), 1.84 (sextet, 2H, $J = 7.3$ Hz), 0.84 (t, 3H, $J = 7.3$ Hz); ^{13}C NMR: δ 151.9, 143.2, 142.2, 139.0, 128.1, 127.7, 124.9, 123.3, 121.0 (q, $J = 319.4$ Hz), 51.4, 36.7, 23.9, 10.7; ^{19}F NMR: δ −79.8 (s, 6F); MS (solid probe) (EI) m/z (%) 202 (M^+, 100), Anal. Calcd for $C_{14}H_{16}F_6N_4O_4S_2$ (482.05): C, 34.86; H, 3.34; N 11.61. Found: C, 34.59; H, 3.26; N, 11.54.

1-Butyl-2-pyridyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide (3f). Pale-yellow liquid, yield: 93%. ^{1}H NMR: δ 8.95 (d, 1H, $J = 4.6$ Hz), 8.20–8.25 (m, 1H), 8.10 (d, 1H, $J = 7.8$ Hz), 7.92 (d, 1H, $J = 2.0$ Hz), 7.87 (d, 1H, $J = 1.9$ Hz), 7.77–7.81 (m, 1H), 4.35 (t, 2H, $J = 7.4$ Hz), 4.01 (s, 3H), 1.82 (quintet, 2H, $J = 7.4$ Hz), 1.27 (sextet, 2H, $J = 7.5$ Hz), 0.82 (t, 3H, $J = 7.4$ Hz); ^{13}C NMR: δ 152.0, 143.3, 142.3, 139.1, 128.2, 127.8, 125.0, 123.4, 121.0 (q, $J = 319.4$ Hz), 49.8, 36.8, 32.7, 19.9, 13.5; ^{19}F NMR: δ −79.8 (s, 6F); MS (solid probe) (EI) m/z (%) 216 (M^+, 100), Anal. Calcd for $C_{15}H_{18}F_6N_4O_4S_2$ (496.07): C, 36.29; H, 3.65; N 11.29. Found: C, 35.90; H, 3.64; N, 11.13.

1-Hexyl-2-pyridyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide (3g). Pale-yellow liquid, yield: 92%. ^{1}H NMR: δ 8.94–8.96 (m, 1H), 8.19–8.25 (m, 1H), 8.08–8.11 (m, 1H), 7.92 (d, 1H, $J = 2.1$ Hz), 7.86 (d, 1H, $J = 2.0$ Hz), 7.77–7.85 (m, 1H), 4.35 (t, 2H, $J = 7.4$ Hz), 4.00 (s, 3H), 1.83 (quintet, 2H, $J = 7.3$ Hz), 1.16–1.30 (m, 6H), 0.81 (t, 3H, $J = 7.0$ Hz); ^{13}C NMR: δ 152.0, 143.6, 142.3, 139.1, 128.1, 127.3, 125.0, 123.4, 121.0 (q, $J = 319.4$ Hz), 50.0, 36.8, 31.6, 30.6, 26.3, 22.9, 14.0; ^{19}F NMR: δ −79.8 (s, 6F); MS (solid probe) (EI) m/z (%) 244 (M^+, 100), Anal. Calcd for $C_{17}H_{22}F_6N_4O_4S_2$ (524.1): C, 38.93; H, 4.23; N 10.68. Found: C, 39.09; H, 4.24; N, 10.83.

1-(4,4,4-Triflurobutyl)-2-pyridyl-3-propylimidazolium bis(trifluoromethanesulfonyl) amide (3h). Pale-yellow liquid, yield: 85%. ^{1}H NMR: δ 8.89–8.91 (m, 1H), 8.13–8.17 (m, 1H), 8.02–8.05 (m, 1H), 7.89 (d, 1H, $J = 2.1$ Hz), 7.85 (d, 1H, $J = 2.1$ Hz), 7.72–7.77 (m, 1H), 4.36 (t, 2H, $J = 7.4$ Hz), 4.21 (t, 2H, $J = 7.3$ Hz), 2.08–2.25 (m, 4H), 1.81 (sextet, 2H, $J = 7.3$ Hz), 0.81 (t, 3H, $J = 7.4$ Hz); ^{13}C NMR: δ 152.1, 143.7, 142.0, 139.1, 128.1, 127.8 (q, $J = 273.8$ Hz), 127.8, 127.2, 123.7, 123.4, 120.8 (q, $J = 318.9$ Hz), 51.4, 48.4, 30.8 (q, $J = 29.5$ Hz), 23.8, 23.5 (q, $J = 3.3$ Hz), 10.6; ^{19}F NMR: δ −66.9 (t, 3F, $J = 10.4$ Hz), −79.9 (s, 6F); MS (solid probe) (EI) m/z (%) 298 (M^+, 100), Anal. Calcd for $C_{17}H_{19}F_9N_4O_4S_2$ (578.07): C, 35.30; H, 3.31; N 9.69. Found: C, 35.14; H, 3.32; N, 9.57.

1-Butyl-2-pyridyl-3-ethylimidazolium bis(trifluoromethanesulfonyl)amide (3i). Pale-yellow liquid, yield: 92%. ^{1}H NMR: δ 8.94–8.96 (m, 1H), 8.19–8.24 (m, 1H), 8.06–8.09 (m, 1H), 7.93 (d, 2H, $J = 1.2$ Hz), 7.77–7.82 (m, 1H), 4.26–4.35 (m, 4H), 1.81 (quintet, 2H, $J = 7.4$ Hz), 1.46 (t, 3H, $J = 7.2$ Hz), 1.26 (sextet, 2H, $J = 7.5$ Hz), 0.81 (t, 3H, $J = 7.3$ Hz); ^{13}C NMR: δ 152.1, 143.3, 142.3, 139.1, 128.0, 127.8, 123.6, 123.0, 121.0 (q, $J = 319.4$ Hz), 49.6, 45.3, 32.6, 19.9, 15.5, 13.5; ^{19}F NMR: δ −79.8 (s, 6F); MS (solid probe) (EI) m/z (%) 230 (M^+, 100), Anal. Calcd for $C_{16}H_{20}F_6N_4O_4S_2$ (510.08): C, 37.65; H, 3.95; N 10.98. Found: C, 37.57; H, 3.91; N, 11.12.

1-Butyl-2-pyridyl-3-propylimidazolium bis(trifluoromethanesulfonyl)amide (3j). Colorless solid, yield: 86%. ^{1}H NMR: δ 8.95–8.98 (m, 1H), 8.21–8.26 (m, 1H), 8.08–8.11 (m, 1H), 7.96 (d, 2H, $J = 1.1$ Hz), 7.79–7.83 (m, 1H), 4.25–4.33 (m, 4H), 1.77–1.89 (m, 4H), 1.26 (sextet, 2H, $J = 7.4$ Hz), 0.78–0.87 (m, 6H); ^{13}C NMR: δ 152.1, 143.3, 139.1, 128.1, 127.8, 123.5, 123.4, 121.0 (q, $J = 319.4$ Hz), 51.3, 49.6, 32.5, 23.9, 19.8, 13.4, 10.7; ^{19}F NMR: δ −79.8 (s, 6F); MS (solid probe) (EI) m/z (%) 244 (M^+, 100), Anal. Calcd for $C_{17}H_{22}F_6N_4O_4S_2$ (524.1): C, 38.93; H, 4.23; N 10.68. Found: C, 38.95; H, 4.18; N, 10.68.

1-(4,4,4-Triflurobutyl)-2-pyridyl-3-butylimidazolium bis(trifluoromethanesulfonyl) amide (3k). Pale-yellow liquid, yield: 83%. ^{1}H NMR: δ 8.94–8.96 (m, 1H), 8.20–8.25 (m, 1H), 8.09–8.12 (m, 1H), 7.98 (d, 2H, $J = 10.96$ Hz), 7.78–7.82 (m, 1H), 4.42 (t, 2H, $J = 7.1$ Hz), 4.30 (t, 2H, $J = 7.0$ Hz), 2.15–2.34 (m, 4H), 1.80 (quintet, 2H, $J = 7.4$ Hz), 1.25 (sextet, 2H, $J = 7.3$ Hz), 0.79 (t, 3H, $J = 7.3$ Hz); ^{13}C NMR: δ 152.1, 143.6, 142.0, 139.2, 128.2, 127.9 (q, $J = 273.8$ Hz), 127.8, 127.2, 123.7, 122.4, 120.9 (q, $J = 319.2$ Hz), 49.6, 48.4, 32.4, 30.8 (q, $J = 29.5$ Hz), 23.5 (q, $J = 3.3$ Hz), 19.8, 13.4; ^{19}F NMR: δ −66.9 (t, 3F, $J = 10.4$ Hz), −79.9 (s, 6F); MS (solid probe) (EI) m/z (%) 312 (M^+, 100), Anal. Calcd for $C_{18}H_{21}F_9N_4O_4S_2$ (592.09): C, 36.49; H, 3.57; N 9.46. Found: C, 36.50; H, 3.60; N, 9.66.

1-Hexyl-2-pyridyl-3-butylimidazolium bis(trifluoromethanesulfonyl)amide (3l). Pale-yellow liquid, yield: 92%. ^{1}H NMR: δ 8.95–8.97 (m, 1H), 8.20–8.26 (m, 1H), 8.08–8.11 (m, 1H), 7.95 (s, 2H), 7.78–7.83 (m, 1H), 4.30 (t, 4H, $J = 7.4$ Hz), 1.75–1.87 (m, 4H), 1.15–1.32 (m, 8H), 0.78–0.83 (m, 6H); ^{13}C NMR: δ 152.2, 143.5, 142.4, 139.2, 128.2, 127.9, 123.6, 123.5, 121.0 (q, $J = 319.5$ Hz), 49.9, 49.7, 32.6, 31.6, 30.5, 26.3, 22.9, 19.9, 14.0, 13.5; ^{19}F NMR: δ −79.8 (s, 6F); MS (solid probe) (EI) m/z (%) 286 (M^+, 100), Anal. Calcd for $C_{20}H_{28}F_6N_4O_4S_2$ (566.15): C, 42.40; H, 4.98; N 9.89. Found: C, 41.73; H, 4.83 N, 9.78.

Palladium(II) [1-butyl-2-pyridyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide] dichloride (4)

$PdCl_2$ (0.035 g, 0.2 mmol) was added to a stirred solution of **3f** (0.199 g, 0.4 mmol) in methanol (10 ml). The mixture was stirred for 12 h at 25 °C. Slow evaporation of the resulting solution gave rise to pale-yellow crystals. Yield: (0.21 g, 90%). ^{1}H NMR: δ 9.31 (s, 2H), 8.50–8.55 (m, 2H), 8.36 (d, 2H, $J = 7.7$ Hz), 8.29 (d, 2H, $J = 2.0$ Hz), 8.20 (s, 2H), 8.03–8.12 (m, 2H), 4.53 (t, 4H, $J = 7.3$

Hz), 4.03 (s, 6H), 1.86 (quintet, 4H, $J = 7.6$ Hz), 1.29 (sextet, 4H, $J = 7.5$ Hz), 0.82 (t, 6H, $J = 7.8$ Hz); ^{13}C NMR: δ 157.3, 143.6, 139.1, 130.1, 128.1, 126.3, 124.9, 123.3, 121.0 (q, $J = 319.4$ Hz), 51.4, 37.8, 32.7, 20.0, 13.5; ^{19}F NMR: δ −79.8 (s, 12F); MS (solid probe) (EI) m/z (%) 216 ([(M − $PdCl_2$)/2]$^+$, 100). Anal. Calcd for $C_{30}H_{36}Cl_2F_{12}N_8O_8PdS_4$ (1170.22): C, 30.79; H, 3.10; N 9.58. Found: C, 30.98; H, 3.36; N, 9.57.

Crystal data: $C_{30}H_{36}Cl_2F_{12}N_8O_8PdS_4$, $M_r = 1170.21$, monoclinic, space group $P2_1/n$, $a = 8.8615(12)$, $b = 24.322(3)$, $c = 11.2807(16)$ Å, $\beta = 111.633(2)°$, $V = 2260.0(5)$ Å^3, $F(000) = 1176$, $T = 87(2)$ K, $Z = 2$, $D_c = 1.720$ g cm^{-3}, $\lambda = 0.71073$ Å, $\mu = 0.818$ mm^{-1}; of 33709 measured reflections, 4080 were unique ($R_{int} = 0.0297$, $1.67 \leq \theta \leq 25.25°$), $R_1 = 0.0382$, $wR_2 = 0.0864$, GOF = 1.081 for 297 parameters, final difference map extremes +1.178 and −0.499 e Å^{-3}. CCDC reference number 286255. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b616529j.

Synthesis of 1-butyl-2-(2-phenyl)imidazole (5)

The compound was synthesized using 1-butyl iodide and 2-phenylimidazole by following the same procedure as for 1-butyl-2-(2-pyridyl)imidazole. Pale-yellow liquid, yield: 90%. ^{1}H NMR ($CDCl_3$): δ 7.52–7.56 (m, 2H), 7.34–7.45 (m, 3H), 7.10 (d, 1H, $J = 1.1$ Hz), 6.98 (d, 1H, $J = 1.2$ Hz), 3.97 (t, 2H, $J = 7.4$ Hz), 1.70 (quintet, 2H, $J = 7.3$ Hz), 1.25 (sextet, 2H, $J = 7.6$ Hz), 0.84 (t, 3H, $J = 7.3$ Hz); ^{13}C NMR ($CDCl_3$): δ 147.7, 131.1, 128.9, 128.6, 128.5, 128.4, 120.3, 46.5, 33.1, 19.7, 13.5; GC–MS (EI) m/z (%) 200 (M$^+$, 53).

Synthesis of 1-butyl-2-phenyl-3-methylimidazolium bis(trifluoromethanesulfonyl) amide (6)

The compound was synthesized using **5** and methyl iodide by following the same procedure as for **3a–3l**. Pale-yellow liquid, yield: 95%. ^{1}H NMR: δ 7.60–7.69 (m, 3H), 7.49–7.52 (m, 2H), 7.40–7.42 (m, 2H), 3.94 (t, 2H, $J = 7.5$ Hz), 3.67 (s, 3H), 1.67 (quintet, 2H, $J = 7.5$ Hz), 1.19 (sextet, 2H, $J = 7.5$ Hz), 0.78 (t, 3H, $J = 7.5$ Hz); ^{13}C NMR: δ 144.7, 132.9, 130.1, 130.0, 123.6, 121.6, 120.7, 119.8 (q, $J = 319.5$ Hz), 48.8, 35.8, 31.7, 19.2, 13.0; ^{19}F NMR: δ −79.9 (s, 12F); MS (solid probe) (EI) m/z (%) 215 (M$^+$, 100). Anal. Calcd for $C_{16}H_{19}F_6N_3O_4S_2$ (495.07): C, 38.79; H, 3.87; N 8.48. Found: C, 39.13; H, 4.11; N, 8.38.

General procedure for Heck reactions in ionic liquids

Palladium(II) complex **4** (23.4 mg, 0.02 mmol) was dissolved in ionic liquid **3f** (3 g), and the solvent was degassed under reduced pressure at 60 °C for 1 h before nitrogen was introduced. The aryl halide (1.0 mmol), olefin (1.25 mmol) and triethylamine (1.5 mmol) were subsequently added under nitrogen at 25 °C. The resulting mixture was stirred at 120 °C for the appropriate time. The product was extracted from the reaction mixture by addition of ethyl ether–hexane (1 : 1, 3 ml), followed by decanting off the solution of the product. This was repeated three times (3 × 3 ml), and the combined organic layers concentrated by rotary evaporation. The residue was purified by flash chromatography on silica gel to give the desired product. The identity of the products was confirmed by comparison with literature spectroscopic data. The catalytic solution was washed three times with water (3 × 3 ml) to remove excess of base and its salt, dried under reduced pressure at 60 °C for 4 h to remove traces of water and other residues, and then employed for the next cycle.

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References

1 (*a*) J. Dupont, R. F. de Souza and P. A. Z. Suarez, *Chem. Rev.*, 2002, **102**, 3667–3691; (*b*) P. Wasserscheid and W. Keim, *Angew. Chem., Int. Ed.*, 2000, **39**, 3773–3789; (*c*) R. Sheldon, *Chem. Commun.*, 2001, 2399–2407; (*d*) T. Welton, *Chem. Rev.*, 1999, **99**, 2071–2083.
2 (*a*) R. D. Rogers and K. R. Seddon, *Science*, 2003, **302**, 792–793; (*b*) K. E. Gutowski, G. A. Broker, H. D. Willauer, J. G. Huddleston, R. P. Swatloski, J. D. Holbrey and R. D. Rogers, *J. Am. Chem. Soc.*, 2003, **125**, 6632–6633; (*c*) A. Perosa, P. Tundo, M. Selva, S. Zinovyev and A. Testa, *Org. Biomol. Chem.*, 2004, **2**, 2249–2252; (*d*) J. Pernak, K. Sobaszkiewicz and J. Foksowicz-Flaczyk, *Chem. Eur. J.*, 2004, **10**, 3479–3485.
3 (*a*) D. Zhao, Z. Fei, T. J. Geldbach, R. Scopelliti and P. J. Dyson, *J. Am. Chem. Soc.*, 2004, **126**, 15876–15882; (*b*) D. Zhao, Z. Fei, R. Scopelliti and P. J. Dyson, *Inorg. Chem.*, 2004, **43**, 2197–2205.
4 A. Kamal and G. Chouhan, *Tetrahedron Lett.*, 2005, **46**, 1489–1491.
5 T. Sasaki, C. Zhong, M. Tada and Y. Iwasawa, *Chem. Commun.*, 2005, 2506–2508.
6 (*a*) J. D. Holbrey, M. B. Turner, W. M. Reichert and R. D. Rogers, *Green Chem.*, 2003, **5**, 731–736; (*b*) L. Zhou and L. Wang, *Synthesis*, 2006, 2653–2658.
7 K.-S. Kim, D. Demberelnyamba and H. Lee, *Langmuir*, 2004, **20**, 556–560.
8 (*a*) T. L. Merrigan, E. D. Bates, S. C. Dorman and J. H. Davis, Jr., *Chem. Commun.*, 2000, 2051–2052; (*b*) H. Xue and J. M. Shreeve, *Eur. J. Inorg. Chem.*, 2005, 2573–2580 and references therein.
9 (*a*) L. Xu, W. Chen and J. Xiao, *Organometallics*, 2000, **19**, 1123–1127; (*b*) F. McLachlan, C. J. Mathews, P. J. Smith and T. Welton, *Organometallics*, 2003, **22**, 5350–5357; (*c*) A. C. Sentman, S. Csihony, R. M. Waymouth and J. L. Hedrick, *J. Org. Chem.*, 2005, **70**, 2391–2393.
10 (*a*) V. K. Aggarwal, I. Emme and A. Mereu, *Chem. Commun.*, 2002, 1612–1613; (*b*) L. Magna, Y. Chauvin, G. P. Niccolai and J.-M. Basset, *Organometallics*, 2003, **22**, 4418–4425; (*c*) N. D. Clement, K. J. Cavell, C. Jones and C. J. Elsevier, *Angew. Chem., Int. Ed.*, 2004, **43**, 1277–1279.
11 C. J. Mathews, P. J. Smith and T. Welton, *J. Mol. Catal. A: Chem.*, 2004, **214**, 27–32.
12 D. J. Brauer, K. W. Kottsieper, C. Liek, O. Stelzer, H. Waffenschmidt and P. Wasserscheid, *J. Organomet. Chem.*, 2001, **630**, 177–184.
13 (*a*) J. C. Xiao, B. Twamley and J. M. Shreeve, *Org. Lett.*, 2004, **6**, 3845–3847; (*b*) J. C. Xiao and J. M. Shreeve, *J. Org. Chem.*, 2005, **70**, 3072–3078; (*c*) J. C. Xiao, C. F. Ye and J. M. Shreeve, *Org. Lett.*, 2005, **7**, 1963–1965; (*d*) C. M. Jin, B. Twamley and J. M. Shreeve, *Organometallics*, 2005, **24**, 3020–3023; (*e*) R. Wang, M. M. Piekarski and J. M. Shreeve, *Org. Biomol. Chem.*, 2006, **4**, 1878–1886; (*f*) R. H. Wang, C. M. Jin, B. Twamley and J. M. Shreeve, *Inorg. Chem.*, 2006, **45**, 6396–6403.
14 K. A. Reeder, E. V. Dose and L. J. Wilson, *Inorg. Chem.*, 1978, **17**, 1071–1075.
15 P. K. Byers and A. J. Canty, *Organometallics*, 1990, **9**, 210–220.
16 (*a*) K. R. Seddon, A. Stark and M. J. Torres, *Pure Appl. Chem.*, 2000, **72**, 2275–2287; (*b*) P. A. Z. Suarez, S. Einloft, J. E. L. Dullius, R. F. de Souza and J. Dupont, *J. Chim. Phys. Phys.-Chim. Biol.*, 1998, **95**, 1626–1639.

17 (*a*) J. D. Holbrey and K. R. Seddon, *J. Chem. Soc., Dalton Trans.*, 1999, 2133–2139; (*b*) E. A. Turner, C. C. Pye and R. D. Singer, *J. Phys. Chem. A*, 2003, **107**, 2277–2288 and references therein.
18 (*a*) P. Bonhôte, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram and M. Grätzel, *Inorg. Chem.*, 1996, **35**, 1168–1178; (*b*) A. Mele, C. D. Tran and S. H. De Paoli Lacerda, *Angew. Chem., Int. Ed.*, 2003, **42**, 4364–4366.
19 K. R. Seddon, *J. Chem. Technol. Biotechnol.*, 1997, **68**, 351–356.
20 (*a*) J. L. Anderson, R. F. Ding, A. Ellern and D. W. Armstrong, *J. Am. Chem. Soc.*, 2005, **127**, 593–604; (*b*) X. Han and D. W. Armstrong, *Org. Lett.*, 2005, **7**, 4205–4208.
21 (*a*) N. Audic, H. Clavier, M. Mauduit and J.-C. Guillemin, *J. Am. Chem. Soc.*, 2003, **125**, 9248–9249; (*b*) Q. Yao and Y. Zhang, *Angew. Chem., Int. Ed.*, 2003, **42**, 3395–3398; (*c*) H. Clavier, N. Audic, J.-C. Guillemin and M. Mauduit, *J. Organomet. Chem.*, 2005, **690**, 3585–3599 and references therein.

